Batch and Column Studies for Metal Removal/Uptake under Uncontrolled/Controlled pH Conditions by Granular Activated Alumina from Mono-, Binary- and Ternary-Metal Ion Systems of Cu(II), Pb(II) and Cr(III) at Fixed Total Initial Concentrations

Thesis submitted to the
Indian Institute of Technology Guwahati
for the award of the degree
of

Doctor of Philosophy

By

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August 2015

Statement

I do hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Civil Engineering, Indian Institute of Technology Guwahati, Guwahati, Assam, India.

In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

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Certificate

This is to certify that the thesis entitled **"Batch and Column Studies for Metal Removal/Uptake under Uncontrolled/Controlled pH Conditions by Granular Activated Alumina from Mono-, Binary- and Ternary-Metal Ion Systems of Cu(II), Pb(II) and Cr(III) at Fixed Total Initial Concentrations"** submitted by **Patil Ravindra Jaysing** Registration No. 09610412 to the Indian Institute of Technology Guwahati, for the award of the degree of Doctor of Philosophy in Civil Engineering is a record of bonafide research work carried out by him under my supervision and guidance. The thesis work, in my opinion, has reached the requisite standard fulfilling the requirement for the degree of Doctor of Philosophy.

The results contained in this thesis have not been submitted in part or full to any other University or Institute for award of any degree or diploma.

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List of Abbreviations/Notations

A	:	Cross sectional area of the bed
β_R	:	Radke–Prausnitz model exponent
b	:	Langmuir adsorption constant
b_s	:	Sips model isotherm constant
b_T	:	Sorption affinity parameter
B	:	Binary
BET	:	Brunauer-Emmer-Teller
BDST	:	Bed depth service time
C_{BET}	:	BET adsorption isotherm
C_o	:	Initial metal concentration
C_e	:	Equilibrium metal concentration in solution
C_s	:	Adsorbate monolayer saturation concentration
C_f	:	Equilibrium concentration of adsorbate in solution
$C_{e,j}$	:	Equilibrium concentration of metal ion '*j*'
C_t	:	Effluent metal concentration
DMW	:	De-mineralized water
DR	:	Dubinin–Radushkevich
ED	:	Elecrtodialysis
F_w	:	Flow rate
G	:	An exponent having value between 0 and 1
GAA	:	Granular activated alumina
h	:	Hour

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IAST	:	Ideal adsorption solution theory
IDA	:	Iminodiacetic acid
k	:	Freundlich constant
K_a	:	Overall mass transfer coefficient
k_{ads}	:	Adsorption rate constant
K_h	:	Henry's constant
K_p	:	Intra-particle diffusion rate constant
K_R	:	R-P isotherm constant
k_{TH}	:	Thomas model rate constant
m	:	Mass of adsorbent
min.	:	Minute
M	:	Mono
MPSD	:	Marquardt's percent standard deviation
MIOC	:	Mont-morillonite iron oxide composite
n	:	Freundlich adsorption intensity
n_T	:	Heterogeneity parameter
NF	:	Nanofiltration
N_o	:	Dynamic bed capacity
pH_{zpc}	:	Point of zero charge
PRH	:	Phosphate treated rice husk
q_e	:	Equilibrium uptake
q_m	:	Maximum adsorbate uptake by adsorbent
$q_{e,i}$	:	Equilibrium uptake of metal ion
q_i	:	Equilibrium uptake of component
$q_{e,exp}$	:	Experimental metal uptake capacity

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q_{em}	:	Metal uptake capacity at equilibrium
q_{em}	:	Total metal uptake capacity
Q	:	Volumetric flow rate
Q_o	:	Maximum solid-phase concentration
$Q_{e,exp}$	:	Experimental metal removal at equilibrium
Q_{em}	:	Metal removal at equilibrium
Q_e	:	Equilibrium metal removal
R	:	Gas constant
RO	:	Reverse osmosis
R-P	:	Redlich-Peterson
RRH	:	Raw rice husk
SRS	:	Sheindorf-Rebuhn-Sheintuch
SS	:	Stock solution
t	:	Time
t_B	:	Breakthrough time
t_E	:	Exhaustion time
t_s	:	Service time
T	:	Ternary
Temp.	:	Temperature
TQ_t	:	Total metal removal at time 't'
$TQ_{e,exp}$	:	Experimental total metal removal at equilibrium
$Tq_{e,exp}$	:	Experimental total metal uptake capacity
Tq_t	:	Total metal uptake at time 't'
TQ_e	:	Total metal removal at equilibrium
Tq_e	:	Total metal uptake at equilibrium

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TC_e	:	Total residual metal concentration at equilibrium
U	:	Linear flow rate
V_t	:	Throughput volume
V	:	Solution volume
VAAC	:	Van apple pulp
Z	:	Packed bed column depth
Z_o	:	Critical bed depth

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Abstract

Adsorption is one of the most widely applied techniques for environmental remediation of heavy metals. The removal of heavy metals from mono- and multi-metal ion systems through the process of adsorption have been investigated and reported in published literatures. The main focus of multi-metal ion adsorption studies was to investigate the competition of metal ions for adsorption sites keeping higher total initial metal ions concentration on mass basis in aqueous phase compared to mono-metal ion systems. Further, most of the batch and continuous mode column studies have been investigated by mentioning the initial pH of the solution. However, no attentions were paid to monitor and report variations in solution pH during the course of experiments as well as the impact of changes in solution pH on the metal ions removal. Also, no literatures are available to throw light on the potential of adsorbent for metal removal when exposed to a metal ions repeatedly followed by exposure to another metal ions and consequently migration of already adsorbed metal ions. Further, the main focus of multi-metal ion systems column studies were to compare the breakthrough curves of metal ions from multi-metal ion systems with mono-metal ions systems. However scanty literatures are available which investigate adsorption of metal ions on already loaded column bed and consequently fate of the already adsorbed metal ions in terms of possible migration back into effluent solution if any. In the present work attempts have been made to address some of these issues.

The present work is aimed at carrying out kinetics, equilibrium and column studies for metal removal/uptake under uncontrolled/controlled pH conditions by granular activated alumina (GAA) from mono-, binary- and ternary-metal ion systems of Cu(II), Pb(II) and Cr(III) at fixed total initial metal ion concentration in the solution. The presence of Cu(II), Pb(II) and Cr(III) metal ions together in aqueous phase had substantial effect on their availability with variation in solution pH. The total residual metal ions concentration remaining in solution from selected combinations of Cu(II)+Pb(II), Cr(III)+Pb(II) and Cu(II)+Cr(III) binary-metal ion systems investigated under uncontrolled and controlled pH conditions with total initial metal ion concentration of approximately 0.60 meq/L overlapped within 95% confidence interval. It indicated that the concentration of total metal ions remaining in aqueous phase was fairly independent of proportion of initial metal ion concentration in selected binary-metal ion systems as long as total initial metal ions concentration was approximately the same. Further, the total metal uptakes under controlled pH conditions and total metal removals under uncontrolled pH conditions were observed to be similar and fairly independent of proportion of initial metal ion concentrations present in selected combinations of binary- and ternary-metal ion systems as long as total initial metal ions concentration in the combinations was approximately 0.60 meq/L even though ionic radius, valence and atomic weights of the metal ions were different from each other. During two sets of batch tests, displacement of already adsorbed target mono-metal ions back into solution was observed along with non-target metal removal under uncontrolled pH conditions and non-target metal uptake under controlled pH conditions. When GAA loaded with a mono-metal ion system during the first three loading cycles was exposed to another mono-metal ion system in the fourth loading cycle, additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions of the other metal ion was observed along with migration of metal ions loaded onto GAA during the first three loading cycles to bulk solution. Two mathematical relationships i.e. power and polynomial curves well predicted metal ion removals at equilibrium from mono-, binary- and ternary-metal ion systems investigated under uncontrolled pH conditions while Freundlich isotherm model well described metal ion uptakes at equilibrium from mono-, binary- and ternary-metal ion systems investigated under controlled

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pH conditions. The variations in metal removals at equilibrium from mono-metal ion systems generally appeared to overlap at 95% confidence intervals with variations in total metal removals at equilibrium from the combinations of binary-metal ion systems and varied within a small band with the ternary-metal ion system having total initial metal ion concentration of 0.60 meq/L. Similarly total metal uptakes at equilibrium from mono-, binary- and ternary-metal ion systems having total initial metal ion concentration of 0.60 meq/L varied within small band. It indicated that the metal removals at equilibrium and metal uptakes at equilibrium depend on the total initial metal ion concentration present in the solution rather than on ionic radius, valence and atomic weights of individual metal ions. During initial phases of column operation of virgin beds loading and washed beds reloading with mono- and binary-metal ion systems, the effluent solution pH coming out of the virgin and washed beds were observed to increase rapidly from initially adjusted pH of 5.00 under uncontrolled pH conditions and initially buffered pH of 5.00 under controlled pH conditions to higher levels and then decreased back close to initially adjusted and buffered pH levels. This variation in effluent solution pH observed during column operation of virgin beds loading and washed beds reloading was unusual compared to variation in solution pH observed during kinetics and equilibrium studies. The column beds had shown additional metal removal capability when virgin beds loaded with a mono-metal ion system or a combination of binary-metal ion system followed by reloading of washed beds with another mono-metal ion system or another combination of binary-metal ion system under uncontrolled and controlled pH conditions. When the virgin beds loaded with mono-metal ion system (termed as the first metal) were washed and then reloaded with another mono-metal ion system (termed as the second metal) under uncontrolled and controlled pH conditions, migration of the first metal ion from the washed beds to the effluent solution took place. This migration was less for Cr(III) metal compared to Cu(II) and Pb(II) metal ions. When virgin beds loaded with B[Cu(0.45)+Pb(0.15)] combination were washed and reloaded with B[Cu(0.15)+Pb(0.45)] combination under uncontrolled and controlled pH conditions, the effluent Cu(II) concentration was observed to be higher than 0.15 meq/L after initial period of column operation. It indicated migration of Cu(II) from the washed beds which was previously loaded with B[Cu(0.45)+Pb(0.15)] combination. However, during column studies with other combinations of binary-metal ion systems, such a migration of metal ions during reloading of washed bed was not observed. With the increase in bed depths from 3.0 cm to 6.0 cm, the breakthrough curves with mono- and binary-metal ion systems under uncontrolled and controlled pH conditions appeared to shift to the right yielding an increased service times and breakthrough throughput volumes. The order of loading and reloading of virgin and washed beds with mono- and binary-metal ion systems under uncontrolled and controlled pH conditions appeared to have bearing on higher amounts of metals removals by the column beds.

Keywords: Adsorption, Heavy metals, Copper, Lead, Chromium, Mono- and multi-metal systems, Granular activated alumina, Uncontrolled pH, Controlled pH, Batch studies, Column studies.

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CHAPTER 1

INTRODUCTION

A large number of batch studies have been reported for heavy metal adsorption from mono-metal ion systems on different adsorbents over the past few decades (Ayoob & Gupta, 2008; Babel & Kurniawan, 2003; Febrianto et al., 2009; Foo & Hameed, 2009). However, industrial wastewaters rarely contain a single heavy metal ion. For example, waste effluent from mining, metallurgical, tannery, chemical and battery manufacturing contain Cu(II), Pb(II) and Cd(II) in varying concentrations (Li et al., 2011; Meena et al., 2005). Ni(II) and Cd(II) ions are frequently encountered in mine drainage, effluents from plating plants, paint and ink formulation units (Srivastava et al., 2006). Even groundwater may be contaminated with more than one metal ion such as As(III), Fe(II), Mn(II), Cu(II) and Pb(II) in varying proportions (Murugesan et al., 2006; Vilensky et al., 2002). Adsorption process is considered as one of the preferred methods for removal and recovery of heavy metals from industrial effluents and groundwater. In the recent past, a few efforts have been directed to understand kinetics and equilibrium of heavy metal adsorption from binary- and multi-metal ion systems which are critically reviewed in subsequent paragraphs.

The kinetics of metal biosorption from binary-metal ion system comprising of Cr(VI) and Fe(III) on *C. vulgaris* and *R. arrhizus* have been investigated with an aim to compare the effect of increase in concentration of Cr(VI) ion on the initial adsorption rate of Fe(III) or vice-versa (Sağ et al., 1998a). It reported decrease in initial adsorption rate of one metal ion with increase in concentration of the other and the combined biosorptive action of Cr(VI) and Fe(III) ions on C. *vulgaris* and *R. arrhizus* was found to be antagonistic. Similar studies were also carried out for biosorption of Cu(II) and Zn(II) on *R. arrhizus* (Sağ et al., 1998b). However, these studies did not address the variation in solution pH during the process and consequently the metal removal mechanisms i.e. either by precipitation or adsorption or combination of both. Further these studies have failed to investigate simultaneous biosorption of metal ions from binary-metal ion system.

The kinetics of metal uptake was investigated from mono-metal ion systems of Cd(II) and Ni(II) onto bagasse fly ash (Srivastava et al., 2006). The solution pH was observed to increase from an initial pH of 6.0 to 8.4 for Cd(II) and 8.3 for Ni(II) within a short span of

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about 20 min. At a pH value of 6.0, the cadmium was present in the Cd^{2+} form while at pH value of > 8.0, the predominating form of cadmium was $Cd(OH)^{+}$ thereby ensuring cent percent Cd(II) availability in the solution. However, Ni(II) formed settleable hydroxide precipitate at a pH value of > 7.7. The availability of Cd(II) ions and formation of Ni(II)-hydroxide precipitate with change in solution pH could only be assessed if the experiments were carried out using binary-metal ion system of Cd(II) and Ni(II), which was not attempted in this study (Srivastava et al., 2006). Further, simultaneous adsorption of both the metal ions from the binary-metal ion system might have taken place on the adsorbent. It indicates a need to carry out kinetic studies with binary-metal ion system to evaluate the overall metal removal under varying or a fixed pH conditions.

The importance of simultaneous adsorption of two or more heavy metal ions and presence of interactive effects between metal ions have led to an elaborate investigation to understand the competitive binding of Cu(II), Pb(II) and Cd(II) onto an iminodiacetic acid (IDA) chelating resin from mono- and binary-metal ion systems (Li et al., 2011). The kinetics were carried out using fixed initial concentrations of 0.5, 1.0 and 2.0 mmol/L for the target metal ion in presence of equi-molar concentration of interferential metal ion in the binary-metal ion systems. The metal uptake profiles from binary-metal ion systems indicated decreased metal uptake compared to respective mono-metal ion system with increase in interferential metal ion concentration indicating competition amongst metal ions for adsorption sites. However, total metal uptake capacities obtained from binary-metal ion systems investigated were quite higher compared to the same of mono-metal ion systems. The difference in metal uptake capacities from mono- and binary-metal ion systems could be attributed to increased total metal ion concentration initially present in the solution in case of binary-metal ion systems, thereby increasing the driving force – concentration gradient, compared to mono-metal ion systems for the fixed number of adsorption sites available. The kinetics of metal uptake should have also been investigated by maintaining a fixed total initial metal ion concentration in the solution thereby keeping the driving force unchanged in mono- and binary-metal ion systems. Similarly multi-metal ion adsorption equilibrium studies were investigated wherein increased total initial metal ion concentration in multi-metal ion systems resulted in decreased uptake of metal ions compared to uptake from mono-metal ion systems and based on these results interactive effect of metal ions have been discussed (Baig et al., 2009; Sağ et al., 2001; Srivastava et al., 2006). Further, the results of most of the metal removal studies by adsorption processes from mono- and multi-metal ion systems have been

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reported on mass basis. As long as only mono-metal ion systems are being handled, this approach appears to be logical. However, when adsorption processes are applied for binary- and/or multi-metal ion systems where all the metals are going onto the surface of the adsorbent in different proportions simultaneously, then possibly expressing results on mass basis may lead to complicacy. Many of the authors working on the removal of metal ions from multi-metal ion systems have reported their results on mass basis considering only a particular metal ion while indicating the presence of other metal ions in the aqueous phase without quantifying its fate in the aqueous phase (Baig et al., 2009; Sağ et al., 2001; Srivastava et al., 2006). This approach fails to indicate the overall metal-uptake capacity of adsorbents tested. Some of the authors have investigated the kinetics and/or equilibrium by considering a fixed initial concentration of individual metal ions both in the mono- as well as multi-metal ion systems and have attempted to compare the results. However, in this case, the concentration gradients might have been entirely different in mono- and multi-metal ion systems and therefore, the comparison of adsorption results might not be justified. Further in many adsorption studies, pH of the solution was not controlled during adsorption process which might have resulted in removal of metal ions by precipitation along with adsorption.

Although batch laboratory adsorption studies provide useful information on the application of adsorption to the removal of specific waste constituents, continuous column studies provide the most practical application of this process in water/wastewater treatment. A few multi-metal column studies such as the biosorption of Cu(II), Pb(II), Zn(II) and Ni(II) from a mixed solution of the metals on polyurethane immobilised biomass (Zhang & Banks, 2006), removal of Pb(II), Cu(II), Zn(II) and Mn(II) from the leachate collected from the open dumping site on rice husk (Mohan & Sreelakshmi, 2008) and biosorption of Pb(II) and Cd(II) from aqueous solutions by protonated *Sargassum glaucescens* biomass (Naddafi et al., 2007) have aimed to study preferential adsorption of metal ions by comparing obtained breakthrough curves for metal ions from mono-metal ion system with the same obtained from mixture of metal ions. However, different experimental conditions in terms of total initial metal ions concentration was employed in mono- and multi-metal ions systems which eventually resulted in competition among metal ions for adsorption sites. Hence it is necessary to carry out mono- and multi-metal ion system column studies with fixed total initial metal ions concentration in solution. Further after exhaustion of column bed with one metal, its regeneration was carried out using different eluents. However literature is not

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available to address whether already exhausted column bed accommodates other metal ion and if so, up to what extent and what happens to already adsorbed metal ions.

Hence present research work was aimed to investigate metal removal from mono-, binary- and ternary-metal ion systems with a fixed total initial metal ion concentration in the solution. The studies were carried out under uncontrolled and controlled pH conditions so as to compare metal removals under uncontrolled pH conditions and metal uptakes under controlled pH conditions. The metal ions concentrations were expressed on equivalent basis so as to take into account the differences in valence and atomic weights of selected metal ions as well as to facilitate algebraic summation of concentrations of metal ions which will eventually help in comparison of overall metal removal and overall metal uptake from mono-, binary- and ternary-metal ion systems. Batch studies for mono-, binary- and ternary-metal ion systems were carried out with an aim to investigate (a) the availability of metal ions in aqueous phase at different solution pH (b) effect of variation in contact time on metal ion concentration remaining in solution under uncontrolled and controlled pH conditions (c) kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions and (d) equilibrium metal removal under uncontrolled pH conditions and equilibrium metal uptake under controlled pH conditions. Further, potential of previously loaded adsorbent with a metal ion or combination of binary-metal ion system for additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions for the same metal ion and/or to another metal ion or combination of binary-metal ion system were also investigated. The continuous mode column studies were also carried out for mono- and binary-metal ion systems by maintaining a fixed value of total initial metal ion concentrations in the solution under uncontrolled and controlled pH conditions. The continuous mode column studies in this work have been planned to investigate variation in pH of effluents coming out of the column beds, additional metal removal potential of exhausted/loaded bed if reloaded with another metal ion and migration of previously removed metal ion from the bed into the effluent when reloaded with another metal ion, if any.

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CHAPTER 2
LITERATURE REVIEW

Most of the heavy metals present in surface waters are generally coming from untreated or treated industrial effluents dealing with metal processing works. The solubility of trace heavy metals in surface waters is predominately controlled by the water pH, the type and concentration of ligands with which the heavy metal ions can form soluble metal ligand complexes and oxidation state of mineral components. Similarly, the groundwater may also contain considerable amounts of heavy metals due to geological formation of the location. Simple physical processes like screening, settling and filtration are inadequate to separate heavy metal ions present at trace levels in water/wastewater. Several methods have been developed and applied to remove heavy metal ions present in water/wastewater at trace levels, which include ion-exchange, membrane processes, electrochemical techniques and biological process.

Chemical precipitation is a preferred method for heavy metal removal from water/wastewater containing higher concentrations of metal ions. It involves addition of chemicals to alter the physical state of dissolved and suspended heavy metal ions to settleable form and facilitate their removal by sedimentation (Tchobanoglous et al., 2003). Common forms of precipitants include hydroxides (OH^-), sulphide (S^{-2}) and carbonates (CO_3^{-2}). For precipitation of metal ions as hydroxides, every metal has a distinct and different pH level at which the precipitation occurs. Precipitation is accompanied by formation of large amounts of sludge containing heavy metals. Metal bearing sludge-especially metal-hydroxide sludges are inherently susceptible to leaching into groundwater when sludges are disposed off in landfills.

Ion exchange is a unit process in which ions of a given species are displaced from an insoluble exchange material by ions of a different species present in solution (Tchobanoglous et al., 2003). Materials used for the exchange of metals include zeolites, weak and strong anionic and cationic resins, chelating resins, and microbial and plant biomass. Chelating resins such as aminophosphonic and iminodiacetic resins have been manufactured to have a high selectivity for specific metals, such as Cu, Ni, Cd, and Zn. Most of the ion exchange resins are expensive and release other cations such as H^+ or Na^+ in aqueous solution. Process

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efficiency is strongly pH dependent as most metals bind better at higher pH, due to less competition from protons for adsorption sites (Tchobanoglous et al., 2003). High concentrations of influent total suspended solids may plug the ion exchange bed and cause high head loss and inefficient operation. The exhausted ion-exchange medium is highly concentrated with heavy metal ions and requires careful disposal. Presence of oxidants, particles, solvents and polymers may affect the performance of ion-exchange resins.

Reverse osmosis (RO), nanofiltration (NF) and elecrtodialysis (ED) are the membrane separation processes which are used for the removal of heavy metals (Tchobanoglous et al., 2003). RO and NF involve an ionic exclusion process where small particles are rejected by the water layer adsorbed on the surface of the membrane which is known as dense of the membrane. In case of ED, ions are transported through semi permeable membrane under the influence of an electric potential. These membrane processes are expensive as high capital and operating costs are required by the higher energy input to develop pressure needed for operation. Other recognizable limitations include membrane fouling and deterioration with time resulting from deposition of soluble materials, organic materials, suspended and colloidal particles and other contaminants thus requiring high level of pretreatments.

The methods to remove heavy metals from water/wastewater using precipitation, ion exchange and membrane processes are expensive or ineffective, especially when the metal concentration is less than 100 ppm (Miretzky et al., 2006; Schiewer & Volesky, 1995). The sludge generated in the precipitation method poses challenges in its handling, treating and land-filling. Ion exchange usually requires a high capital cost of the equipment as well as a high operational cost due to use of chemicals for resin regeneration. Electrolysis allows the removal of metal ions from the solution in a solid metallic form for recycling. The advantage of this method is that there is no need for additional chemicals, and hence, there is no sludge generation. However, it is inefficient at a low metal concentration. Membrane processes such as RO and ED tend to suffer from the instability of the membranes in salty or acidic conditions and fouling by inorganic and organic substances present in wastewater (Doan et al., 2008).

Adsorption techniques have gained favour in recent years because of its proven efficiency in the removal of heavy metals present at trace levels in the water/wastewater. Adsorption is looked upon as better technology due to its simplicity and high efficiency

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performance even for a minute amount of heavy metals (Choy et al., 2000). Adsorption process is a surface phenomenon by which multi-component fluid (gas or liquid) mixture is attracted to the surface of a solid adsorbent and forms attachments via physical or chemical bonds, is recognized as the most efficient, promising and widely used fundamental approach in water/wastewater treatment processes (Foo & Hameed, 2009, 2010).

Development of activated carbon as an adsorbent with its large porous surface area has been witnessed in terms of its versatility for removal of a broad type of organic and inorganic pollutants dissolved in aqueous media (Foo & Hameed, 2010; Mohan & Pittman Jr, 2006). Despite activated carbons prolific use in adsorption processes, the biggest barrier of its application by industries is its cost-prohibitiveness adsorbent and difficulties associated with its regeneration (Ahmaruzzaman, 2008; Foo & Hameed, 2010). Realizing the complication, a growing exploitation to evaluate the feasibility and suitability of natural, renewable and low-cost materials (such as bamboo dust, peat, chitosan, lignite, fungi, moss, bark husk, chitin, coir pith, maize cob, pinewood sawdust, rice husk, sugar cane bagasse, tea leaves, sago waste, etc.) as alternative adsorbents in water pollution control, remediation and decontamination processes has been undertaken over the past few decades (Ahmaruzzaman, 2008; Foo & Hameed, 2010; Kalderis et al., 2008).

Equilibrium data, commonly known as adsorption isotherms and kinetic models, are the basic requirements for the design of adsorption systems. Adsorption isotherm is an invaluable curve describing the phenomenon governing retention or release or mobility of a substance from the aqueous media to a solid-phase at a constant temperature (Foo & Hameed, 2010). Adsorption isotherms describe how pollutants interact with the adsorbent materials, and thus are critical for optimization of the adsorption mechanism pathways, expression of the surface properties and capacities of adsorbents, and effective design of the adsorption systems. Adsorption isotherm is a mathematical expression to depict the distribution of solute between the solid and liquid phase at a fixed temperature. The isotherm models relate the amount of solute adsorbed per unit weight of adsorbent (q_e) with amount of solute retained in solvent (C_e) at equilibrium. Generally, the q_e amount increases with increase in C_e value, but not in direct proportion. Over the years, a wide variety of single component isotherm models (such as Henry's law, Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Hill, Flory–Huggins and Radke–Prausnitz isotherm) have been developed for the modeling of adsorption of metal ions

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from single metal ion systems (Foo & Hameed, 2010). Industrial wastewater rarely contain single metal ion in aqueous phase and hence few models have also been developed to describe equilibrium in multi-metal ion systems. Further, continuous mode column studies provide most practical application of adsorption studies and hence few efforts have also been directed to carry out multi-metal ion adsorption column studies. Subsequent sections describe most of the single and multi-metal ions adsorption isotherm models available in the literature and studies carried out related to adsorption of metal ions from multi-metal ion systems.

2.1 Single component adsorption isotherm models

2.1.1 Single parameter isotherms

For adsorption on a uniform surface at sufficiently low concentrations such that all molecules are isolated from their nearest neighbours, the equilibrium relationship between fluid phase and adsorbed phase concentrations will be linear. This linear relationship is commonly known as Henry's law (Ruthven, 1938) as presented in Table 2.1. This is the simplest model having a single parameter. This model is applicable at low effluent concentration only (Maurya & Mittal, 2010). Henry's law model was applied to describe the experimental data obtained for the sorption of Hg(II) onto *C. papaya* (Basha et al., 2008). This study revealed that this model completely failed to predict the equilibrium isotherm for biosorption of Hg(II). This might be due to the unavailability of sorption data in the lower range of Hg(II) concentration. Henry's model was also applied to describe the experimental data obtained from the sorption of Methylene Blue and Rhodamin B on the surface of activated carbon and fungal biomass (Maurya & Mittal, 2006). This model again completely failed to predict the equilibrium isotherm of any of the adsorbate–adsorbent systems mainly due to unavailability of sorption data in the lower range of dye concentrations.

2.1.2 Two parameter isotherms

Langmuir isotherm model (Table 2.1) is the empirical model which assumes monolayer adsorption i.e. adsorbed layer is only one molecule thick. Adsorption occurs at fixed number of definite localized sites that are identical and equivalent, with no lateral interaction between adsorbed molecules, even on adjacent sites. Langmuir isotherm refers to homogeneous adsorption, which each molecule possess constant enthalpies and sorption activation energy (Langmuir, 1918). This is one of the most widely used isotherm models for

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Table 2.1: Single component adsorption isotherm models.

Isotherm model	Number of parameter(s) involved	Mathematical Expressions	General Remarks	References
Henry's Law	1	$q_e = K_h \times C_e$ where K_h = Henry's constant (L/g), q_e = equilibrium uptake (mg/g), C_e = equilibrium concentration of adsorbate (mg/L)	• Applicable at low effluent concentrations only • Very simple equation	Ruthven, 1938
Langmuir model	2	$q_e = \frac{q_m b C_e}{1 + b C_e}$ where q_e = equilibrium uptake (mg/g), q_m = maximum adsorbate uptake by adsorbent (mg/g), b = Langmuir adsorption constant (L/mg), C_e = adsorbate concentration in solution at equilibrium (mg/L)	• Monolayer sorption • Homogeneous adsorption energy	Langmuir, 1918
Freundlich model	2	$q_e = k \times C_e^{\frac{1}{n}}$ where k = Freundlich constant, $1/n$ = adsorption intensity, C_e = adsorbate concentration in solution at equilibrium (mg/L), q_e = equilibrium uptake (mg/g)	• Simple expression • Empirical in nature • Heterogeneous adsorption energy	Freundlich, 1926
Brunauer-Emmer- Teller (BET) model	2	$q_e = \frac{q_s \times C_{BET} \times C_e}{(C_s - C_e)\left[1 + (C_{BET} - 1)\left(\frac{C_e}{C_s}\right)\right]}$ where C_{BET} = BET adsorption isotherm (L/mg), C_s = adsorbate monolayer saturation concentration (mg/L), q_s = theoretical isotherm saturation capacity (mg/g), q_e = equilibrium adsorption capacity (mg/g) and C_e = adsorbate concentration in solution at equilibrium (mg/L)	• Multiple sorption • Applicable for gas phase adsorption	Bruanuer et al., 1938
Temkin isotherm	2	$q_e = \left(\frac{RT}{b}\right) \times \ln(A C_e)$ where R = gas constant (8.314 J/mol K), T = absolute temperature (K), A and b = constants	• Temperature dependent expression • Excellent for predicting the gas phase equilibrium	Basha et al., 2008; Tempkin & Pyzhev, 1940

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Table 2.1 continues.....

Dubinin – Radushkevich (DR) isotherm model	2	$q_e = q_s \times \exp\left(-B \times \varepsilon^2\right)$ where, $\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right]$, B = DR model constant (mol^2/kJ^2), q_s = DR model constant (mg/g), and R, T and C_e represent the gas constant (8.314 J/mol k), absolute temperature (K) and adsorbate equilibrium concentration (mg/L) respectively	• Rarely applied onto liquid-phase adsorption • Temperature dependent expression	Dubinin & Radushkevich, 1947; Febrianto et al., 2009; Foo & Hameed, 2010
Redlich–Peterson (R-P) isotherm model	3	$q_e = \frac{K_R \times C_e}{1 + a_R \times C_e^g}$ where K_R = R-P isotherm constant (L/g), a_R = constant $(L/mg)^g$, g = an exponent having value between 0 and 1, C_e = equilibrium liquid phase concentration of the adsorbate (mg/L), q_e = equilibrium adsorbate loading onto the adsorbent (mg/g)	• Can be applied either in homogeneous or heterogeneous systems • Empirical equation	Febrianto et al., 2009; Redlich & Peterson, 1959
Sips model (Combination of Langmuir and Freundlich)	3	$q_e = \frac{q_m (b_s C_e)^\gamma}{1 + (b_s C_e)^\gamma}$ where b_s = Sips model isotherm constant (L/g), γ = Sips model exponent, q_m = maximum adsorbate uptake by adsorbent (mg/g), C_e = adsorbate concentration in solution at equilibrium (mg/L)	• Combination of Langmuir and Freundlich • Reduces to Freundlich at low concentrations • Predicts a monolayer adsorption capacity of Langmuir model at higher concentrations	Sips, 1948
Toth equation	3	$q_e = \frac{q_{max} \times b_T \times C_e}{\left[1 + (b_T C_e)^{n_T}\right]^{\frac{1}{n_T}}}$ where, q_{max} = maximum sorption capacity (mg/g), b_T = sorption affinity parameter (L/mg), n_T = heterogeneity parameter, C_e = adsorbate concentration in solution at equilibrium (mg/L), q_e = equilibrium uptake (mg/g)	• Improvement over Langmuir and Freundlich • Empirical equation	Toth, 1971

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Table 2.1 continues.....

Radke-Prausnitz isotherm model	3	$q_e = \frac{a_R r_R C_f^{B_R}}{a_R + r_R C_f^{B_R - 1}}$ where a_R and r_R = Radke–Prausnitz model constants, β_R = Radke–Prausnitz model exponent, q_e = equilibrium uptake (mg/g), C_f = equilibrium concentration of adsorbate in solution (mg/L)	• Simple expression • Empirical • Uses three parameters	Vijayaraghavan et al., 2006
Weber and van Vliet	4	$C_e = a_1 \times Q^{(a_2 Q^{a_3} + a_4)}$ where a_1, a_2, a_3 and a_4 = Weber and van Vliet parameters	• Successfully applied for adsorption of hydrocarbon on activated carbon	Maurya & Mittal, 2006
Fritz–Schluender	5	$Q_e = \frac{\alpha_1 C_e^{\beta_1}}{(\alpha_1^{'} + \alpha_2 C_e^{\beta_2})}$ where α'_1, α_1, α_2, β_1 and β_2 = Fritz- Schluender constants	• Improvement over Langmuir and Freundlich • Uses five parameters	Maurya & Mittal, 2006

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describing aqueous phase equilibria of metal adsorption (Foo & Hameed, 2009, 2010).

Freundlich isotherm (Table 2.1) is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. The Freundlich model for heterogeneous surface energy could be derived by assuming a logarithmic decrease in the heat of adsorption with the fraction of surface covered by the adsorbed solute (Freundlich, 1926). Freundlich isotherm has the ability to fit nearly all experimental adsorption-desorption data, and is especially excellent for fitting data from highly heterogeneous adsorbent systems (Foo & Hameed, 2009, 2010).

The Brunauer-Emmer-Teller (BET) model assumes that number of layers of adsorbate accumulates at the surface and that the Langmuir model applies to each layer (Bruanuer et al., 1938). The kinetics concept proposed by Langmuir is applied to this multiple layer process, that is the rate of adsorption on any layer is equal to the rate of desorption from that layer. The BET equation is generally used for gas-phase adsorption, where multilayer adsorption is frequently encountered (Bruanuer et al., 1938; Foo & Hameed, 2010). Superb applicability of this model was shown for the biosorption of Cr(VI) using *Lyngbya putealis* exopolysaccharides, claiming multilayer adsorption occurring in the system (Kiran & Kaushik, 2008). However, simple curve fitting procedure and high value of correlation coefficient was not valid enough to justify the occurrence of multilayer adsorption. Ideal assumptions within this model namely all sites are energetically identical along with no horizontal interaction between adsorbed molecules may be correct for heterogeneous material and simple non-polar gases but not for complex systems involving heterogeneous adsorbent such as biosorbents and metals. For that reason, this equation is unpopular in the interpretation of liquid phase adsorption data for complex solids.

Temkin isotherm (Table 2.1) was proposed to describe adsorption of hydrogen on platinum electrodes within acidic solutions (Basha et al., 2008; Tempkin & Pyzhev, 1940). The derivation of the Temkin isotherm is based on the assumption that the decline of the heat of sorption as a function of temperature is linear rather than logarithmic. Temkin isotherm is excellent for predicting the gas phase equilibrium (Febrianto et al., 2009). In case of liquid phase adsorption especially in heavy metals adsorption using biosorbent, this model falls short in representing the equilibrium data (Febrianto et al., 2009). Adsorption in the liquid phase is a more complex phenomenon than gas phase adsorption as the adsorbed molecules

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do not necessarily organize in a tightly packed structure. The presence of solvent molecules and formation of micelles from adsorbed molecules add to the complexity of liquid phase adsorption. Numerous factors including pH, solubility of adsorbate in the solvent, temperature and surface chemistry of the adsorbent influence adsorption from liquid phase. Since the basis of derivation for Temkin equation is a simple assumption, complex phenomenon involved in liquid phase adsorption is not taken into account by this equation (Febrianto et al., 2009) and as a result this equation is often not suitable for representation of experimental data in complex systems. Dubinin and his co-workers (Dubinin & Radushkevich, 1947) conceived Dubinin–Radushkevich (DR) isotherm model for subcritical vapors in micropore solids where the adsorption process followed a pore filling mechanism onto energetically non-uniform surface (Foo & Hameed, 2009, 2010). The Dubinin–Radushkevich (DR) model is excellent for interpreting organic compounds sorption equilibria (in gas phase condition) in porous solids (Foo & Hameed, 2009). DR model is rarely applied onto liquid-phase adsorption due to the complexities associated with other factors such as pH and ionic equilibria inherent in these systems. This approach was usually applied to distinguish the physical and chemical adsorption of metal ions (Apiratikul & Pavasant, 2008; Febrianto et al., 2009; Vijayaraghavan et al., 2006).

2.1.3 Three parameter isotherms

Redlich-Peterson (R-P) isotherm model (Table 2.1) is a hybrid isotherm featuring both Langmuir and Freundlich isotherms, which incorporate three parameters into an empirical equation (Redlich & Peterson, 1959). The model has a linear dependence on concentration in the numerator and an exponential function in the denominator to represent adsorption equilibria over a wide concentration range, that could be applied either in homogeneous or heterogeneous systems due to its versatility. This model is quite popular for the prediction of heavy metals biosorption equilibria data (Febrianto et al., 2009). This model fits the experimental data accurately in several systems, namely adsorption of cadmium and nickel onto bagasse fly ash (Srivastava et al., 2006), biosorption of chromium using suspended and immobilized cells of *Rhizopus arrhizus* (Preetha & Viruthagiri, 2007) as well as sorption of lead onto peat (Ho, 2006).

Sips isotherm (Table 2.1) is a combined form of Langmuir and Freundlich expressions (Sips, 1948) deduced for predicting heterogeneous adsorption systems (Günay et

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al., 2007) and circumventing the limitation of the rising adsorbate concentration associated with Freundlich isotherm model. At low adsorbate concentrations, it reduces to Freundlich isotherm; while at high concentrations, it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm. As a general rule, the equation parameters are governed mainly by the operating conditions such as the alteration of pH, temperature and concentration of adsorbate. Sips isotherm provides a reasonably accurate prediction of heavy metal biosorption experimental results with high value of correlation coefficient (R^2) (Apiratikul & Pavasant, 2008; Febrianto et al., 2009; Vijayaraghavan et al., 2006).

Toth isotherm model (Table 2.1) is another empirical equation developed to improve Langmuir isotherm fittings (Toth, 1971) and useful in describing heterogeneous adsorption systems, while satisfying both low and high-end boundary of the concentration (Vijayaraghavan et al., 2006). Its correlation presupposes an asymmetrical quasi-Gaussian energy distribution with most of its sites have adsorption energy lower than the peak (maximum) or mean value. Vijayaraghavan et al. (2006) used this isotherm for describing adsorption equilibria of Ni(II) onto *Sargassum wightii.* Toth equation offered the best model for nickel biosorption data at all pH conditions examined. However this isotherm is still unable to predict the isotherm in a particular heterogeneous system as in the biosorption of Hg(II) into *C. papaya* (Basha et al., 2008). Vijayaraghavan et al. (2006) used Radke-Prausnitz isotherm model for modeling equilibria of adsorption of Ni(II) onto *Sargassum wightii.* The Ni(II) biosorption data did not correlate well with Radke-Prausnitz model.

2.1.4 Four parameter isotherm

The Weber and van Vliet model (Table 2.1) is an empirical equation having four parameters (Maurya & Mittal, 2006) and similar to the three-parameter isotherms it also expresses adsorption capacity as an explicit function of equilibrium concentration. It provided a poor fit in comparison to most of the isotherm models having two degrees of freedom used to describe biosorption equilibria of two cationic dyes on activated carbon (Maurya & Mittal, 2006). The applicability of the Weber and van Vliet model has also been reported to be less satisfactory compared to Langmuir and Freundlich (Ting & Mittal, 1999; Wang et al., 1997).

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2.1.5 Five parameter isotherm

The Fritz-Schluender isotherm model (Table 2.1) is also an empirical equation of five degrees of freedom and successfully applied to liquid-phase adsorption of organic solute to the activated carbon surface (Maurya & Mittal, 2006). Maurya and Mittal (2006) applied sixteen numbers of adsorption isotherms to represent biosorption of two cationic dyes onto activated carbon. A comparison of the Fritz-Schluender isotherm model having the highest correlation coefficient with the most widely used isotherm models (i.e. Langmuir and Freundlich isotherm models) showed that there was improvement in the predictions by the Fritz-Schluender model over either the Langmuir or Freundlich model, but it was not substantial. Besides, application of the Fritz-Schluender model was not as simple. Thus, the Langmuir and Freundlich models could be used for predicting the adsorptive processes.

Many researchers have successfully employed Lamgmuir isotherm model for adsorption of heavy metals ions by various adsorbents. The applicability of the Langmuir isotherm were tested to describe Cd(II) adsorption by hematite and monolayer coverage (q_m) was observed as 0.24, 0.23, and 0.22 mg/g at 20, 30, and 40 ^oC respectively at pH 9.2 (Singh et al., 1998). The applicability of the Langmuir, Freundlich, Redlich-Peterson and Temkin adsorption models were tested for Cu(II) adsorption by *Tectona grandis* L.f. leaves powder (Prasanna Kumar et al., 2006). Langmuir model interpreted the experimental data well with maximum adsorption capacity of 15.43 mg/g of Cu(II) ion. Equilibrium biosorption of Cd(II) and Cu(II) metal ions was investigated using wheat straw as an adsorbent (Dang et al., 2009). Among the model tested, namely the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms, the biosorption equilibrium for both Cd(II) and Cu(II) was best described by the Langmuir model.

Maurya and Mittal (2006) investigated the applicability of equilibrium isotherm models for biosorptive uptake of Methylene Blue and Rhodamin B (cationic dyes) on two types of macrofungi biosorbents and they compared results with adsorption on activated carbon. Results showed that in general the accuracy of models to fit experimental data improved with the degree of freedom (i.e. number of parameters in the expression). The Fritz-Schluender model gave the most accurate fit (R^2 values in the range of 0.85–0.99) to all experimental data in comparison to other models used both for activated carbon and the biosorbent. But based on the study, Maurya and Mittal (2006) concluded that most widely

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used isotherm models, i.e., Langmuir and Freundlich, could be used to describe the sorption equilibrium of biosorptive processes with a fair degree of accuracy, owing to the mathematical ease in the use of these models.

2.2 Competitive isotherm models

One of the major concerns arising from the adsorption of heavy metals from water/wastewater is the simultaneous presence of more than one metal ion in water/wastewater. The interference and competition between different metal ions, metal and solvents as well as metals and adsorption site are significant enough to take into account. Only few isotherms have been developed to describe equilibrium in multi-metal ion systems. These models range from simple ones based on the individual isotherm parameters only to more complex ones exploiting the individual isotherm parameters along with correction factors.

2.2.1 Competitive multicomponent isotherm models obtained using single component isotherm parameters

Non-modified competitive Langmuir model: The extension of basic Langmuir model to competitive adsorption is formulated as (McKay & Al Duri, 1989).

$$q_{e,i} = \frac{q_i b_i C_i}{1 + \sum_{j=1}^{n} b_j C_j} \tag{2.1}$$

where C_i and C_j are the concentrations of the adsorbates *'i'* and *'j'* remaining in liquid at equilibrium (mg/L), $q_{e,i}$ is the equilibrium uptake of the adsorbate *'i'* in the multicomponent system (mg/g), b_i and b_j are the Langmuir adsorption constants of the adsorbates in single component systems (L/g) and *'q_i'* is the Langmuir adsorption capacity of the adsorbate *'i'* (equivalent to q_m) in the single-component system (mg/g). The non-modified competitive Langmuir isotherm is based on the same basic assumptions as the single component Langmuir isotherm that the energy of adsorption between the specific adsorbing species and the surface site is constant and equal for each site, there is no interaction between components and there is equal competition between species for adsorption sites (McKay & Porter, 1997). But this model uses single component isotherm parameters for prediction of multicomponent isotherm and if sizeable difference in the monolayer saturation capacities of metal ions

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(obtained from single component isotherms for metals in system) exists then the competition and interaction among the metal ions will be significant. Therefore this model will not be suitable for representing the systems in which sizeable difference in monolayer capacity exist (McKay & Porter, 1997). Nevertheless, because of its simple and easy to handle formulation, particularly when it is considered more like a numerical description without any theoretical base than rigorous description of the thermodynamic phenomena encountered during the adsorption process, this competitive model remains one of the most employed in the literature.

Langmuir partially competitive multicomponent model: The partially competitive Langmuir isotherm allows for a partial competition in the adsorption of multiple adsorbates. For two-adsorbate systems, the isotherm could be written as (Jain & Vernon, 1973):

$$q_{e1} = \frac{(q_1 - q_2) \times b_1 \times C_1}{1 + b_1 C_1} + \frac{q_1 \times b_1 \times C_1}{1 + b_1 C_1 + b_2 C_1} \tag{2.2}$$

$$q_{e2} = \frac{q_2 \times b_2 \times C_2}{1 + b_1 C_1 + b_2 C_2} \tag{2.3}$$

where q_1, q_2 are maximum uptake capacities for metal '1' and '2' in single component systems respectively (mg/g); b_1, b_2 are Langmuir isotherms parameters for metal '1' and '2' in single component system (L/g); q_{e1}, q_{e2} are equilibrium uptake of metal ions '1' and '2' respectively (mg/g) and C_1, C_2 are equilibrium concentrations of metal ions in equilibrium (mg/L). The first term of the right-hand side of Eq. (2.2) accounts for the amount of solute '1' adsorbed without competition. The second term, which is based on the original modified Langmuir isotherm, is for the amount of solute '1' adsorbed under competition with solute '2'. Eq. (2.3) is for the amount of solute '2' adsorbed under competition with solute '1'.

Redlich-Peterson multicomponent model: Three parameter isotherm of Redlich-Peterson that has been empirically developed for multi-component mixtures is given as (Mathews, 1975)

$$q_i = \frac{K_i \times C_i}{1 + \sum_{j=1}^{N} a_j \times C_j^{g_j}} \tag{2.4}$$

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where K_i, a_j, g_j are Redlich-Peterson parameters given by the individual Redlich-Peterson isotherms. However, details with respect to applicability of this model are not available.

2.2.2 *Competitive multicomponent isotherm models obtained using single component isotherm parameters with application of correction factors*

All the previously mentioned approaches have the aim of deducing competitive multicomponent isotherms only from single component isotherms, without any information other than from experimental competitive adsorption data. Better accuracy may be achieved by extracting additional coefficients from experimental competitive isotherms. Some of the models in this category are described below.

Modified competitive Langmuir model: Single component adsorption constants may not describe the interactions between individual metal ions as also between an individual metal ion and the mixture of metal ions in a system. The interactive effect could be incorporated in the single component isotherm models by correcting the individual adsorbate concentration by an interaction term, η_i. η_i is a characteristic of each species and depends on the concentrations of the other components in the solution. η_i can be estimated from the competitive adsorption data. The modified competitive Langmuir isotherm along with interaction term (η_i) is given as (Bellot & Condoret, 1993)

$$q_{e,i} = \frac{q_i b_i (C_{e,i}/\eta_i)}{1 + \sum_{j=1}^{n} b_j (C_{e,j}/\eta_j)} \tag{2.5}$$

where q_i and b_i are derived from the corresponding single component Langmuir isotherm models, $q_{e,i}$ is the equilibrium uptake of metal ion (mg/g) and $C_{e,j}$ is equilibrium concentration of metal ion (mg/L). The term *'η_i'* is estimated by minimizing the variance between experimental and calculated equilibrium data. The modified competitive Langmuir model approach provided excellent prediction of the binary adsorption data of Cu(II)-Cd(II), Pb(II)-Cd(II), and Pb(II)-Cu(II) on calcium alginate beads (Papageorgiou et al., 2009).

Sheindorf-Rebuhn-Sheintuch (SRS) model: The multi-component Freundlich isotherm could be expressed as (Sheindorf et al., 1981)

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$$q_i = K_i C_i \left(\sum_{j=1}^{z} a_{ij} C_j \right)^{n_i - 1} \tag{2.6}$$

where q_i is the equilibrium uptake of component *'i'* (mg/g); C_i and C_j are the concentrations of components *'i'* and *'j'* in the equilibrium solution (mg/L); K_i and n_i are the Freundlich constants obtained for *'i'* in a single-component system and a_{ij} is the competition coefficient for the adsorption of component *'i'* in the presence of component *'j'* which describe the inhibition to the adsorption of component *'i'* by component *'j'* and could be determined from experimental data of multicomponent systems. The Freundlich multi-component model along with extended Langmuir model was used for representing three metal biosorption equilibria using a fungal biosorbent (Sağ et al., 2001). Competition coefficients of Freundlich multicomponent model (a_{12}, a_{13}, a_{21}, a_{23}, a_{31}, *and* a_{32}) for three metal system i.e. of Cr(VI), Fe(III) and Cu(II) were estimated from the competitive biosorption data of Cr(VI), Fe(III) and Cu(II) ions using an MS excel 7.0 computer program. Extended Langmuir model showed better fits to the data from ternary systems than the multicomponent Freundlich model. All the parameters of the extended Langmuir model were estimated from the three-metal equilibrium data. On the other hand, the pre-exponential coefficients and exponents of the monocomponent isotherms are also parameters of the multicomponent Freundlich isotherm. The additional six parameters of the multicomponent Freundlich model were determined from the competitive adsorption data. This argument was put forward for the better fit to experimental data of extended Langmuir model compared to Freundlich multicomponent model.

Extended Freundlich isotherm model: This isotherm is an empirical extension of Freundlich model (Fritz & Schluender, 1974), restricted to binary mixtures

$$q_{e,1} = \frac{k_1 \times C_{e,1}^{\frac{1}{n_1}+x_1}}{C_{e,1}^{x_1} + y_1 \times C_{e,2}^{z_1}} \tag{2.7}$$

$$q_{e,2} = \frac{k_2 \times C_{e,2}^{\frac{1}{n_2}+x_2}}{C_{e,2}^{x_2} + y_2 \times C_{e,1}^{z_2}} \tag{2.8}$$

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where k_1, k_2, n_1 *and* n_2 are derived from single component Freundlich isotherms. The six other parameters are correction factors (x_1, y_1, z_1, x_2, y_2, z_2). Competitive extended Freundlich model fitted the binary adsorption equilibrium data of cadmium and nickel onto bagasse fly ash satisfactorily and adequately (Srivastava et al., 2006). Similar observations were made for binary adsorption equilibrium data of Cr(VI) and Fe(III) ions on *C. vulgaris* (Sağ et al., 1998a).

Ideal adsorption solution theory (IAST) – Freundlich isotherm model: This model is a simplification of the multi-component Freundlich isotherm and could be expressed as (Hand et al., 1985)

$$C_1 = \frac{q_i}{\sum_{j=1}^{N} q_j} \left(\frac{\sum_{j=1}^{N} n_j \times q_j}{n_i \times K_i} \right)^{n_i} \tag{2.9}$$

where '*i*' and '*j*' are the adsorbates in the multi-component system, C_i is the concentration of adsorbate remaining in solution at equilibrium, q_i is the equilibrium uptake of adsorbate at equilibrium and K_i, n_i are the Freundlich constants for the adsorbates in the single component system. IAST models are based on the ideal adsorbed solute theory, which assumes that the solutes in binary or multi-component mixtures behave independently of each other, without competition, interaction, or displacement effects. Thus, the IAST models fail to provide accurate prediction of the binary adsorption behavior, especially in cases where strong competition between the metal ions is present (Papageorgiou et al., 2009).

P-Factor model: This method is another correlative technique that has been developed (McKay & Al Duri, 1989). This P-factor model uses basic thermodynamic parameters characteristics of each system's Langmuir isotherm model and is based on adsorption capacity. It is easy method to use based on capacity factor P_i expressed as

$$P_i = \frac{\left(K^o/b^o\right)_{i,\,Single}}{\left(K/b\right)_{i,\,mixture}} \tag{2.10}$$

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where $K = q_{max} \times b$, (K^o/b^o) is adsorbent monolayer capacity for metal ion in single system (mg/g) i.e. q_{max} and (K/b) is adsorbent monolayer capacity for component in multi solute system (mg/g). This model assumes Langmuir isotherm, hence for each component '*i*' the multicomponent isotherm equation is described as

$$q_{e,i,multi} = \frac{1}{P_i} \times \frac{q_{max,i}\, b_i\, C_{e,i,multi}}{1 + b_i C_{e,i,multi}} \tag{2.11}$$

This model was used along with modified competitive Langmuir model, non-modified competitive Langmuir model for describing sorption of Cu(II), Cd(II) and Zn(II) onto the peat in multicomponent systems (McKay & Porter, 1997). Among the models used to describe the multicomponent equilibria, P- Factor model showed best fit to experimental data.

Extended Langmuir model: Assuming that the surface sites are uniform, and that all the adsorbate ions in the solution compete for the same surface sites, extended Langmuir equation for multi-component systems is derived (Yang, 1987) as

$$q_{e,i} = \frac{q_{max} b_i C_{e,i}}{1 + \sum_{j=1}^{n} b_j C_{e,j}} \tag{2.12}$$

where $q_{e,i}$ is equilibrium uptake of metal ion '*i*' (mg/g), q_{max} is maximum uptake capacity (mg/g), $C_{e,i}$ is equilibrium concentration of metal ion '*i*' (mg/L), b_i and b_j are constants (L/g). Here, the values of q_{max} and b_i can be obtained from the optimized fitting of Eq. (2.12) with the experimental data for the equilibrium adsorption of components in the multi-component system.

2.2.3 Multi-component adsorption equilibrium studies

Over the years, some of the models discussed above have been used to predict the equilibrium uptake of heavy metals in single as well as multi-component systems using adsorbents such as activated carbon, various biosorbents, natural occurring minerals, etc. Some of these studies are highlighted below:

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Equilibrium metal uptake performance of *Rhizopus arrhizus* was studied using aqueous solutions containing Cr(VI), Fe(III) and Cu(II) ions in ternary mixtures at an initial pH value of 2.0 (Sağ et al., 2001). The single component isotherms for Cr(VI), Fe(III) and Cu(II) were determined by varying the concentrations of metals over the 571-4170, 604-3342, 437-3015 µmol/L ranges respectively (25-200 mg/L on the basis of weight) while using the fixed amount of adsorbent (i.e. 1 g/L). The applicability of multicomponent adsorption models to the simultaneous biosorption of Cr(VI), Fe(III) and Cu(II) ions from ternary metal mixtures by *R. arrhizus* were carried out using initial concentrations of Cr(VI) ions between 446 and 2970 µmol/L while the Fe(III) and Cu(II) ion concentrations in each metal mixture were held constant over the range of 339-2538 and 429-2278 µmol/L respectively while keeping the adsorbent dose of 1 g/L. The multi-component biosorption equilibria were described by the extended Langmuir and Freundlich multi-component model. The extended Langmuir model described the experimental results better than the multi-component Freundlich model. The maximal capacity, q_{max} resulting from single and ternary systems was 605 µmol/g [for Cr(VI) alone] and 689 µmol/g [for Cr(VI) + Cu(II) + Fe(III)] respectively. By comparing the maximal adsorption capacities, the adsorption sites of Cu(II) and Fe(III) were likely to be overlapped. Thus the basic information provided from the maximal capacities, q_{max} violated the basic assumptions of the extended Langmuir model which proposed that the entire adsorbent surface is homogeneous and that there is no lateral interaction between adsorbate molecules, and thus the affinity of each binding site for the adsorbate molecules should be uniform. As a result, the adsorbent should have identical maximum capacity for each adsorbate present. Therefore, the extended Langmuir model cannot account for the adsorption equilibrium when the adsorbent appeared to have specific binding sites and distinct preference for each adsorbate. Also, it is important to note that for the ternary system [comprising of Cr(VI) + Fe(III) + Cu(II)], the total minimum and maximum initial concentrations considered were 1245 and 7599 µmol/L respectively which yielded the maximal capacity of 689 µmol/g while the maximal capacity for Cr(VI) was obtained as 605 µmol/g but the Cr(VI) concentration varied between 446 and 2970 µmol/L – much lower than the ternary system. As the equilibrium uptake is a function of concentration gradient existing in the system, there is need to carry out investigation on the uptake of metal components present in the mixture while maintaining the similar total initial metal ion concentrations in mono- and multi-metal ion systems. Although the equilibrium studies have been investigated on mole basis, no efforts were made to investigate the overall adsorption based on equivalents of metal ions going on to the surface of the adsorbent even though the

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valency of metal ions (i.e. adsorbates) used in this study were different. Further, in this investigation only initial pH of the solution has been mentioned and no information has been provided about pH of the solution at equilibrium and consequently exact removal process of metal ions from aqueous phase.

The capability of wheat straw to adsorb Ni(II) and Zn(II) in single and binary system was investigated using batch system in the initial concentration range of 5-150 ppm (Baig et al., 2009). For single metal solutions, among the three models tested, namely the Langmuir, Freundlich, and Temkin isotherms; the Freundlich model was suitable to describe the adsorption equilibrium for Ni(II) and Zn(II). To evaluate the different multi-component model's goodness of fit to the experimental data, an averaged error was used. For bimetal solutions, the IAST-Freundlich multi-component isotherm best fitted the experimental data, among the four models investigated i.e. the modified Langmuir multi-component model, the Langmuir partial competitive model, the Freundlich multi-component model and the IAST-Freundlich multi-component model. It appeared that the total initial metal ion concentration in single component system was different from multi-component system of Ni(II) and Zn(II). Consequently, different experimental conditions were adopted in mono- and binary-metal ion systems as far as total initial metal ion concentration in solution was concerned. Therefore, there is a need to carry out investigation maintaining the similar total initial metal ion concentration in mono- and multi-component systems. Also, no efforts were made to investigate the overall adsorption based on equivalents of metal ions going on to the surface of the adsorbent even though valency of metal ions (i.e. adsorbates) used in this system were the same.

The adsorption of Cd(II) and Ni(II) in competition was studied using bagasse fly ash (BFA) as an adsorbent at an optimum pH of 6.0 (Srivastava et al., 2006). For single system, initial metal ion concentration was varied from 10 to 100 mg/L. In binary metal ion mixture, for each initial concentration of Cd(II) solution (i.e. 10, 20, 30, 50, 100 mg/L), Ni(II) concentration was varied in the range of 10-100 mg/L (i.e. 10, 20, 30, 50, 100 mg/L). The isotherm parameters of all multi-component models were determined by minimizing Marquardt's percent standard deviation (MPSD). The single ion equilibrium adsorption data were fitted to the non-competitive Langmuir, Freundlich and Redlich-Peterson (R-P) isotherm models. The R-P and the Freundlich models represent the equilibrium data better than the Langmuir model in the studied initial metal concentration range (10-100 mg/L).

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Equilibrium isotherms for the binary adsorption of Cd(II) and Ni(II) ions onto bagasse fly ash (BFA) have been analyzed by using non-modified Langmuir, modified Langmuir, extended Langmuir, extended Freundlich and the Freundlich multi-component model (SRS) models. Based on MPSD error function, competitive extended Freundlich model fitted the binary adsorption equilibrium data satisfactorily and adequately. In this study also, the total initial metal ion concentration in single component systems were different from the multi-component systems. Also in order to analyze the antagonistic adsorption interaction of the two metal ions, the adsorption yields of single and binary-component systems were compared (Srivastava et al., 2006). It was expected that total adsorption yield must be equal to 54.80% for the total metal ion concentration of 200 mg/L (100 mg/L of each metal in mixture). However, the total experimental adsorption yield was only 25.70% for total metal ions concentration of 200 mg/L consisting of 100 mg/L each of Cd(II) and Ni(II). Based on single and binary system adsorption yields, competition among metal ions for adsorption sites have been described. Further, since the equilibrium studies have been investigated on mass basis, considerable difference in the atomic weights of metal ions will cause sizeable difference in their concentrations in terms of mole or equivalent basis. Hence it is necessary to investigate the mono- and multi-metal ion adsorption studies on equivalent basis with fixed total initial metal ions concentration in solution to facilitate the comparison of overall metal uptake capacities. Further, this study do not present pH of the solution at equilibrium from binary-metal ion system equilibrium studies, which again cannot help to elucidate the metal removal process exactly i.e., due to only adsorption or combined effect of precipitation and adsorption.

The simultaneous biosorption of Cr(VI) and Fe(III) was investigated on *C. vulgaris* and *R. arrhius* (Sağ et al., 1998a). In the single metal ion system, the adsorption isotherms were developed for optimum conditions and adsorption equilibrium data fitted to both the non-competitive Langmuir and Freundlich models. To determine adsorption characteristics of Cr(VI) ions in binary metal mixtures, the initial concentrations of Cr(VI) ions were varied between 25 and 150 mg/L while the Fe(III) ion concentration in each biosorption medium was held constant at 10, 25, 50, 75, 100, 150 and 250 mg/L. To determine adsorption characteristics of Fe(III) ions in binary metal mixtures, the initial concentrations of Fe(III) ions were varied between 10 and 250 mg/L while the Cr(VI) ion concentration in each biosorption medium was held constant at 10, 25, 50, 100 and 150 mg/L. The pH of biosorption media was adjusted to pH 2.0, the optimum value for the biosorption of Cr(VI)

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and Fe(III) ions by *C. vulgaris* and *R. arrhius* and microorganisms concentration in each binary system was kept constant at 1 g/L. For the modeling of multi-component adsorption equilibrium, non-modified competitive Langmuir model, modified competitive Langmuir model and extended Freundlich model were used. The extended Freundlich model for binary metal mixtures was satisfactory for most adsorption equilibrium data of Cr(VI) and Fe(III) ions on *C. vulgaris,* while the non-modified competitive Langmuir model and the modified Langmuir model were used successfully to characterize competitive adsorption of Cr(VI) and Fe(III) ions from two component systems by *R. arrhizus*. The main focus of this study was to investigate the competitive adsorption of metal ions by providing different total initial metal ion concentrations in the single and binary systems for the fixed number of adsorption sites. Hence it is necessary to investigate single and binary systems adsorption studies by keeping fixed total initial metal ions concentration in solution. Further, the study was carried out on the mass basis and no efforts were made to investigate the overall adsorption based on equivalents of metal ions going onto the surface of the adsorbent even though valency of metal ions (i.e. adsorbates) used in this system were different. Further, in this investigation also only initial pH of the solution has been mentioned and no information has been provided about pH of the solution at equilibrium which again cannot help to elucidate the metal removal process exactly i.e., due to only adsorption or combined effect of precipitation and adsorption.

The binary adsorption of Cu(II)-Cd(II), Pb(II)-Cd(II) and Pb(II)-Cu(II) mixtures onto Ca-Alginate beads, prepared from *Laminaria digitata,* was studied using batch experiments (pH = 4.5, 1 g/L alginate beads) (Papageorgiou et al., 2009). Competitive uptake of metal ions from binary systems were investigated on mmol/L basis. Competitive sorption models including extended Sips, non-modified competitive Langmuir model, the Langmuir partially competitive multi-component model (JS modified) as well as IAST-Freundlich models were applied to predict the binary adsorption using single component adsorption parameters. To test the validity of the predictive models, the sum of square errors (SSE) between the experimental data and the theoretically predicted points were used. The modified competitive Langmuir and Langmuir partially competitive model approaches provided excellent prediction of the binary adsorption, while the extended Sips failed to predict the experimental data, giving only fair results in the case of Pb(II)-Cu(II) mixture. On the contrary, the IAST models, though it was more complicated, provided less accurate estimation of sorption in binary metal ion solutions. This study concluded that single component adsorption

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parameters could be effectively used for the prediction of materials adsorption performance in binary metal ion solutions. In this study also total initial metal ions concentration (on mmol basis) in the binary system was different from the single component system. Hence the single and multi-metal ion systems are needed to be investigated with fixed total initial metal ions concentration in solution based on equivalents of metal ions that will eventually help in comparison of total metal uptake capacities from the mono and multi metal ion systems. Further, in this investigation also final pH of the solution has not been mentioned which consequently cannot help to elucidate the metal removal process exactly.

Simultaneous biosorption of Cr(VI) and Ni(II) on to dried activated sludge from binary mixture was investigated and compared with single Cr(VI) or single Ni(II) situation in batch stirred system containing 0.5 g/L of adsorbent (Aksu et al., 2002). They determined the single component isotherms for optimum pH [Cr(VI), pH = 1: Ni(II), pH = 4.5] by varying initial concentrations of Cr(VI) or Ni(II) in the range of 25 to 500 mg/L while the amount of biosorbent in each sample was kept constant at 0.5 g/L. To determine the effects of initial Cr(VI) and Ni(II) ion concentrations on the equilibrium uptake of Cr(VI), the initial Cr(VI) concentrations were varied between 25 to 500 mg/L while the initial concentration in each biosorption medium was held constant at 0, 25, 50, 100, 250 or 500 mg/L at pH 1 and 4.5. They utilized non-modified competitive Langmuir model, modified Langmuir model and extended Freundlich model to describe simultaneous biosorption of Cr(VI) and Ni(II) onto dried activated sludge. Based on this study, it was concluded that Freundlich multi-component model agreed well with the results found experimentally in the studied initial mixture concentration range (25 to 500 mg/L). The obtained results showed that the dried activated sludge biomass selectively adsorbed Ni(II) ions at pH 4.5 while Cr(VI) ions were preferentially adsorbed by the biomass at pH 1.0 indicating the impact of variation in pH level for the metal adsorption from the binary system. Equilibrium uptake of Cr(VI) and Ni(II) in the binary mixture were found to be decreasing due to the levels of Cr(VI) and Ni(II) concentrations because of the antagonistic interaction between the components. In this study also, total initial metal ions concentration in the binary system was different from the single component system for fixed number of adsorption sites. Further, this study also failed to investigate/compare overall uptake from mono and multi metal ion systems by keeping fixed total initial metal ions concentration in solution on equivalent basis even though valency of the metal ions were different. Other studies have also been reported in the literatures, investigating competitive adsorption of metal ions by providing different total

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initial metal ions concentration in mono- and multi-metal systems for fixed number of adsorption sites (Depci et al., 2012; Hossain et al., 2014; Liu et al., 2013; Ma et al., 2015; Mohan & Singh, 2002; Prasad et al., 2008; Roy & Bhattacharya, 2013).

2.3 Kinetics of heavy metal adsorption

For the purpose of investigating the mechanism of adsorption and its potential rate-controlling steps that include mass transport and chemical reaction processes, kinetic models have been exploited to test the experimental data. In addition, information on the kinetics of metal uptake is required to select the optimum condition for full-scale batch metal removal processes. In practice, kinetic studies have been carried out in batch reactions using various initial adsorbate concentrations, adsorbent doses, particle sizes, agitation speeds, pH values and temperatures along with different adsorbent and adsorbate types. Then, linear regression is used to determine the best-fitting kinetic rate equation (Ho, 2006).

Several adsorption kinetic models have been established to understand the adsorption kinetics and rate-limiting steps. These include pseudo-first- and pseudo-second-order rate model, Weber and Morris sorption kinetic model, Adam-Bohart-Thomas relation (Djeribi & Hamdaoui, 2008), first-order reversible reaction model (Baral et al., 2006), external mass transfer model (Apiratikul & Pavasant, 2008), Elovich's model and Ritchie's equation. However, the pseudo-first- and pseudo-second-order kinetic models are the most extensively used models to study the adsorption kinetics of heavy metals and quantify the extent of uptake in adsorption kinetics.

2.3.1 Sorption kinetic model based on reaction order

***Pseudo-first-order kinetic model*:** The Lagergren first-order rate expression based on solid capacity is generally expressed (Lagergren, 1898) as follows,

$$\frac{dq}{dt} = k_1 (q_e - q) \tag{2.13}$$

Integration of Eq. (2.13) with the boundary conditions as follow: $t = 0$, $q = 0$, and at $t = t$, $q = q_t$, gives

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$$q_t = q_e\left(1 - e^{-k_1 \times t}\right) \tag{2.14}$$

Eq. (2.14) can be written in the linear form as

$$\ln(q_e - q_t) = \ln q_e - k_1 \times t \tag{2.15}$$

where q_t is uptake of adsorbate at time 't' (mg/g), q_e is equilibrium uptake (mg/g), k_1 is first order rate constant (min^{-1}) and t is time (min). The linearized form of rate equation is used to evaluate k_1 value graphically provided q_e value had already been evaluated experimentally (Gupta et al., 2007). However in the absence of experimentally determined q_e value, the evaluation of k_1 value graphically appears to be difficult. But, the values of k_1 and q_e can be determined simultaneously and independently using the experimental values of various q_t obtained at different time 't' using method of least squares (Tchobanoglous et al., 2003) as explained in Appendix A. Non-linear regression analysis procedure for fitting of Eq. (2.14) is another way to achieve the predicted values of q_e and k_1.

***Pseudo-second-order kinetic model*:** Predicting the rate of adsorption for a given system is among the most important factors in adsorption system design, as the system kinetic determines adsorbate residence time and the reactor dimensions. Pseudo-second-order model is derived on the basis of the sorption capacity of the solid phase (Ho, 2006) expressed as

$$\frac{dq}{dt} = k_2 (q_e - q)^2 \tag{2.16}$$

Integration of Eq. (2.16) with the boundary conditions $t = 0$, $q = 0$, and at $t = t$, $q = q_t$, results in

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{2.17}$$

where q_t is uptake of adsorbate at time 't' (mg/g), q_e is equilibrium uptake (mg/g), k_2 is second order rate constant (g/mg.min) and t is time (min). Eq. (2.17) can be linearized to different linear forms as shown in Table 2.2 to evaluate q_e and k_2 (Kumar, 2006).

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Table 2.2: Different linear forms of pseudo-second-order kinetic model (Source: Kumar, 2006).

Type	Linear form	Plot	Slope and intercept
Type 1	$\frac{t}{q_t}=\frac{t}{q_e}+\frac{1}{k_2 q_e^2}$	t/q_t *vs.* t	$\text{slope}=\frac{1}{q_e}$ $\text{intercept}=\frac{1}{k_2\times q_e^2}$
Type 2	$\frac{1}{q_t}=\left(\frac{1}{k_2 q_e^2}\right)\frac{1}{t}+\frac{1}{q_e}$	$1/q_t$ *vs.* $1/t$	$\text{slope}=\frac{1}{k_2\times q_e^2}$ $\text{intercept}=\frac{1}{q_e}$
Type 3	$\frac{1}{t}=\left(\frac{k_2 q_e^2}{q_t}\right)-\frac{k_2 q_e^2}{q_e}$	$1/t$ *vs.* $1/q_t$	$\text{slope}=k_2\times q_e^2$ $\text{intercept}=\frac{k_2\times q_e^2}{q_e}$
Type 4	$\frac{q_t}{t}=k_2 q_e^2-\frac{k_2 q_e^2\, q_t}{q_e}$	q_t/t *vs.* q_t	$\text{slope}=\frac{k_2\times q_e^2}{q_e}$ $\text{intercept}=k_2\times q_e^2$
Type 5	$\frac{1}{q_e-q_t}=\frac{1}{q_e}+k_2 t$	$\frac{1}{q_e-q_t}$ vs. t	$\text{slope}=k_2$ $\text{intercept}=\frac{1}{q_e}$

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2.3.2 Sorption kinetic model based on reaction mechanism

To understand the sorption mechanism, additional details from kinetic data can be studied using sorption kinetic models based on mechanism. Generally the adsorption includes 4 basic steps as follows: (1) adsorbate transfer from bulk solution to boundary film, (2) adsorbate transfer from the boundary film to surface of adsorbent (external mass transfer step), (3) adsorbate transfer from the adsorbent surface to intraparticle active site or binding site (intraparticle diffusion step) and (4) adsorption of the adsorbate on the active or binding sites of adsorbent. Steps 1 and 4 generally occur rapidly and not considered as the rate limiting steps while the slower steps 2 or 3 or both are mainly considered as rate limiting steps.

Weber and Morris intra-diffusion sorption kinetic model: Weber and Morris sorption kinetic model (Weber & Morris, 1963) can be expressed as:

$$q = I + K_{WM} \times \sqrt{t} \tag{2.18}$$

where K_{WM} is Weber and Morris intra-particle diffusion rate $\left(\frac{mg}{g\ min^{0.5}}\right)$, and I is intercept of vertical axis (mg/g). The determination of the two parameters can be achieved by plotting q vs. $\sqrt{t}$. The linear region of the curve is selected for fitting with the model using linear regression analysis where the slope and intercept represented K_{WM} and I respectively. The *y*-axis interception (adsorption capacity axis) in the plot of q vs. $\sqrt{t}$ could be employed to examine the relative significance of the two transport mechanisms of the solute, i.e. intra-particle diffusion and external mass transfer. If $I = 0$, the intra-particle diffusion is considered as the rate limiting step, while, at $I > 0$, both external mass transfer and intra-particle diffusion were considered as rate limiting step (Kalavathy et al., 2005).

2.4 Multi-component kinetic studies

Simultaneous biosorption of Cr(VI) and Fe(III) were investigated on *C. vulgaris* and *R. arrhius* (Sağ et al., 1998a). In kinetic study of binary mixtures, the initial adsorption rate was obtained by calculating the slope of a plot of the adsorbed metal ion quantity 'q' per gram of dried microorganism (mg/g) versus time (min) t = 0. A comparison of the effect of initial Cr(VI) ion concentration on the initial adsorption rates of Cr(VI) ions to *C. vulgaris*

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and *R. arrhizus,* with the Cr(VI) ions present as the single metal and in the presence of Fe(III) ions was carried out. Similar study was carried out for Fe(III) metal ion. The initial biosorption rates of Cr(VI) ions on *R. arrhizus* were significantly reduced by Fe(III) ions. The presence of Fe(III) ions at low concentrations did not appreciably affect the instantaneous uptake of Cr(VI) ions by *C. vulgaris*. In the single Cr(VI) situation, for *R. arrhizus a* maximum initial adsorption rate of Cr(VI) ions at an initial Cr(VI) concentration of 150 mg/L was measured as 8.43 mg/g.min. Maximum initial adsorption rates of Cr(VI) ions on *C. vulgaris* were obtained at initial metal ion concentrations in the range 150 to 250 mg/L, and determined to be 4.62 and 4.98 mg/g.min respectively. When 50 mg/L of Fe(III) was added to biosorption media containing 150 mg/L of Cr(VI), the initial adsorption rates of Cr(VI) ions on *R. arrhizus* and C. *vulgaris* decreased to 4.42 and 4.44 mg/g.min respectively, compared with the single ion situation. The inhibitory effects of Fe(III) ions on the initial biosorption rates of Cr(VI) ions on *C. vulgaris* increased with increasing initial Fe(III) concentrations, e.g. the adsorption rate of Cr(VI) ions on *C. vulgaris* decreased to 3.46 mg/g.min on increasing the initial Fe(III) concentration to 247.5 mg/L. Since the initial biosorption rates decreased with increasing concentration of the other metal ion, the combined action of Cr(VI) and Fe(III) ions on C. *vulgaris* and *R. arrhizus* was found to be antagonistic. However, this decrease in adsorption rates for metal ions could be attributed to different concentration gradient existed in mono- and binary-metal ion systems for fixed number of adsorption sites. Since the study had been carried out on 'mg' basis in binary metal systems and it is well known that metal ions adsorption take place on mole or equivalent basis, the moles or equivalents of 1 mg/L concentration of one particular metal ion is not equal to 1 mg/L of other metal ions i.e., the concentration gradient posed by Cr(VI) and Fe(III) metal ions will be different due to their varying molecular weights and valency. Further, no information has been provided about the variation in values of pH during the study, which again cannot help to elucidate the removal process exactly i.e., due to only adsorption or combined effect of precipitation and adsorption. Similar study was carried out for the simultaneous biosorption of Cu(II) and Zn(II) on *Rhizopus arrihizus* (Sağ et al., 1998b). The effects of the presence of Cu(II) and Zn(II) ions together on the biosorption of Cu(II) and Zn(II) ions was investigated in terms of initial rates of biosorption.

Simultaneous adsorption of Cu(II), Pb(II) and Cd(II) onto an iminodiacetic acid (IDA) chelating resin was investigated from mono and binary metal systems (Li et al., 2011). The kinetics were carried out using fixed initial concentrations of 0.5, 1.0 and 2.0 mmol/L for the

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target metal ion in presence of equi-molar concentration of interferential metal ion in the binary metal systems. The metal uptake profiles from binary systems indicated decreased metal uptake compared to respective mono system with increase in interferential metal ion concentration indicating competition amongst metal ions for adsorption sites. However, total metal uptake capacities obtained from binary systems investigated were quite higher compared to the same from mono systems. The difference in metal uptake capacities from mono- and binary-metal systems could be attributed to increased total metal ion concentration initially present in the solution in case of binary systems, thereby increasing the driving force − concentration gradient, compared to mono systems for the fixed number of adsorption sites available. The kinetics of metal uptakes should have also been investigated by maintaining a fixed total initial metal ions concentration in the solution thereby keeping the driving force unchanged in mono- and binary-metal systems. Further, this study do not present the variation in solution pH during binary systems kinetic studies, which again cannot help to elucidate the removal process exactly i.e., due to only adsorption or combined effect of precipitation and adsorption.

The competitive adsorption kinetic study had been carried out for removal of Cd(II), Ni(II) and Zn(II) onto iron rich tourmaline (Liu et al., 2013). In mono-metal ion systems, initial concentrations for each metal ion was 100 mg/L while in binary-metal ion systems total metal ion concentration on mass basis was 200 mg/L (100 mg/L for each metal in the mixture). The study was carried out at an initial pH value of 4, temperature of 25 ^{o}C and tourmaline dose of 6 g/L (Liu et al., 2013). It was observed that in the Cd(II)+Zn(II) and Cd(II)+Ni(II) binary-metal systems, Cd(II) ions were always favourably adsorbed on tourmaline relative to Zn(II) and Ni(II) ions. Within first 5 min., the uptake capacity for Cd(II) was measured as 5.12 and 8.50 mg/g in the presence of Zn(II) and Ni(II) ions, respectively. At equilibrium time of 1440 min., maximum uptake capacities for Cd(II) were measured to be approximately 5.45 and 8.77 mg/g from Cd(II)+Zn(II) and Cd(II)+Ni(II) binary-metal systems respectively. The observed uptake capacities for Cd(II), Zn(II) and Ni(II) from binary-metal systems were less compared to their respective capacities from mono-metal systems. This decrease in adsorption capacities for Cd(II) metal ions could be attributed to different concentration gradient existed in mono- and binary-metal ion systems for fixed number of adsorption sites. Since the study had been carried out on ‘mg’ basis in binary-metal systems and it is well known that metal ions adsorption take place on mole or equivalent basis, the moles or equivalents of 1 mg/L concentration of one particular metal ion

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is not equal to 1 mg/L of other metal ions i.e., the concentration gradient posed by metal ions will be different due to their varying molecular weight and valence. Further, no information has been provided about the variation in values of pH during the study, which again cannot help to elucidate the removal process exactly i.e., due to only adsorption or combined effect of precipitation and adsorption. Similar kind of work has been carried out to investigate the kinetics of Pb(II) and Zn(II) metal uptake from multi solute systems on activated carbon prepared from Van apple pulp (VAAC) in which uptake of both the metal from multi solute systems decreased compared to mono solute systems due to different total initial metal ions concentration provided in mono and multi solute systems for fixed number of adsorption sites (Depci et al., 2012).

2.5 Column studies

Although batch laboratory adsorption studies provide useful information on the application of adsorption to the removal of specific waste constituents, continuous column studies provide the most practical application of this process in water/wastewater treatment. Batch reactors were easy to use in the laboratory study, but less convenient for industrial applications. In static mode adsorption studies, the same solution remains in contact with a given quantity of the adsorbent where the driving force of concentration gradient keeps on decreasing with time. The adsorption process continues, however, till equilibrium between the solute concentration in solution, and the solute adsorbed per unit weight of the adsorbent is reached. This equilibrium established is static in nature, as it does not change further with time for the system being investigated. In dynamic column adsorption, solution continuously enters and leaves the column, so that the complete equilibrium is never established at any stage between the solute in solution and the amount adsorbed (Dwivedi et al., 2008). Adsorption efficiency by column mode depends on flow rate, bed height and influent adsorbate initial concentration. However, adsorption takes place under a fixed concentration gradient. Generally the performance of the continuous column mode operation is usually described through the concept of breakthrough curve which is the typical 'S' shape profile of exit concentration (C) as a function of lapse time (t) or throughput volume (V_t).

2.5.1 Mathematical models

Optimization of parameters in the continuous adsorption process by experimental methods is an expensive and time consuming proposition. It would be much cheaper and

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faster to use mathematical modeling to predict the duration of the column bed before regeneration becomes necessary (Warchoł & Petrus, 2006). Some of the known mathematical models applied for column mode operation are bed depth service time (BDST) model, Thomas model, theoretical breakthrough curve etc.

Bed depth service time (BDST) model: The Bohart-Adams equation which is based on surface reaction rate theory can be represented as (Bohart & Adams, 1920).

$$ln\left(\frac{C_o}{C_b}-1\right)=ln\left(e^{k_{ads}N_0(Z/u)}-1\right)-K_{ads}C_0t_s \tag{2.19}$$

The Bohart-Adams equation is further modified and a linear relationship is obtained between the bed depth and service time which requires only three fixed bed tests to collect the necessary data (Hutchins, 1973). The modified equation is represented as,

$$t_s=\frac{N_oZ}{C_ou}-\frac{1}{k_{ads}C_o}ln\left(\frac{C_o}{C_b}-1\right) \tag{2.20}$$

where t_s is the service time at breakthrough point (h), N_o is the dynamic bed capacity (mg/g), Z is the packed bed column depth (cm), u is the linear flow rate (cm/h) defined as the ratio of volumetric flow rate Q (cm^3/h) to the cross sectional area of the bed A (cm^2), C_o and C_b are respectively the influent and the breakthrough adsorbate concentration (mg/L) and k_{ads} the adsorption rate constant (L/mg.h). Plotting service time (t_s) versus bed depth (Z) will generate a straight line equation having slope of $\frac{N_o}{C_ou}$ and intercept of $\frac{1}{k_{ads}C_o}ln\left(\frac{C_o}{C_b}-1\right)$. Critical bed depth ($Z_o$) represents the theoretical minimum depth of column that will be able to prevent the concentration from exceeding C_b. It is obtained when breakthrough is immediate and it can be calculated by substituting $t_s = 0$ in Eq (2.20) as shown below.

$$Z_o=\frac{u}{k_{ads}N_o}ln\left(\frac{C_o}{C_b}-1\right) \tag{2.21}$$

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According to linearized BDST model [Eq. (2.20)], data collected from one flow rate experiment can predict the system with different flow rate. When an experiment conducted at flow rate Q_1 yields equation of the form

$$t_s = a_1 Z + b_1 \tag{2.22}$$

the predicted equation for new flow rate Q_2 is given by

$$t_s = a_2 Z + b_1 \tag{2.23}$$

$$a_2 = a_1 \frac{Q_1}{Q_2} \tag{2.24}$$

where a_1 and a_2 are the slopes at the flow rate Q_1 and Q_2 respectively. However the intercept b_1 remained same since it is independent of flow rate in linearized BDST model [Eq. (2.20)]. BDST model can also be used to design the systems for treating other influent solute concentrations using the data of previous laboratory experiment of one influent solute concentration. When an experiment conducted at initial concentration C_1, yields an equation of the form

$$t = r_1 X + s_1 \tag{2.25}$$

The predicted equation for new flow rate Q_2, is given by:

$$t = r_2 X + s_2 \tag{2.26}$$

The new slope and intercept values can be determined as:

$$r_2 = r_1 + \frac{C_1}{C_2} \tag{2.27}$$

$$s_2 = s_1 \frac{C_1}{C_2} \times \frac{ln\left[\frac{C_2}{C_F} - 1\right]}{ln\left[\frac{C_1}{C_b} - 1\right]} \tag{2.28}$$

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where r_1 and r_2 is slopes at influent concentration C_1 and C_2 respectively, s_1 and s_2 are intercepts at influent concentration C_1 and C_2 respectively, C_F is effluent concentration at influent concentration C_2 and C_b is effluent concentration at influent concentration C_1.

Thomas model: Thomas model assumes Langmuir kinetics of adsorption-desorption and no axial dispersion. It is derived with the assumption that the rate driving force obeys pseudo second order reversible reaction kinetics. Thomas equation is given by (Naddafi et al., 2007; Thomas, 1944)

$$\frac{C_o}{C} = 1 + exp\left[\frac{k_{TH}}{Q}\left(Q_o M - C_o V_t\right)\right] \tag{2.29}$$

where C_o is the initial adsorbate concentration (mg/L), C is the effluent adsorbate concentration (mg/L), k_{TH} is the Thomas model rate constant (mL/min.mg), M the total mass of the adsorbent loaded in the column (g), Q_o the maximum solid-phase concentration of the solute (mg/g), V_t is the throughput volume. Linearized form of Thomas Model is as follows:

$$ln\left(\frac{C}{C_o} - 1\right) = \frac{k_{TH} Q_o M}{Q} - \frac{k_{TH} C_o}{Q} V_t \tag{2.30}$$

Theoretical breakthrough curve (Based on mass transfer model): The breakthrough curve of a continuous fixed bed operation mode can be evaluated using the data obtained from the batch isotherm studies. The batch data are first transformed into a theoretical breakthrough curve which serves as a basis for design. Thus column operation can be designed from batch experiment data without running the column experiment and the procedure is given below.

1) Equilibrium curve is plotted (C_e vs q_e) using batch data.
2) Further operating line needs to be drawn passing through the origin and intersecting the equilibrium curve at C_o. The significance of this operating line is that the data of fixed bed reactor and the data of mixed batch reactor are identical at these two points.
3) The rate of transfer of solute from solution over a differential depth column dh is given by

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$$F_w dC = K_a (C - C_e) dh \tag{2.31}$$

where F_w is the flow rate, K_a is overall mass transfer coefficient, which include resistance offered by film diffusion and pore diffusion, C_e equilibrium concentration of the adsorbate in the solution corresponding to a adsorbed concentration q_e. C is the concentration of the adsorbate at a given instant of time t (Benefield et al., 1982).

4) The term $(C-C_e)$ is the driving force for the adsorption and is equal to the difference between the operating line and equilibrium curve at a given q_e value. Integrating the Eq (2.31) and solving for the height of adsorption zone (h_z) at saturation yields

$$h_z = \frac{F_w}{K_a} \int_{C_B}^{C_E} \frac{dC}{(C - C_e)} \tag{2.32}$$

where C_B and C_E are the concentrations of adsorbate in effluent at breakthrough and at exhaustion point respectively.

5) Further plot between C versus $(C-C_e)^{-1}$ is made to determine the area under the curve by graphical integration to evaluate the term

$$\int_{C_B}^{C_E} \frac{dC}{(C - C_e)}$$

Since $(C-C_e)^{-1}$ approaches infinity as C approaches C_o, it is necessary to terminate the plot of C at a value somewhat less than C_o or at $C = 0.95C_o$ (point of exhaustion of adsorption columns). For any value of h less than h_z corresponding to a concentration $C_B < C < C_E$, Eq (2.32) can be written as

$$h_z = \frac{F_w}{K_a} \int_{C_B}^{C} \frac{dC}{(C - C_e)} \tag{2.33}$$

Dividing Eq (2.33) by Eq (2.32) results in

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$$\frac{h}{h_z} = \frac{\int_{C_B}^{C} \frac{dC}{(C - C_e)}}{\int_{C_B}^{C_E} \frac{dC}{(C - C_e)}} = \frac{V - V_B}{V_E - V_B} \tag{2.34}$$

where V_B and V_E are throughput volumes at breakthrough and exhaustion respectively and V is throughput volume within V_E for an effluent concentration C within C_E.

6) Finally the theoretical curves are generated by plotting $\frac{V - V_B}{V_E - V_B}$ vs $\frac{C}{C_0}$

For successful application of adsorption to practical applications, the focus of research and development has to be on continuous-flow processes as the results from batch experiments, where metal ions are depleted from solution without further metal ion addition, cannot usefully be used for this purpose. In this regard numbers of study have been carried out for the removal of metal ions in continuous mode. Some of the studies have been discussed in subsequent paragraphs.

2.5.2 Column studies with multi metal ion systems

The biosorption of Cu(II), Pb(II), Zn(II) and Ni(II) from a mixed solution of metals was investigated in continuous flow packed columns containing polyurethane immobilised biomass (Zhang & Banks, 2006). The characteristics and biosorption properties of *Sphagnum moss*, the brown seaweed *Ascophyllum nodosum*, waste biomass from the preparation of sunflower oil, and whole plant maize were compared in this study. The column was a simple glass tube with an inner diameter of 3.8 cm, and length of 50 cm. Ten grams of the immobilized biomass was packed into the centre of the column, yielding an approximate length of 20 cm with a packing density of 44 g/L. The metal solutions for adsorption pumped in an upflow mode and elution solutions used for desorption pumped in a downflow mode at 2 L/h into the column using a peristaltic pump. All biosorption experiments were carried out using either a solution containing a single metal, with a mixture of two metals (binary) or a solution of four mixed metals (multi-metal solution). In all cases the influent pH was adjusted to 4.0. The concentration of each metal ion in solution was kept near to 10 mg/L when experiments were run at equal mass concentration and 0.16 mmol/L when experiments were run at equal molar concentrations. All the biomass types showed a preference for the

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sequestration of Pb(II) followed by Cu(II), with Ni(II) and Zn(II) having roughly equal affinity. With continuous metal loading to the column there was an initial binding of all metals and then a displacement of the lower affinity metals by those with a high affinity. This led to a chromatographic effect in the column with breakthrough concentrations for low-affinity metals higher than the concentration in the feed. A similar phenomenon was observed on desorption using acidic solutions where low-affinity metals were desorbed preferentially. The results also indicated that despite competitive displacement of one metal species by another the biomass appeared to succeed in retaining some low-affinity metal species indicating that there may be selective sites present with different affinity characteristics. The results clearly showed that in the initial stages of column operation metal ions of all species attach to binding sites but then metals of lower affinity are progressively displaced giving an early breakthrough and chromatographic concentrating effect. The present study was carried out at initially adjusted influent pH but it was not monitored for the effluents coming out of the adsorbent bed which again cannot help to elucidate the removal process exactly i.e., due to only adsorption or combined effect of precipitation and adsorption. Further, displacement of low affinity metal ions was observed from the column bed when all the metal ions were exposed to column bed simultaneously. However less or no studies are available in the literatures which show additional metal removal potential of exhausted column bed if reloaded with another metal ion and migration of previously removed metal ion from the bed into the effluent when reloaded. Further, mono- and multi-metal ion system column studies have been carried out with different total initial metal ions concentration in influent solution. The mono- and multi-metal ion system column studies can be investigated by keeping fixed total initial metal ions concentration in influent solution in order to compare total metal removal from column bed.

A performance of low-cost adsorbent such as raw rice husk (RRH) and phosphate treated rice husk (PRH) was investigated in removing heavy metals such as Pb(II), Cu(II), Zinc(II) and Mn(II) from the leachate collected from the open dumping site (Mohan & Sreelakshmi, 2008). The heavy metal concentration in the leachate was observed at around 10 mg/L and thus this concentration level was selected for column study. The fixed bed column experiments were conducted with 10 mg/L synthetic single metal solutions using the columns at a constant flow rate of 20 mL/min. The samples were collected from the ports at bed depths of 10, 20 and 30 cm at 1 h regular time interval. The adsorbent materials adopted were found to be an efficient media for the removal of heavy metals in continuous mode using

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fixed bed column. The breakthrough time was found to increase from 1.3 to 3.5 h for Pb(II), 4.0 to 9.0 h for Cu(II), 12.5 to 25.4 h for Zn(II) and 3.0 to 11.3 h for Mn(II) with increase in bed height from 10 to 30 cm for PRH. Different column design parameters like depth of exchange zone, adsorption rate, adsorption capacity, etc. were evaluated. It was observed that the adsorption capacity and adsorption rate constant increased and the minimum column bed depth required reduced when the rice husk is treated with phosphate, when compared with that of RRH. In this study also pH of the effluent solution coming out of the adsorbent bed was not monitored which again cannot help to elucidate the removal process exactly i.e., due to only adsorption or combined effect of precipitation and adsorption. Further, mono- and multi-metal ion system column studies have been carried out with different total initial metal ions concentration in influent solution on mass basis. Therefore, in order to compare total metal removal from column bed, mono- and multi-metal ion system column studies are need to be investigated by keeping fixed total initial metal ions concentration in influent solution on equivalent basis.

Biosorption of Pb(II) and Cd(II) from aqueous solutions by protonated *Sargassum glaucescens* biomass was studied in a continuous packed bed column (Naddafi et al., 2007). The selective uptake of Pb(II) and Cd(II) was investigated in a binary system with initial concentration of 1mM for each metal ion with an empty bed contact time (EBCT) of 30 min. The column was a simple glass tube with inner diameter of 4 cm, bed depth of 40 cm and bed volume of 503 mL. The experiments were conducted by pumping a metal solution (pH = 5.00, adjusted to optimum value based on batch study experiments) in upflow mode through the packed bed column with a peristaltic pump. The selective uptake capacities of Pb(II) and Cd(II) at complete exhaustion point were obtained as 1.18 and 0.22 mmol/g respectively. The Thomas model gave a suitable fitness with the experimental data ($R^2 > 0.90$) at all different operation stages. In this study also pH of the effluent solution was not monitored and mono- and multi-metal ion system column studies have been carried out with different total initial metal ions concentration in influent solution.

Green coconut shell was used as an adsorbent for the removal of toxic metal ions [Cu(II), Pb(II), Cd(II), Zn(II) and Ni(II)] from aqueous effluents using column adsorption (Sousa et al., 2010). A polyethylene column filled with a known mass of adsorbent corresponding to 5, 10 and 18 cm bed heights was percolated with 150 mL of multi-component model solution (100 mg/L at pH 5.0) at flow rates of 2, 4, 6 and 15 mL/min. The

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results showed that a flow rate of 2 mL/min and a bed height of 10 cm were most feasible. The breakthrough curves for multiple elements gave the order of adsorption capacity as Cu(II)>Pb(II)>Cd(II)>Zn(II)>Ni(II). In this study also pH of the effluent solution was not monitored and mono- and multi-metal ion system column studies have been carried out with different total initial metal ions concentration in influent solution.

Mono- and multi-metal ion adsorption of selected heavy metals (As, Cd, Cr, Cu, Hg, Pb and Zn) in a sediment from a coastal Louisiana forested swamp used for wastewater treatment was investigated in continuous mode column studies (Seo et al., 2008). Column experiments were conducted for determining both mono- and multi-metal adsorption characteristics of the seven heavy metals. Eight columns were constructed of PVC cylinder (inside diameter: 25 mm, height: 150 mm) and each column was packed with 10.25 g of wet sediment (water content 51.2%). Column experiments were carried out by expressing metal concentrations on weight basis and no efforts were made to measure the variation in pH during column operation. Metal solutions containing 50 mg/L of each metal for the mono-metal system and mixed metal solution (50 mg/L of all seven metal ions) for the multi-metal system were supplied continuously at a rate of approximately 30 mL/d using a constant-head feeding tank. Samples of the effluent were collected each day over a 4 week period. The samples were filtered and the metal concentrations in filtrate were analysed. Result showed that the maximum adsorption capacity (mg/g) of metals was in the order of Pb (96.5) >> Hg (56.6) > Cr (31.3) > Cd (17.5) > Cu (13.4) > Zn (9.3) >> As (1.1) from mono-metal system, and Hg (36.0) >> Cr (12.3) >> Pb (3.9) > Cu (2.5) > Zn (1.5) > Cd (1.3) > As (0.6) from multi-metal system. Results from the column experiments showed that Pb from multi-metal system lost its adsorption capacity significantly as the result of competition with other metals. In this study also pH of the effluent solution coming out of the adsorbent bed was not monitored which again cannot help to elucidate the metal removal process exactly. Mono- and multi-metal ion system column studies have been carried out with different total initial metal ions concentration in influent solution on mass basis. However, in order to compare total metal removal from column bed, column studies could have been investigated by keeping fixed total initial metal ions concentration in influent solution on equivalent basis.

The fixed bed column study was carried out to investigate competitive adsorption of Pb(II) and Cu(II) metals on chaff (Han et al., 2006). Experiments were carried out to determine the breakthrough curves both in single-metal ion system and binary-metal ion

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system. Chaff was packed into a glass column (1.5 cm inner diameter and 30 cm height). The mass of chaff in the column was 4.24 g. The metal solution containing Pb(II) or Cu(II) or Pb(II)+Cu(II) both were applied to the column. The pH of metal solution was adjusted to 5.0 and was not monitored or controlled during the column operation. The metal solution was pumped to the column in a downflow direction by a peristaltic pump at a rate of 7.5 mL/min. Effluent samples were collected at regular intervals and the concentration of free metal ions in the effluent was analyzed. To investigate the effect of coexistence ions on the adsorption of chaff, column study were performed in three sets (a) the column of chaff was saturated by Cu(II) solution of 9.97 mg/L, then Pb(II) solution of 32.5 mg/L, equal mol-concentration with Cu(II) solution, was passed through the column, (b) column of chaff was saturated by Pb(II) of 24.4 mg/L, then the Cu(II) solution of 7.49 mg/L, equal mol-concentration with Pb(II) solution, was passed through the column, (c) Cu(II) and Pb(II) adsorbed synchronously by chaff were studied. The content of solute was that the metal ions concentration of Cu(II) and Pb(II) were 14.7 mg/L and 50.6 mg/L respectively. It was observed that in first two sets of experiment, when the exhausted column with one metal ion system was again exposed with the second metal ion system, there was displacement of already adsorbed metal ion from the surface of chaff. The studies of the competitive adsorption of Cu(II) and Pb(II) revealed that the mechanism of the two metal ions was in homology nearly. The tendency for adsorbed Pb(II) was higher than that for Cu(II). The whole experiment was performed on molar basis and total metal ions concentration in binary-metal ion system was different from the mono-metal ion systems. This might be the reason for the reduction in adsorption capacities (expressed in mg/g basis) of Pb(II) and Cu(II) metal ions from binary-metal ion systems compared to mono-metal ion systems. This work is also silent about the total metal removed by the column bed on molar or equivalent basis from binary systems. Hence, it is necessary to investigate the mono- and multi-metal systems column studies with fixed total initial metal ions concentration in solution on equivalent basis to compare the total metal removal from the systems.

A competitive and comparative adsorption column studies had been performed for the removal of Cs(I) and Sr(II) onto mont-morillonite iron oxide composite (MIOC) (Ararem et al., 2013). The study elucidated the effect of bed depth, flow rate and initial metal ion concentration on the breakthrough curves. The columns used for the study were of 0.9 cm inner diameter, bed depth of 5, 10 and 15 cm, initial metal ion concentration of 2, 20, 50 mg/L and flow rate of 2, 5, 8 mL/min. The study revealed that (a) as the bed depth increased

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the residence time increased and the breakthrough curve shifted towards right. (b) An increase in initial metal ion concentration resulted in steeper breakthrough curves. (c) Increase in flow rate also shifted the breakthrough to the left due to reduced residence time. The observed results indicated that in single metal systems, the affinity for Sr(II) onto MIOC was more than Cs(I) and in binary metal ion system, the presence of competitive metal has slightly reduced the affinity for Sr(II) and strongly for Cs(I). However, this study also failed to investigate the overall adsorption capacities under fixed total initial metal ions concentration in mono- and multi-metal systems.

2.6 Concluding remarks

Literature review highlighted successful deployment of different adsorbents for the removal of metal ions from mono- and multi-metal ion systems under various operational and environmental conditions. The available literature also enlightened with the development in modeling of equilibrium, kinetic and column data for mono- as well as multi-metal ion systems. The results of most of the metal removal studies by adsorption processes from mono- and multi-metal ion systems have been reported on mass basis. As long as only mono-metal ion systems are being handled, this approach appears to be logical. However, when adsorption processes are applied for binary- and/or multi-metal ion systems where all the metals are going on the surface of the adsorbent in different proportions, then possibly expressing results on mass basis may lead to complicacy. Hence there is need to carry out mono- and multi-metal ion adsorption studies on equivalent basis so as to take into account the sizeable difference in atomic weights and valence of metal ions. Expressing the concentrations of metal ions on equivalent basis in multi-metal ion systems will facilitate the algebraic summation of concentrations of metal ions and eventually will help in to estimate overall metal removal from the multi-metal ion systems. The aspiration for the multi-metal ion adsorption equilibrium studies were to scrutinize the preferential adsorption of metal ions by providing higher total initial metal ion concentration in solution of multi-metal systems in contrast to mono-metal systems based on mass rather than equivalents. However no studies are available in literatures which compare the overall metal removal at equilibrium from mono- and multi-metal ion systems investigated with fixed total initial metal ions concentration in aqueous phase on equivalent basis. Further, the main focus of multi-metal ion kinetic studies has been restricted only to investigate the effect on the adsorption rate of target metal in presence of non-target metal. However, no or scanty literatures are available

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which compare the overall metal removal with time from mono- and multi-metal ion systems kinetic studies investigated with fixed total initial metal ions concentration in aqueous phase on equivalent basis. The studies are also unavailable which focus on kinetic of adsorption when adsorbent loaded with one metal ion, reloaded with same metal ion for several times and also migration of already adsorbed metal ions from the adsorbent when the same is exposed to another metal ion. Similarly, the main focus of multi-metal ion systems column studies were to compare the breakthrough curves of metal ions from multi-metal ion systems with mono-metal ion systems and eventually based on the results competition among metal ions for adsorption sites were estimated. However, scanty literatures are available which describe adsorption of different metal ion on already exhausted column bed and consequently possible migration of already adsorbed metal ion back into effluent solution. Further, there are fewer literatures available which describe the working pH conditions and also variation in pH during the course of adsorption process, which is very essential to describe the exact process of metal ion removal i.e., either by adsorption or combined effects of precipitation and adsorption.

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CHAPTER 3

OBJECTIVES AND SCOPE OF THE WORK

Ample of work has been reported on the removal of heavy metal from mono-metal ion systems, through adsorption process without controlling the variation in pH during the experiments. The adsorption process of metal removal from multi-metal ion systems is yet to be fully understood as compared to metal removal from mono-metal ion systems. Although research in recent times have made an effort to understand the preferential adsorption from multi-metal ion systems, the systems are judged on varying initial concentration gradients in solution on mass basis rather than equivalent basis. The same approach may not be directly applicable when dealing with metal removal from multi-metal ion systems through the process of adsorption. Therefore, there is a need to understand the kinetics and equilibrium of metal adsorption in batch mode from multi-metal ion systems at the selected environmental conditions. Many of the research have also evaluated numerous low cost adsorbents, regeneration techniques to recover the metal ions and to reuse the adsorbent. There are fewer efforts to understand the possibilities of further adsorption of metal ion onto metal loaded adsorbent when exposed to same metal repeatedly and subsequent migration of already adsorbed metal ion when exposed to another metal ion. The present research is an effort to fill these gaps which are essential for the proper understanding of adsorption process through mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) metal ions. Hence, the broad objective of this research work may be presented as follows:

1. To investigate effect of variation in solution pH on the availability of metal ions from mono-, binary- and ternary-metal ion systems.
2. To investigate effect of contact time on metal ion concentration remaining in aqueous phase with fixed total initial metal ions concentration in solution on equivalent basis under uncontrolled and controlled pH conditions.
3. To investigate kinetics of metal removal from mono-, binary- and ternary-metal ion systems with fixed total initial metal ions concentration in solution on equivalent basis under uncontrolled and controlled pH conditions.
4. Batch tests to investigate additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions when adsorbent exposed to (i) a metal ion only once followed by exposure to another metal ion and (ii) a metal ion

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repeatedly for 6-10 cycles followed by exposure to another metal ion while keeping the fixed total initial metal ion concentration in solution.

5. To understand the kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions when adsorbent repeatedly exposed to three loading cycles of one mono-metal ion system or one combination of binary-metal ion system followed by fourth loading cycle of another mono-metal ion system or another combination of binary-metal ion system.
6. To investigate equilibrium studies of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from mono-, binary- and ternary-metal ion systems with fixed total initial metal ions concentration in solution on equivalent basis.
7. To investigate column studies of metal removal from mono- and binary-metal ion systems with fixed total initial metal ions concentration in solution on equivalent basis under uncontrolled and controlled pH conditions. The investigation encompasses to assess the (i) variation in pH of effluents coming out of the column beds, (ii) additional metal removal potential of exhausted bed if reloaded with another metal ion, and (iii) migration of previously removed metal ion from the bed in the effluent, if any (iv) total metal removal from mono- and binary- metal ion systems.

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CHAPTER 4

MATERIALS AND METHODS

4.1 Materials

The commercial grade granular activated alumina (GAA) was procured from M/S Siddhartha Industries, Surat (India) and used as an adsorbent in this study. The physical and chemical properties of GAA are presented in Table 4.1. The surface area and pore volume of the GAA were also estimated by nitrogen adsorption/desorption isotherm method (Model: ASIQM0000-4, Autosorb IQ, Quantachrome Instruments, Boynton Beach, FL, USA) at 196^{o} C and shown in Table 4.1. The GAA was used as procured without any additional treatment. Furthermore, copper [Cu(II)], lead [Pb(II)] and chromium [Cr(III)] metal ions were selected as adsorbates. The characteristics of the selected metal ions are presented in Table 4.2. The criteria used for selection of the metal ions were (i) similar valence but different atomic weights in the case of Cu(II) and Pb(II); (ii) different valence but atomic weights close to each other in the case of Cu(II) and Cr(III); and (iii) different valence and atomic weights in the case of Pb(II) and Cr(III).

Table 4.1: Properties of granular activated alumina (GAA) (Source: M/S Siddhartha Industries, Surat, India).

Characteristics		Manufacturer provided value	Estimated value
Physical	Particle form	Granular	–
	Particle size (mm)	0.40 – 1.20	–
	Surface area (m^2/g) (minimum)	360.00	355.69
	Pore volume (cc/g)	0.50	0.37
	Packed bulk density (g/cm^3)	0.72	0.99
	Bed crushing strength (wt. %) (minimum)	99.20 – 99.90	–
	Loss on abrasion (wt. %) (maximum)	0.50	–
Chemical	Al_2O_3 (%)	92.50	–
	SiO_2 (%)	0.02	–
	Na_2O (%)	0.30	–

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Table 4.2: Characteristics of selected heavy metal ions (Sources: Hawari & Mulligan, 2007; Pauling, 1960; Sawyer et al., 2003).

Metal ion	Valence	Representation	Atomic weight (g)	Ionic radius (A^o)	Electronegativity
Copper	+2	Cu(II)	63.546	0.72	1.90
Lead	+2	Pb(II)	207.190	1.20	1.87
Chromium	+3	Cr(III)	51.996	0.70	1.60

4.2 Methods

Stock solutions of known concentrations of Cu(II), Pb(II) and Cr(III) mono-metal ions were prepared by dissolving required amounts of analytical grade copper sulfate [$Cu(SO_4).5H_2O$)], lead nitrate [$Pb(NO_3)_2$] and chromium nitrate [$Cr(NO_3)_3.9H_2O$] respectively in de-mineralized water (DMW) as indicated in Table 4.3. The copper sulfate, lead nitrate and chromium nitrate salts were dried overnight in a hot air drying oven (Model: PSI, M/S Mahindra Scientific Instrument Co., India) at 50 ^oC, 70 ^oC and 38 ^oC respectively and cooled in a dessicator before weighing out the required quantity using an analytical balance (Model: AB304S, M/S Mettler Instrument AG, Switzerland). The drying temperatures for the metal ions were adopted based on the thermal decomposition analysis of the metal ions reported in published literatures (Galwey & Brown, 1999; Melnikov et al., 2013; Vratny & Gugliotta, 1963). The DMW was prepared through RO process (Model: Milli-Q Water, M/S Millipore S.A.S., Molsheim, France). The characteristics of de-mineralized water are presented in Table 4.4.

Table 4.3: Stock solutions of selected metal ions.

Metal ion		
Cu(II)	Pb(II)	Cr(III)
Dissolved 3.9292 g of $Cu(SO_4).5H_2O$ in de-mineralized water and made final volume to 1000 mL. 1.00 mL of stock solution contained 0.0315 meq (1.00 mg) of Cu(II).	Dissolved 1.5985 g of $Pb(NO_3)_2$ in de-mineralized water and made final volume to 1000 mL. 1.00 mL of stock solution contained 0.0097 meq (1.00 mg) of Pb(II).	Dissolved 7.6958 g of $Cr(NO_3)_3.9H_2O$ in de-mineralized water and made final volume to 1000 mL. 1.00 mL of stock solution contained 0.0577 meq (1.00 mg) of Cr(III).

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Table 4.4: Characteristics of de-mineralized water (DMW) used.

Parameters	Value
Electrical conductivity (mmho/cm)	0.002±0.001
Total alkalinity (mg/L as $CaCO_3$)	9.00±0.10
Total hardness (mg/L as $CaCO_3$)	2.00±0.20
Temperature (°C)	23.0±1.0
pH (pH unit)	6.60±0.30
Sulphate (mg/L)	0.58±0.10
Chloride (mg/L)	1.00±0.10
Calcium (mg/L)	1.29±0.03
Sodium (mg/L)	0.11±0.05
Potassium (mg/L)	0.07± 0.04
Cu(II) (mg/L)	Not detected
Pb(II) (mg/L)	Not detected
Cr(III) (mg/L)	Not detected

Data presented in xx±yy format where xx is the average value and yy is the standard deviation estimated using a minimum of three independent data points.

4.2.1 Combinations of mono-, binary- and ternary-metal ion systems

The studies for metal removal and metal uptake from mono-, binary- and ternary-metal ion systems were carried out by selecting different combinations of metal ion systems with a fixed desired total initial metal ion concentration in the solution. The selection of combinations was primarily based on metal ion system (either mono or binary or ternary), metal ion(s) present in the system and desired initial concentration of metal ions in the system (expressed in meq/L). In the case of mono-metal ion systems comprising of Cu(II), Pb(II) and Cr(III); all the systems were having a fixed desired initial metal ion concentration of 0.60 meq/L in the solution [which on mass basis equaled to 19.06 mg/L for Cu(II), 62.16 mg/L for Pb(II) and 10.40 mg/L for Cr(III)]. The combination of mono-metal ion systems were designated as M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] respectively for Cu(II), Pb(II) and Cr(III) metal ion systems where M represented the mono-metal ion system while square brackets included the metal ion along with its desired initial concentration expressed in meq/L. The selected metal ions for the study [viz. Cu(II), Pb(II) and Cr(III)] yielded three different binary-metal ion systems of Cu(II)+Pb(II), Pb(II)+Cr(III) and Cr(III)+Cu(II). Each of the binary-metal ion systems have been further grouped into four different combinations by selecting different desired initial concentration of each of the metal ions present in the combination. The four different combinations of binary-metal ion system of Cu(II)+Pb(II) on the basis of different desired initial concentration of metal ions were (a) 0.45 meq/L of Cu(II)

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+ 0.15 meq/L of Pb(II) which was designated as B[Cu(0.45)+Pb(0.15)], (b) 0.30 meq/L of Cu(II) + 0.30 meq/L of Pb(II) – designated as B[Cu(0.30)+Pb(0.30)], (c) 0.15 meq/L of Cu(II) + 0.45 meq/L of Pb(II) – designated as B[Cu(0.15)+Pb(0.45)] and (d) 0.60 meq/L of Cu(II) + 0.60 meq/L of Pb(II) – designated as B[Cu(0.60)+Pb(0.60)] where B represented the binary-metal ion system while square brackets included the metal ions along with its desired initial concentration expressed in meq/L. In the first three combinations, the desired total initial metal ion concentration were fixed at 0.60 meq/L – similar to the metal ion concentrations maintained in mono-metal ion systems while in the fourth combination, the desired total initial metal ion concentration was fixed at 1.20 meq/L – double of the concentration maintained in mono-metal ion systems. The selection of initial concentration of a mono-metal ion as 0.60 meq/L was helpful in making the first three combinations of binary-metal ion system by maintaining a definite proportion of each of the metal ions in the combination. Similarly, four different combinations for each of binary-metal ion systems of Pb(II)+Cr(III) and Cr(III)+Cu(II) were also grouped and designated. Further, the selected metal ions yielded two different combinations of ternary-metal ion systems of Cu(II)+Pb(II)+Cr(III) on the basis of different desired initial concentration of metal ions as (a) 0.20 meq/L of Cu(II) + 0.20 meq/L of Pb(II) + 0.20 meq/L of Cr(III) which was designated as T[Cu(0.20)+Pb(0.20)+Cr(0.20)] and (b) 0.60 meq/L of Cu(II) + 0.60 meq/L of Pb(II) + 0.60 meq/L of Cr(III) – designated as T[Cu(0.60)+Pb(0.60)+Cr(0.60)] where T represented the ternary-metal ion system while square brackets included the metal ions along with its desired initial concentration expressed in meq/L. In the first combination, the desired total initial metal ion concentration was fixed at 0.60 meq/L – similar to the metal ion concentrations maintained in mono-metal ion systems while in the second combination, the desired total initial metal ion concentration was fixed at 1.80 meq/L – triple of the concentration maintained in mono-metal ion systems. The details of selected combinations of mono-, binary- and ternary-metal ion systems with unique designations are presented in Table 4.5.

4.2.2 Solution pH conditions in combinations of mono-, binary- and ternary-metal ion systems

The studies of metal removal from aqueous phase and metal uptake by adsorbent from mono-, binary- and ternary-metal ion systems have been carried out under two different conditions of solution pH. In the first condition, the initial pH of the solution was adjusted to

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Table 4.5: Details of combinations of mono-, binary- and ternary-metal ion systems selected for investigation in the present study.

System	Metal ion	Combination and desired initial metal ion concentration	Designation assigned
Mono (M)	Cu(II)	0.60 meq/L of Cu(II)	M[Cu(0.60)]
	Pb(II)	0.60 meq/L of Pb(II)	M[Pb(0.60)]
	Cr(III)	0.60 meq/L of Cr(III)	M[Cr(0.60)]
Binary (B)	Cu(II)+Pb(II)	0.45 meq/L of Cu(II) + 0.15 meq/L of Pb(II)	B[Cu(0.45)+Pb(0.15)]
		0.30 meq/L of Cu(II) + 0.30 meq/L of Pb(II)	B[Cu(0.30)+Pb(0.30)]
		0.15 meq/L of Cu(II) + 0.45 meq/L of Pb(II)	B[Cu(0.15)+Pb(0.45)]
		0.60 meq/L of Cu(II) + 0.60 meq/L of Pb(II)	B[Cu(0.60)+Pb(0.60)]
	Cr(III)+Pb(II)	0.45 meq/L of Cr(III) + 0.15 meq/L of Pb(II)	B[Cr(0.45)+Pb(0.15)]
		0.30 meq/L of Cr(III) + 0.30 meq/L of Pb(II)	B[Cr(0.30)+Pb(0.30)]
		0.15 meq/L of Cr(III) + 0.45 meq/L of Pb(II)	B[Cr(0.15)+Pb(0.45)]
		0.60 meq/L of Cr(III) + 0.60 meq/L of Pb(II)	B[Cr(0.60)+Pb(0.60)]
	Cu(II)+Cr(III)	0.45 meq/L of Cu(II) + 0.15 meq/L of Cr(III)	B[Cu(0.45)+Cr(0.15)]
		0.30 meq/L of Cu(II) + 0.30 meq/L of Cr(III)	B[Cu(0.30)+Cr(0.30)]
		0.15 meq/L of Cu(II) + 0.45 meq/L of Cr(III)	B[Cu(0.15)+Cr(0.45)]
		0.60 meq/L of Cu(II) + 0.60 meq/L of Cr(III)	B[Cu(0.60)+Cr(0.60)]
Ternary (T)	Cu(II)+Pb(II)+Cr(III)	0.20 meq/L of Cu(II) + 0.20 meq/L of Pb(II) + 0.20 meq/L of Cr(III)	T[Cu(0.20)+Pb(0.20)+Cr(0.20)]
		0.60 meq/L of Cu(II) + 0.60 meq/L of Pb(II) + 0.60 meq/L of Cr(III)	T[Cu(0.60)+Pb(0.60)+Cr(0.60)]

M, B and T represented mono-, binary- and ternary-system respectively while square brackets included the metal ion along with its desired initial concentration expressed in meq/L.

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a pre-decided level/value of 5.00 in the beginning of the experiment by using appropriate strengths of either hydrochloric acid (1 N, 0.1N, 0.01N HCl) or sodium hydroxide (1 N, 0.1N, 0.01N NaOH). However, the variations in the adjusted pH level/value were not checked or maintained at the same level/value during the course of experiment, hence the experiments were termed as carried out under uncontrolled pH conditions in this study. In the second condition, the initial pH of the solution was buffered to a pre-decided level/value of 5.00 in the beginning of the experiment by adding 8 mL of acetate buffer {prepared by mixing 680 mL of 0.5M sodium acetate tri-hydrate with 320 mL of 0.5M acetic acid (Asnin et al., 2010)} thereby variations in the solution pH level/value were checked or maintained at the same level/value during the course of experiment. Hence, the experiments were termed as carried out under controlled pH conditions in this study.

4.3 Metal ions availability in aqueous phase with variation in solution pH from mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions

Experiments were designed to assess availability of Cu(II), Pb(II) and Cr(III) metal ions in the aqueous phase from different combinations of mono-, binary- and ternary-metal ion systems with variations in solution pH in the range of 5.00 to 7.00. All the experiments for metal availability from combinations of mono-, binary- and ternary-metal ion systems were carried out by taking a required volume of stock solution of metal ion(s) in 150 mL beakers and added with de-mineralized water to make the solution volume to approximately 70-80 mL as indicated in Table 4.6. The beaker containing the solution was mounted on a magnetic stirrer [Make: Eltek, M/S Elektrocraft (India) Pvt. Ltd., Mumbai, India] and while mixing appropriate amounts of acid (1N, 0.1N, 0.01N HCl) or base (1N, 0.1N, 0.01N NaOH) were added using a glass pipette for adjusting the desired pH with the help of a digital pH meter (Model: µpH System 361, M/S Systronics India Ltd., India). The mixing was continued for approximately 8-10 min. after adjusting the desired pH and then solution content was transferred in to a 100 mL capacity volumetric flask, added with de-mineralized water up to the mark and mixed thoroughly again. Thereafter, the solution mixture was allowed to stand without mixing and other disturbances for 5 min. before withdrawal of samples from the top portion using another glass pipette. The withdrawn sample was centrifuged at 9800-10200 rpm (Model: R24, M/S Remi Instruments Ltd., India) for 4 min. to separate the solids from the liquid and liquid portion (free of solids) was used to estimate the concentration of metal ion remaining in the solution with the help of an atomic absorption spectroscopy (Model: 55

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Table 4.6: Preparation of mono-, binary- and ternary-metal ion combinations for metal ion availability in aqueous phase with variation in solution pH.

Combinations	Components used
M[Cu(0.60)]	1.91 mL of Cu(II) SS added with acid or base to adjust initial desired pH and final volume made to 100 mL using DMW
M[Pb(0.60)]	6.22 mL of Pb(II) SS added with acid or base to adjust initial desired pH and final volume made to 100 mL using DMW
M[Cr(0.60)]	1.04 mL of Cr(III) SS added with acid or base to adjust initial desired pH and final volume made to 100 mL using DMW
B[Cu(0.45)+Pb(0.15)]	1.43 mL of Cu(II) SS & 1.55 mL of Pb(II) SS added with acid or base to adjust initial desired pH and final volume made to 100 mL using DMW
B[Cu(0.30)+Pb(0.30)]	0.95 mL of Cu(II) SS & 3.11 mL of Pb(II) SS added with acid or base to adjust initial desired pH and final volume made to 100 mL using DMW
B[Cu(0.15)+Pb(0.45)]	0.48 mL of Cu(II) SS & 4.66 mL of Pb(II) SS added with acid or base to adjust initial desired pH and final volume made to 100 mL using DMW
B[Cu(0.60)+Pb(0.60)]	1.91 mL of Cu(II) SS & 6.22 mL of Pb(II) SS added with acid or base to adjust initial desired pH and final volume made to 100 mL using DMW
B[Cr(0.45)+Pb(0.15)]	0.78 mL of Cr(III) SS & 1.55 mL of Pb(II) SS added with acid or base to adjust initial desired pH and final volume made to 100 mL using DMW
B[Cr(0.30)+Pb(0.30)]	0.52 mL of Cr(III) SS & 3.11 mL of Pb(II) SS added with acid or base to adjust initial desired pH and final volume made to 100 mL using DMW
B[Cr(0.15)+Pb(0.45)]	0.26 mL of Cr(III) SS & 4.66 mL of Pb(II) SS added with acid or base to adjust initial desired pH and final volume made to 100 mL using DMW
B[Cr(0.60)+Pb(0.60)]	1.04 mL of Cr(III) SS & 6.22 mL of Pb(II) SS added with acid or base to adjust initial desired pH and final volume made to 100 mL using DMW
B[Cu(0.45)+Cr(0.15)]	1.43 mL of Cu(II) SS & 0.26 mL of Cr(III) SS added with acid or base to adjust initial desired pH and final volume made to 100 mL using DMW
B[Cu(0.30)+Cr(0.30)]	0.95 mL of Cu(II) SS & 0.52 mL of Cr(III) SS added with acid or base to adjust initial desired pH and final volume made to 100 mL using DMW
B[Cu(0.15)+Cr(0.45)]	0.48 mL of Cu(II) SS & 0.78 mL of Cr(III) SS added with acid or base to adjust initial desired pH and final volume made to 100 mL using DMW
B[Cu(0.60)+Cr(0.60)]	1.91 mL of Cu(II) SS & 1.04 mL of Cr(III) SS added with acid or base to adjust initial desired pH and final volume made to 100 mL using DMW
T[Cu(0.20)+Pb(0.20)+Cr(0.20)]	0.64 mL of Cu(II) SS, 2.07 mL of Pb(II) & 0.35 mL of Cr(III) SS added with acid or base to adjust initial desired pH and final volume made to 100 mL using DMW
T[Cu(0.60)+Pb(0.60)+Cr(0.60)]	1.91 mL of Cu(II) SS, 6.22 mL of Pb(II) & 1.04 mL of Cr(III) SS added with acid or base to adjust initial desired pH and final volume made to 100 mL using DMW

SS = Stock solution, DMW = De-mineralized water, acid or base (1N, 0.1N, 0.01N) added to adjust initial pH level to 5.0, 5.5, 6.0, 6.5 and 7.0.

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B, M/S Spectra AA Varian, Australia). All the experiments were conducted in triplicate and average values were used for analysis of the results.

The speciation of Cu(II), Pb(II) and Cr(III) metal ions from different combinations of mono-, binary- and ternary-metal ion systems with variation in solution pH were also estimated using MINEQL+ software (Schecher & McAvoy, 1998). The input parameters such as initial concentrations of different components [viz., Cu(II), Pb(II), Cr(III), SO_4^{2-}, NO_3^-, CH_3COO^-, Na^+ etc.] present in aqueous phase were estimated based on the initial experimental conditions adopted as indicated in Table 4.7. The speciation of metal ions under uncontrolled pH conditions was estimated for pH of 5.00, 5.50, 6.00, 6.50 and 7.00 while speciation of metal ions under controlled pH conditions was estimated at buffered pH value of 5.00. The input values for the concentrations of H^+ and OH^- ions under uncontrolled and controlled pH conditions were not entered in the software as their values were taken by the software depending on the initial pH value entered in the MINEQL+ software. All the concentrations of metal species present in ionic form were taken into consideration to estimate the percentage availability of metal ion(s) in the aqueous phase.

4.4 Effect of contact time on metal ion concentration remaining in aqueous phase under uncontrolled and controlled pH conditions from mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions

The effect of contact time on the metal ion concentration remaining in aqueous phase from different combinations of mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) have been investigated under uncontrolled and controlled pH conditions. The stock solutions of mono-metal ions were used to prepare solution of selected combinations of mono-, binary- and ternary-metal ion systems as indicated in Table 4.8. The required amounts (in terms of volume) of stock solutions of mono-metal ions were taken in a 1000 mL capacity glass beaker and added with sufficient amount of de-mineralized water to ensure that pH electrode is safely dipped into the liquid leaving sufficient space below for smooth operation of magnetic stirring bar without touching the lower tip of pH electrode. For experiments carried out under uncontrolled pH conditions, pH of the solution was initially adjusted to a value of 5.00 by adding required amounts (in terms of volume) of either acid (1N, 0.1N, 0.01N HCl) or base (1N, 0.1N, 0.01N NaOH). After adjusting the solution pH to 5.00, the content was transferred in to a 1000 mL capacity volumetric flask, added with de-mineralized water up to the mark and mixed thoroughly again. For experiments carried out

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Table 4.7: Input parameters for mono-, binary- and ternary-metal ion combinations for metal ion availability in aqueous phase under uncontrolled and controlled pH conditions with variation in solution pH using MINEQL+ software.

Combinations	Input parameters with initial concentration (in mol/L)	
	Uncontrolled pH conditions	Controlled pH conditions
M[Cu(0.60)]	Cu(II) = 0.0013, SO_4^{-2} = 0.0003	Cu(II) = 0.0012, CH_3COO^- = 0.0800, Na^+ = 0.0560, SO_4^{-2} = 0.0003
M[Pb(0.60)]	Pb(II) = 0.0012, NO_3^- = 0.0006	Pb(II) = 0.0012, CH_3COO^- = 0.0800, Na^+ = 0.0560, NO_3^- = 0.0006
M[Cr(0.60)]	Cr(III) = 0.0018, NO_3^- = 0.0006	Cr(III) = 0.0012, CH_3COO^- = 0.0800, Na^+ = 0.0560, NO_3^- = 0.0006
B[Cu(0.45)+Pb(0.15)]	Cu(II) = 0.0009, SO_4^{-2} = 0.0002, Pb(II) = 0.0003, NO_3^- = 0.0002	Cu(II) = 0.0009, SO_4^{-2} = 0.0002, Pb(II) = 0.0003, NO_3^- = 0.0002, CH_3COO^- = 0.0800, Na^+ = 0.0560
B[Cu(0.30)+Pb(0.30)]	Cu(II) = 0.0006, SO_4^{-2} = 0.0002, Pb(II) = 0.0006, NO_3^- = 0.0003	Cu(II) = 0.0006, SO_4^{-2} = 0.0002, Pb(II) = 0.0006, NO_3^- = 0.0003, CH_3COO^- = 0.0800, Na^+ = 0.0560
B[Cu(0.15)+Pb(0.45)]	Cu(II) = 0.0003, SO_4^{-2} = 0.0000, Pb(II) = 0.0009, NO_3^- = 0.0005	Cu(II) = 0.0003, SO_4^{-2} = 0.0000, Pb(II) = 0.0009, NO_3^- = 0.0005, CH_3COO^- = 0.0800, Na^+ = 0.0560
B[Cu(0.60)+Pb(0.60)]	Cu(II) = 0.0012, SO_4^{-2} = 0.0003, Pb(II) = 0.0012, NO_3^- = 0.0006	Cu(II) = 0.0012, SO_4^{-2} = 0.0003, Pb(II) = 0.0012, NO_3^- = 0.0006, CH_3COO^- = 0.0800, Na^+ = 0.0560
B[Cr(0.45)+Pb(0.15)]	Cr(III) = 0.0014, Pb(II) = 0.0003, NO_3^- = 0.0006	Cr(III) = 0.0014, Pb(II) = 0.0003, NO_3^- = 0.0006, CH_3COO^- = 0.0800, Na^+ = 0.0560
B[Cr(0.30)+Pb(0.30)]	Cr(III) = 0.0009, Pb(II) = 0.0006, NO_3^- = 0.0006	Cr(III) = 0.0009, Pb(II) = 0.0006, NO_3^- = 0.0006, CH_3COO^- = 0.0800, Na^+ = 0.0560
B[Cr(0.15)+Pb(0.45)]	Cr(III) = 0.0005, Pb(II) = 0.0009, NO_3^- = 0.0006	Cr(III) = 0.0005, Pb(II) = 0.0009, NO_3^- = 0.0006, CH_3COO^- = 0.0800, Na^+ = 0.0560
B[Cr(0.60)+Pb(0.60)]	Cr(III) = 0.0019, Pb(II) = 0.0011, NO_3^- = 0.0012	Cr(III) = 0.0019, Pb(II) = 0.0011, NO_3^- = 0.0012, CH_3COO^- = 0.0800, Na^+ = 0.0560
B[Cu(0.45)+Cr(0.15)]	Cu(II) = 0.0009, SO_4^{-2} = 0.0002, Cr(III) = 0.0004, NO_3^- = 0.0001	Cu(II) = 0.0009, SO_4^{-2} = 0.0002, Cr(III) = 0.0004, NO_3^- = 0.0001, CH_3COO^- = 0.0800, Na^+ = 0.0560
B[Cu(0.30)+Cr(0.30)]	Cu(II) = 0.0006, SO_4^{-2} = 0.0002, Cr(III) = 0.0010, NO_3^- = 0.0003	Cu(II) = 0.0006, SO_4^{-2} = 0.0002, Cr(III) = 0.0010, NO_3^- = 0.0003, CH_3COO^- = 0.0800, Na^+ = 0.0560
B[Cu(0.15)+Cr(0.45)]	Cu(II) = 0.0003, SO_4^{-2} = 0.0000, Cr(III) = 0.0015, NO_3^- = 0.0004	Cu(II) = 0.0003, SO_4^{-2} = 0.0000, Cr(III) = 0.0015, NO_3^- = 0.0004, CH_3COO^- = 0.0800, Na^+ = 0.0560
B[Cu(0.60)+Cr(0.60)]	Cu(II) = 0.0012, SO_4^{-2} = 0.0003, Cr(III) = 0.0020, NO_3^- = 0.0006	Cu(II) = 0.0012, SO_4^{-2} = 0.0003, Cr(III) = 0.0020, NO_3^- = 0.0006, CH_3COO^- = 0.0800, Na^+ = 0.0560
T[Cu(0.20)+Pb(0.20)+Cr(0.20)]	Cu(II) = 0.0004, SO_4^{-2} = 0.0000, Pb(II) = 0.0004, Cr(III) = 0.0007, NO_3^- = 0.0004	Cu(II) = 0.0004, SO_4^{-2} = 0.0000, Pb(II) = 0.0004, Cr(III) = 0.0007, NO_3^- = 0.0004, CH_3COO^- = 0.0800, Na^+ = 0.0560
T[Cu(0.60)+Pb(0.60)+Cr(0.60)]	Cu(II) = 0.0012, SO_4^{-2} = 0.0003, Pb(II) = 0.0012, Cr(III) = 0.0019, NO_3^- = 0.0012	Cu(II) = 0.0012, SO_4^{-2} = 0.0003, Pb(II) = 0.0012, Cr(III) = 0.0019, NO_3^- = 0.0012, CH_3COO^- = 0.0800, Na^+ = 0.0560

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Table 4.8: Preparation of experimental solution of mono-, binary- and ternary-metal ion combinations for investigation of effect of contact time on variations in metal ion concentration remaining in aqueous phase.

Combinations	Components (mL)	
	Uncontrolled pH conditions	Controlled pH conditions
M[Cu(0.60)]	19.06 mL of Cu(II) SS added with acid or base to adjust initial pH 5.00 and final volume made to 1000 mL using DMW	19.06 mL of Cu(II) SS buffered to pH 5.00 with 80 mL of acetate buffer and final volume made to 1000 mL using DMW
M[Pb(0.60)]	62.16 mL of Pb(II) SS added with acid or base to adjust initial pH 5.00 and final volume made to 1000 mL using DMW	62.16 mL of Pb(II) SS buffered to pH 5.00 with 80 mL of acetate buffer and final volume made to 500 mL using DMW
M[Cr(0.60)]	10.40 mL of Cr(III) SS added with acid or base to adjust initial pH 5.00 and final volume made to 1000 mL using DMW	10.40 mL of Cr(III) SS buffered to pH 5.00 with 80 mL of acetate buffer and final volume made to 1000 mL using DMW
B[Cu(0.45)+Pb(0.15)]	14.30 mL of Cu(II) SS & 15.54 mL of Pb(II) SS added with acid or base to adjust initial pH 5.00 and final volume made to 1000 mL using DMW	14.30 mL of Cu(II) SS & 15.54 mL of Pb(II) SS buffered to pH 5.00 with 80 mL of acetate buffer and final volume made to 1000 mL using DMW
B[Cu(0.30)+Pb(0.30)]	9.53 mL of Cu(II) SS & 31.08 mL of Pb(II) SS added with acid or base to adjust initial pH 5.00 and final volume made to 1000 mL using DMW	9.53 mL of Cu(II) SS & 31.08 mL of Pb(II) SS buffered to pH 5.00 with 80 mL of acetate buffer and final volume made to 1000 mL using DMW
B[Cu(0.15)+Pb(0.45)]	4.78 mL of Cu(II) SS & 46.62 mL of Pb(II) SS added with acid or base to adjust initial pH 5.00 and final volume made to 1000 mL using DMW	4.78 mL of Cu(II) SS & 46.62 mL of Pb(II) SS buffered to pH 5.00 with 80 mL of acetate buffer and final volume made to 1000 mL using DMW
B[Cu(0.60)+Pb(0.60)]	19.06 mL of Cu(II) SS & 62.16 mL of Pb(II) SS added with acid or base to adjust initial pH 5.00 and final volume made to 1000 mL using DMW	19.06 mL of Cu(II) SS & 62.16 mL of Pb(II) SS buffered to pH 5.00 with 80 mL of acetate buffer and final volume made to 1000 mL using DMW
B[Cr(0.45)+Pb(0.15)]	7.80 mL of Cr(III) SS & 15.54 mL of Pb(II) SS added with acid or base to adjust initial pH 5.00 and final volume made to 1000 mL using DMW	7.80 mL of Cr(III) SS & 15.54 mL of Pb(II) SS buffered to pH 5.00 with 80 mL of acetate buffer and final volume made to 1000 mL using DMW
B[Cr(0.30)+Pb(0.30)]	5.20 mL of Cr(III) SS & 31.08 mL of Pb(II) SS added with acid or base to adjust initial pH 5.00 and final volume made to 1000 mL using DMW	5.20 mL of Cr(III) SS & 31.08 mL of Pb(II) SS buffered to pH 5.00 with 80 mL of acetate buffer and final volume made to 1000 mL using DMW

Table continued on next page…..

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Table 4.8 continues……

B[Cr(0.15)+Pb(0.45)]	2.60 mL of Cr(III) SS & 46.62 mL of Pb(II) SS added with acid or base to adjust initial pH 5.00 and final volume made to 1000 mL using DMW	2.60 mL of Cr(III) SS & 46.62 mL of Pb(II) SS buffered to pH 5.00 with 80 mL of acetate buffer and final volume made to 1000 mL using DMW
B[Cr(0.60)+Pb(0.60)]	10.40 mL of Cr(III) SS & 62.16 mL of Pb(II) SS added with acid or base to adjust initial pH 5.00 and final volume made to 1000 mL using DMW	10.40 mL of Cr(III) SS & 62.16 mL of Pb(II) SS buffered to pH 5.00 with 80 mL of acetate buffer and final volume made to 1000 mL using DMW
B[Cu(0.45)+Cr(0.15)]	14.30 mL of Cu(II) SS & 2.60 mL of Cr(III) SS added with acid or base to adjust initial pH 5.00 and final volume made to 1000 mL using DMW	14.30 mL of Cu(II) SS & 2.60 mL of Cr(III) SS buffered to pH 5.00 with 80 mL of acetate buffer and final volume made to 1000 mL using DMW
B[Cu(0.30)+Cr(0.30)]	9.53 mL of Cu(II) SS & 5.20 mL of Cr(III) SS added with acid or base to adjust initial pH 5.00 and final volume made to 1000 mL using DMW	9.53 mL of Cu(II) SS & 5.20 mL of Cr(III) SS buffered to pH 5.00 with 80 mL of acetate buffer and final volume made to 1000 mL using DMW
B[Cu(0.15)+Cr(0.45)]	4.78 mL of Cu(II) SS & 7.80 mL of Cr(III) SS added with acid or base to adjust initial pH 5.00 and final volume made to 1000 mL using DMW	4.78 mL of Cu(II) SS & 7.80 mL of Cr(III) SS buffered to pH 5.00 with 80 mL of acetate buffer and final volume made to 1000 mL using DMW
B[Cu(0.60)+Cr(0.60)]	19.06 mL of Cu(II) SS & 10.40 mL of Cr(III) SS added with acid or base to adjust initial pH 5.00 and final volume made to 1000 mL using DMW	19.06 mL of Cu(II) SS & 10.40 mL of Cr(III) SS buffered to pH 5.00 with 80 mL of acetate buffer and final volume made to 500 mL using DMW
T[Cu(0.20)+Pb(0.20)+Cr(0.20)]	6.35 mL of Cu(II) SS, 20.72 mL of Pb(II) & 3.47 mL of Cr(III) SS added with acid or base to adjust initial pH 5.00 and final volume made to 1000 mL using DMW	6.35 mL of Cu(II) SS, 20.72 mL of Pb(II) & 3.47 mL of Cr(III) SS buffered to pH 5.00 with 80 mL of acetate buffer and final volume made to 1000 mL using DMW
T[Cu(0.60)+Pb(0.60)+Cr(0.60)]	19.06 mL of Cu(II) SS, 62.16 mL of Pb(II) & 10.40 mL of Cr(III) SS added with acid or base to adjust initial pH 5.00 and final volume made to 1000 mL using DMW	19.06 mL of Cu(II) SS, 62.16 mL of Pb(II) & 10.40 mL of Cr(III) SS buffered to pH 5.00 with 80 mL of acetate buffer and final volume made to 1000 mL using DMW

SS = Working solution, DMW = De-mineralized water, acid or base (1N, 0.1N, 0.01N) added to adjust initial pH level under uncontrolled pH conditions.

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under controlled pH conditions, pH of the solution was buffered to a value of 5.00 by adding 160 mL of acetate buffer {prepared by mixing 680 mL of 0.5M sodium acetate tri-hydrate with 320 mL of 0.5M acetic acid (Asnin et al., 2010)} for 1000 mL of total solution volume (which worked out to be 8 mL of buffer solution in 50 mL of solution volume). After buffering the solution pH to 5.00, the content was transferred in to a 1000 mL capacity volumetric flask, added with de-mineralized water up to the mark and mixed thoroughly again. These solutions (one prepared for uncontrolled pH conditions experiments while another one prepared for controlled pH conditions experiments) were termed as experimental solution. 50 mL each of the experimental solution was transferred to 9 specimen tubes of 100 mL capacity. Each of the specimen tubes was further added with a fixed dose of 0.6 g GAA (which worked out to be 12 g GAA/L). The capped specimen tubes containing the mixture (i.e. metal ion solution with initial pH adjusted or buffered and GAA) were mounted on an end-over-end rotary shaker (Model: Reico, M/S REICO Equipment & Instrument Pvt. Ltd., Kolkata, India) and mixed at a constant speed of 66 revolutions per minute (rpm) at room temperature (30±1 ^{o}C). The specimen tubes were taken out from the shaker one by one at predetermined time intervals. The liquid phase was separated from the solid phase by using an ordinary filter paper (Make: O Sicerin and Biva, Kolkata, India). The final solution pH and the residual metal ion concentration in the separated liquid phase were estimated. All the experiments were conducted in triplicate and average values were used for analysis of the results.

4.5 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions

The experimental data obtained in the investigation of effect of contact time on metal ion concentration remaining in aqueous phase under uncontrolled and controlled pH conditions from combinations of mono-, binary- and ternary-metal ion systems (as explained in section 4.4) were used to study the kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from the respective combinations of mono-, binary- and ternary-metal ion systems.

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4.6 Batch tests to investigate additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions by GAA when exposed to metal ions repeatedly

Two sets of batch tests were carried out to investigate additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions by GAA when exposed to metal ions repeatedly. In the first set of batch tests, a fixed amount of GAA was exposed up to equilibrium time only once to a mono-metal ion system {either M[Cu(0.60)] or M[Pb(0.60)] or M[Cr(0.60)]} – the metal ion in the system termed as target metal and thereafter, the target metal ion loaded GAA was washed thrice with de-mineralized water to remove the precipitated or un-adsorbed target metal ion without loss of GAA particles and then again exposed up to equilibrium time only once to the non-target metal ion system {for example, if M[Cu(0.60)] taken as target metal then either M[Pb(0.60)] or M[Cr(0.60)] considered as non-target metal}. The experiments were carried out by taking 50 mL of a target metal ion solution {prepared as explained in section 4.4 (Table 4.8)} in a 100 mL capacity specimen tube. The specimen tube was added with a fixed dose of 0.6 g GAA (which worked out as 12 g GAA/L). The capped specimen tube containing the mixture (i.e. experimental solution and GAA) was mounted on an end-over-end rotary shaker and mixed at a constant speed of 66 rpm at room temperature (30±1 ^{o}C) up to equilibrium time as determined in section 4.4. At the end of mixing, the specimen tube was taken out from the shaker and the supernatant liquid containing residual target metal ion was decanted without loss of any GAA particles and decanted supernatant was preserved. The target metal ion loaded GAA was washed thrice with 50 mL of de-mineralized water in each washings to remove the precipitated or un-adsorbed target metal ion without loss of any GAA particles from the specimen tube, the washings were collected together and preserved. The specimen tube containing target metal ion loaded washed GAA was then filled with 50 mL experimental solution of non-target metal ion. The capped specimen tube with the mixture was mounted on an end-over-end rotary shaker and mixed at a constant speed of 66 rpm at room temperature (30±1 ^{o}C) up to equilibrium time as determined in section 4.4. At the end of mixing, the specimen tube was taken out from the shaker and the supernatant liquid containing residual non-target metal ion was decanted without loss of any GAA particles and decanted supernatant was preserved. The preserved decanted supernatant liquids containing residual target and non-target metal ions as well as washings of target metal ion loaded GAA

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were used to estimate the concentration of the metal ions. All the experiments were conducted in triplicate and average values were used for analysis of the results.

In the second set of batch tests, a fixed amount of GAA was exposed up to equilibrium time repeatedly for 6-10 cycles of a mono-metal ion system {either M[Cu(0.60)] or M[Pb(0.60)] or M[Cr(0.60)]} – the metal ion in the system termed as target metal. At the end of exposure with target metal ion in each cycle, the supernatant was decanted without loss of GAA particles. After completion of exposure cycles with the target metal ion, the target metal ion loaded GAA was washed thrice with de-mineralized water to remove the precipitated or un-adsorbed target metal ion without loss of GAA particles. The target metal ion loaded washed GAA was then again exposed only once to the non-target metal ion system {for example, if M[Cu(0.60)] taken as target metal then either M[Pb(0.60)] or M[Cr(0.60)] considered as non-target metal} up to equilibrium time. The first cycle experiment was carried out by taking 50 mL of a target metal ion solution {prepared as explained in section 4.4 (Table 4.8)} in a 100 mL capacity specimen tube. The specimen tube was added with a fixed dose of 0.6 g GAA (which worked out as 12 g GAA/L). The capped specimen tube containing the mixture (i.e. experimental solution and GAA) was mounted on an end-over-end rotary shaker and mixed at a constant speed of 66 rpm at room temperature (30±1 ^{o}C) up to equilibrium time as determined in section 4.4. At the end of the mixing, the specimen tube was taken out from the shaker and the supernatant liquid containing residual target metal ion from the first cycle was decanted without loss of any GAA particles and preserved. Similarly, other 5-9 subsequent cycles of exposure with the same target metal ion were carried out to the target metal ion loaded washed GAA from the previous cycles and the decanted supernatant from each cycles were preserved. The 6-10 cycles of target metal ion loaded GAA was washed thrice with 50 mL of de-mineralized water in each washings to remove the precipitated or un-adsorbed target metal ion without loss of any GAA particles from the specimen tube, the washings were collected together and preserved. The specimen tube containing 6-10 cycles target metal ion loaded washed GAA was then filled with 50 mL experimental solution of non-target metal ion. The capped specimen tube with the mixture was mounted on an end-over-end rotary shaker and mixed at a constant speed of 66 rpm at room temperature (30±1 ^{o}C) up to equilibrium time as determined in section 4.4. At the end of the mixing, the specimen tube was taken out from the shaker and the supernatant liquid containing residual non-target metal ion was decanted without loss of any GAA particles and preserved. The preserved decanted supernatant liquids containing residual target metal ions

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from each cycles and non-target metal ions as well as washings of target metal ion loaded GAA were used to estimate the concentration of the metal ions. All the experiments were conducted in triplicate and average values were used for analysis of the results.

4.7 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for four loading cycles with mono- and binary-metal ions systems comprising of Cu(II), Pb(II) and Cr(III) ions

Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for four loading cycles with mono- and binary-metal ions systems comprising of Cu(II), Pb(II) and Cr(III) metal ions have been investigated. In this investigation, the GAA was exposed to a mono-metal ion system or a combination of binary-metal ion system for consecutive three loading cycles followed by fourth loading cycle of another mono-metal ion system or another combination of binary-metal ion system having the same metal ions under uncontrolled and controlled pH conditions. For example, the GAA was repeatedly exposed to first three loading cycles of M[Cu(0.60)] system followed by fourth loading cycle with M[Pb(0.60)] system and vice-versa. Similarly, in the case of binary-metal ion system, the GAA was exposed to B[Cu(0.45)+Pb(0.15)] combination in the first three loading cycles while it was exposed to B[Cu(0.15)+Pb(0.45)] combination in the fourth cycle.

In the first loading cycle, 50 mL each of the experimental solution of a mono-metal ion system or a combination of binary-metal ion system {prepared as explained in section 4.4 (Table 4.8)} was transferred to 9 specimen tubes of 100 mL capacity. Each of the specimen tubes was further added with a fixed dose of 0.6 g GAA (which worked out to be 12 g GAA/L). The capped specimen tubes containing the mixture (i.e. experimental solution and GAA) were mounted on an end-over-end rotary shaker and mixed at a constant speed of 66 rpm at room temperature (30±1 ^{o}C). The specimen tubes were taken out from the shaker one by one at the predetermined time intervals and allowed to settle the solids. The supernatant liquid containing residual metal ion from the first loading cycle was decanted without loss of any GAA particles. The decanted supernatants were preserved in new specimen tubes while the first cycle loaded GAA particles were preserved in the original specimen tubes. After completion of first loading cycle experiments, the metal loaded GAA of the first cycle were washed thrice with 50 mL of de-mineralized water in each washings to remove the precipitated or un-adsorbed target metal ion without loss of any GAA particles from the

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respective specimen tubes. The first cycle loaded washed GAA was similarly loaded in the second loading cycles while second cycle loaded washed GAA was again loaded in the third cycle with the same mono-metal ion system or combination of binary-metal ion system. All the separated supernatants were preserved separately. The fourth loading cycle was carried out using third cycle loaded washed GAA but exposing with another mono-metal ion system or another combination of binary-metal ion system having the same metal ions in the combination. At the end of fourth loading cycle, all the separated supernatants were preserved separately. The final solution pH and the residual metal ion concentration in the separated supernatants were estimated. All the experiments were conducted in duplicate and average values were used for analysis of the results.

4.8 Equilibrium studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions

The equilibrium studies have been carried out under uncontrolled and controlled pH conditions from combinations of mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions. The equilibrium experiments were carried out by transferring 50 mL of a metal ion system {prepared as explained in section 4.4 (Table 4.8)} in 9 specimen tubes of 100 mL capacity. One specimen tube was kept as a control while other 8 specimen tubes were added with varying doses of GAA starting with lower value of 0.2 g and increasing to a higher value of 1.6 g (which worked out as 4 to 32 g GAA/L). The capped specimen tube containing the mixture (i.e. experimental solution and GAA) was mounted on an end-over-end rotary shaker and mixed at a constant speed of 66 rpm at room temperature (30±1 ^{o}C) for an equilibrium time of 3 h. The specimen tubes were taken out from the shaker at the end of equilibrium time. The liquid and solid phases were separated immediately using ordinary filter paper and the final pH was measured. The separated liquid portions were preserved for estimation of metal ion concentration. All the experiments were conducted in triplicate and average values were used for analysis of the results.

4.9 Continuous mode column studies for metal removal under uncontrolled and controlled pH conditions from mono- and binary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions

Continuous mode column experiments were conducted using a glass tube of 20 mm inner diameter. A schematic of the experimental setup used for the study is shown in Fig. 4.1.

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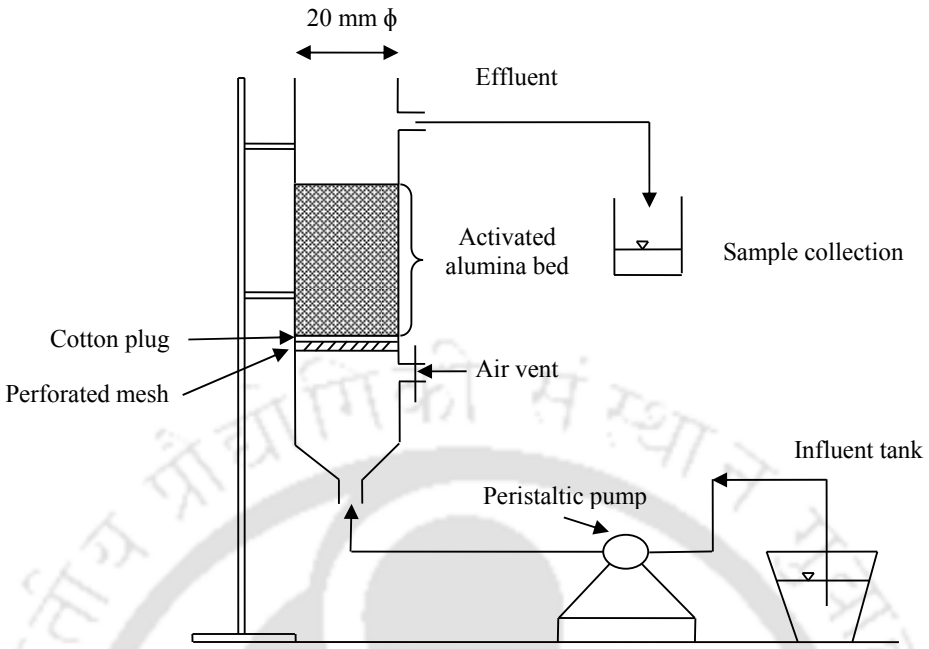

Fig. 4.1: Schematic of the experimental set-up used in the column study.

A perforated (openings less than 2 mm) circular metal plate was fixed at the bottom of the glass tube. A thin layer (approximately 2 mm in thickness) of cotton-wool was placed over the metal plate to prevent the loss of GAA particles through perforated openings. An air venting valve was also provided just below the perforated plate to allow expulsion of trapped air-bubbles in the beginning of the column operation. The columns were packed with GAA by imparting gentle jerks. The bed depths of 3.0, 4.5 and 6.0 cm contained approximately 9.4, 13.2 and 16.8 g GAA respectively.

The column studies have been carried out for metal removal from combinations of mono- and binary-metal ion systems under uncontrolled and controlled pH conditions. The experimental solution {prepared as explained in section 4.4 (Table 4.8)} was fed to GAA column bed in upflow mode using a peristaltic pump (Model: PP20 EX–2C, M/S Miclins, India) at a constant flow rate of 2.0 mL/min. The virgin column bed was first loaded and exhausted with the experimental solution of a mono-metal ion system or a combination of a binary-metal ion system. The loaded bed was then washed with approximately 100 bed volumes of de-mineralized water in downflow mode to remove any of the residual or un-adsorbed metal ions remaining in pore volumes of the bed. The washed bed was then

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reloaded with the experimental solution of another mono-metal ion system or another combination of binary-metal ion system having same metal ions. Samples were collected from the effluent at regular intervals and effluent pH as well as concentration of the metal ions present in the effluents was estimated. All the column studies were conducted in duplicate and average values were used in the analysis of the experimental data. While undertaking column studies in the initial phases, operation of column beds till it exhausted or yielded effluent concentration close to 80% of influent metal concentration became a nightmare as the column operations continued for more than 33 h at a stretch. Therefore, column studies with combinations of mono- and binary-metal ion systems were carried out for time periods as tabulated in Table 4.9.

4.10 Estimation of pH_{zpc} of GAA

The pH_{zpc} value of GAA was estimated by following the procedure as explained by Srivastava et al. (2011). The pH of a solution of 100 mL containing 0.01M NaCl was adjusted in the range between 2.00 and 12.00 by using NaOH (1N, 0.1N, 0.01N NaOH) or HCl (1N, 0.1N, 0.01N HCl). Then 50 mL of 0.01M NaCl was taken in a conical flask and 0.6 g of the GAA was added in conical flasks containing 0.01M NaCl solution of different pH values. These flasks were then kept on horizontal shaker (Model: ICT, M/S International Commercial Trading, Kolkata, India) for mixing for 24 h and after that pH of the solutions was measured by using a pH meter. The point of intersection of the "pH_{final} vs $pH_{initial}$" curves represented the pH_{zpc} of the GAA.

4.11 Estimation techniques used

All the analytical measurements were carried out following Standards Methods (APHA, 2005). The residual concentrations of Cu(II), Pb(II) and Cr(III) metal ions were estimated using atomic absorption spectroscopy (Model: 55 B, M/S Spectra AA Varian, Australia). The instrument(s) and equipment(s) used in the present work are listed in Table 4.10.

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Table 4.9: Column operation periods for combinations of mono- and binary-metal ion systems investigated under uncontrolled and controlled pH conditions.

Uncontrolled pH conditions							
Virgin bed loading				Washed bed reloading			
Combinations	Time for bed depth (min)			Combinations	Time for bed depth (min)		
	3.0 cm	4.5 cm	6.0 cm		3.0 cm	4.5 cm	6.0 cm
M[Cu(0.60)]	1800	1200	1800	M[Pb(0.60)]	1500	1000	1800
M[Cu(0.60)]	1800	2200	2700	M[Cr(0.60)]	700	700	1200
M[Pb(0.60)]	1800	1000	1800	M[Cu(0.60)]	150	1100	1800
M[Pb(0.60)]	1000	1000	1000	M[Cr(0.60)]	600	700	700
M[Cr(0.60)]	1800	2200	2700	M[Cu(0.60)]	700	700	1200
M[Cr(0.60)]	1000	1000	1000	M[Pb(0.60)]	600	700	700
B[Cu(0.45)+Pb(0.15)]	1800	1200	2200	B[Cu(0.15)+Pb(0.45)]	1500	1000	1500
B[Cu(0.15)+Pb(0.45)]	1500	1200	2200	B[Cu(0.45)+Pb(0.15)]	1500	1000	1800
B[Cr(0.45)+Pb(0.15)]	1000	1000	1000	B[Cr(0.15)+Pb(0.45)]	600	700	700
B[Cr(0.15)+Pb(0.45)]	1000	1000	1000	B[Cr(0.45)+Pb(0.15)]	600	700	700
Controlled pH conditions							
Virgin bed loading				Washed bed reloading			
Combinations	Time for bed depth (min)			Combinations	Time for bed depth (min)		
	3.0 cm	4.5 cm	6.0 cm		3.0 cm	4.5 cm	6.0 cm
M[Cu(0.60)]	500	600	600	M[Pb(0.60)]	300	400	400
M[Cu(0.60)]	600	700	900	M[Cr(0.60)]	400	400	400
M[Pb(0.60)]	500	500	600	M[Cu(0.60)]	300	300	600
M[Pb(0.60)]	500	500	600	M[Cr(0.60)]	300	300	400
M[Cr(0.60)]	600	700	900	M[Cu(0.60)]	400	400	400
M[Cr(0.60)]	500	500	600	M[Pb(0.60)]	300	300	400
B[Cu(0.45)+Pb(0.15)]	500	500	500	B[Cu(0.15)+Pb(0.45)]	300	300	300
B[Cu(0.15)+Pb(0.45)]	500	500	500	B[Cu(0.45)+Pb(0.15)]	300	300	300
B[Cr(0.45)+Pb(0.15)]	500	500	500	B[Cr(0.15)+Pb(0.45)]	300	300	300
B[Cr(0.15)+Pb(0.45)]	500	500	500	B[Cr(0.45)+Pb(0.15)]	300	300	300

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Table 4.10: Instrument(s) and equipment(s) used in the present work.

Instrument(s)/Equipment(s)	Manufacturer
Analytical balance	Model: AB304S, M/S Mettler Instrument AG, Switzerland
Atomic absorption spectroscopy	Model: 55 B, M/S Spectra AA Varian, Australia
Conductivity meter	Model: VSI-04ATC, M/S VSI Electronics Pvt. Ltd., India
De-mineralized water prepared through RO process	Model: Milli-Q Water, M/S Millipore S.A.S., Molsheim, France
Digital pH meter	Model: µpH System 361, M/S Systronics India Ltd., India
End-over-end rotary shaker	Model: Reico, M/S REICO Equipment & Instrument Pvt. Ltd., Kolkata, India
Horizontal shaker	Model: ICT, M/S International Commercial Trading, Kolkata, India
Flame photometer	Model: 128, M/S Systronics India Ltd., India
Peristaltic pump	Model: PP20 EX–2C, M/S Miclins, India
Hot air drying oven	Model: PSI, M/S Mahindra Scientific Instrument Co., India
Digital thermometer	Model: St- 9283B, M/S MEXTECH, India
Magnetic stirrer	Make: Eltek, M/S Elektrocraft (India) Pvt. Ltd., Mumbai, India
Centrifuge	Model: R24, M/S Remi Instruments Ltd., India
Autosorb IQ	Model:ASIQM0000-4, Quantachrome Instruments, Boynton Beach, FL, USA

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CHAPTER 5

RESULTS AND DISCUSSION

The present work is aimed at carrying out an investigation of metal removal and metal uptake from mono-, binary- and ternary-metal ion systems having a fixed total initial metal ion concentration in the solution. These studies have been executed under (i) uncontrolled pH conditions as well as (ii) controlled pH conditions. The results obtained shall be useful to understand metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from aqueous phase. The metal ions selected for the present study are Cu(II), Pb(II) and Cr(III) while the selected adsorbent is granular activated alumina (GAA). For the experimental investigations, concentration of metal ion was expressed on equivalent basis so as to take into account the differences in valence and atomic weight of selected metal ions as well as ease in adding concentrations of metal ions algebraically. Batch studies were carried out with a view to determine the availability of metal ions in aqueous phase at different solution pH. The effect of variation in contact time on metal ion concentration remaining in solution was investigated under uncontrolled and controlled pH conditions. The observed results were used to understand kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions. Thereafter, capabilities of GAA for equilibrium metal removal under uncontrolled pH conditions and equilibrium metal uptake under controlled pH conditions were also carried out. The kinetics and equilibrium studies of metal removal and metal uptake from binary- and ternary-metal ion systems were carried out by taking different proportions of individual metal ions but keeping the total initial metal ion concentration to a fixed value. In addition, GAA loaded with a metal ion or a combination of binary-metal ion system was further investigated for its additional potential for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for the same metal ion and/or to another metal ion or combination of binary-metal ion system. The continuous mode column studies were also carried out for mono- and binary-metal ion systems by maintaining a fixed value of total initial metal ion concentrations in the solution (ensuring a constant initial concentration gradient of metal ions) under uncontrolled and controlled pH conditions. Further, the fate of metal ions removed by column bed was investigated when the metal loaded bed reloaded with another metal ion system. Such studies might help to investigate accommodation of

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another metal ion on previously metal loaded column bed and consequently displacement of previously loaded metal ion due to reloading with another metal ion, if any.

5.1 Metal ions availability in aqueous phase with variation in solution pH from mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions

The metal availability in aqueous phase from mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) metal ions was investigated with variation in solution pH. The results of these studies shall be useful to understand the role of solution pH on metal removal from the aqueous phase either by precipitation or adsorption or by both the processes.

5.1.1 Availability of metal ions in aqueous phase with variation in solution pH from mono-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions

The experiments were conducted for mono-metal ion systems of M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] and solution pH was varied from 5.00 to 7.00. This pH range was selected based on the desired initial pH of the solution and final pH observed during the course of a few preliminary tests. The variation in trend of availability of metal ions in aqueous phase from M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] systems is represented in Fig. 5.1. In the case of M[Cu(0.60)] system, Cu(II) metal ion was available 100% in aqueous phase up to solution pH 5.50 while its availability reduced to approximately 95% at pH 6.00, 28% at pH 6.50 and 5% at pH 7.00. The availability of Cu(II) in aqueous phase decreased rapidly between pH 6.00 and 7.00. The theoretically calculated Cu(II) availability in aqueous phase at solution pH 6.00 was 97% (Christophi & Axe, 2000). In the case of M[Pb(0.60)] system, Pb(II) metal ion was available approximately 100% in aqueous phase up to pH 5.50 which reduced to approximately 72% at pH 6.00, 6% at pH 6.50 and 2% at pH 7.00. The availability of Pb(II) in aqueous phase also decreased rapidly between pH 6.00 and 7.00. The theoretically calculated Pb(II) availability in aqueous phase at solution pH 6.00 was 96.4% which was much higher to experimentally observed availability (Christophi & Axe, 2000). In the case of M[Cr(0.60)] system, Cr(III) metal ion was available close to 100% in aqueous phase up to pH 6.00 which reduced to 84% at pH 6.50 and 63% at pH 7.00. Therefore, Cu(II) and Cr(III) may be considered 100% available in aqueous phase up to pH value of 6.00, while availability of Pb(II) in aqueous phase may be considered 72% up to pH value of 6.00. Since

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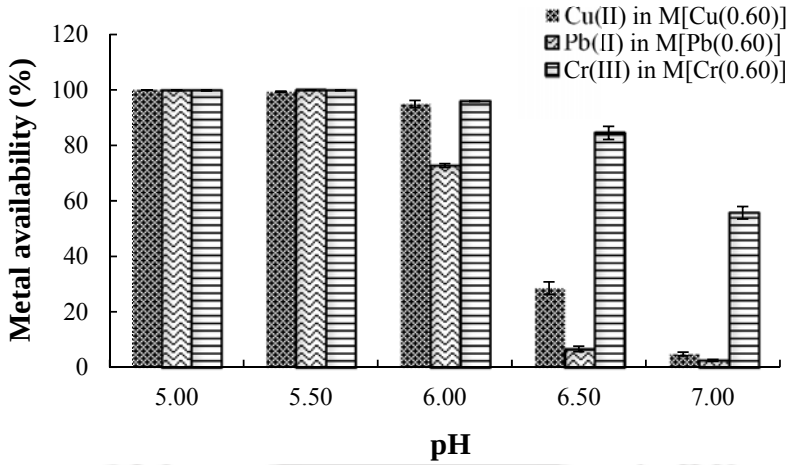

Fig. 5.1: Availability of Cu(II), Pb(II) and Cr(III) metal ions in aqueous phase with variation in solution pH from respective mono-metal ion systems {Initial metal conc. in M[Cu(0.60)] = 0.60±0.00 meq/L, M[Pb(0.60)] = 0.60±0.00 meq/L, M[Cr(0.60)] = 0.60±0.00 meq/L, Temp. = 30±2°C} (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

availability in aqueous phase of close to or more than 70% of Pb(II) and more than 80% of Cu(II) and Cr(III) metal ions are up to pH of 6.00, and hence the same has been considered in the study.

5.1.2 Availability of metal ions in aqueous phase with variation in solution pH from binary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions

The experiments were conducted for binary-metal ion systems comprising of Cu(II)+Pb(II), Cr(III)+Pb(II) and Cu(II)+Cr(III) metal ions with four different combinations of initial metal ion concentrations as described in section 4.2.1 (Table 4.5). The solution pH was varied in the range of 5.00 to 7.00. This pH range was selected based on the desired initial pH of the solution and final pH observed during the course of a few preliminary tests. The percentage of metal ions remaining in aqueous phase estimated at each pH for different combinations of binary-metal ion systems comprising of Cu(II)+Pb(II) is presented in Fig. 5.2. Both the metal ions were 100% available in aqueous phase at pH 5.00 in B[Cu(0.45)+Pb(0.15)], B[Cu(0.30)+Pb(0.30)], B[Cu(0.15)+Pb(0.45)] and B[Cu(0.60)+Pb(0.60)] combinations. The Cu(II) metal ions availability in aqueous phase reduced approximately to 95%, 93%, 96% and 88% in B[Cu(0.45)+Pb(0.15)], B[Cu(0.30)+Pb(0.30)], B[Cu(0.15)+Pb(0.45)] and B[Cu(0.60)+Pb(0.60)] combinations respectively at solution pH 5.50. The availability of Pb(II) metal ions in aqueous phase were

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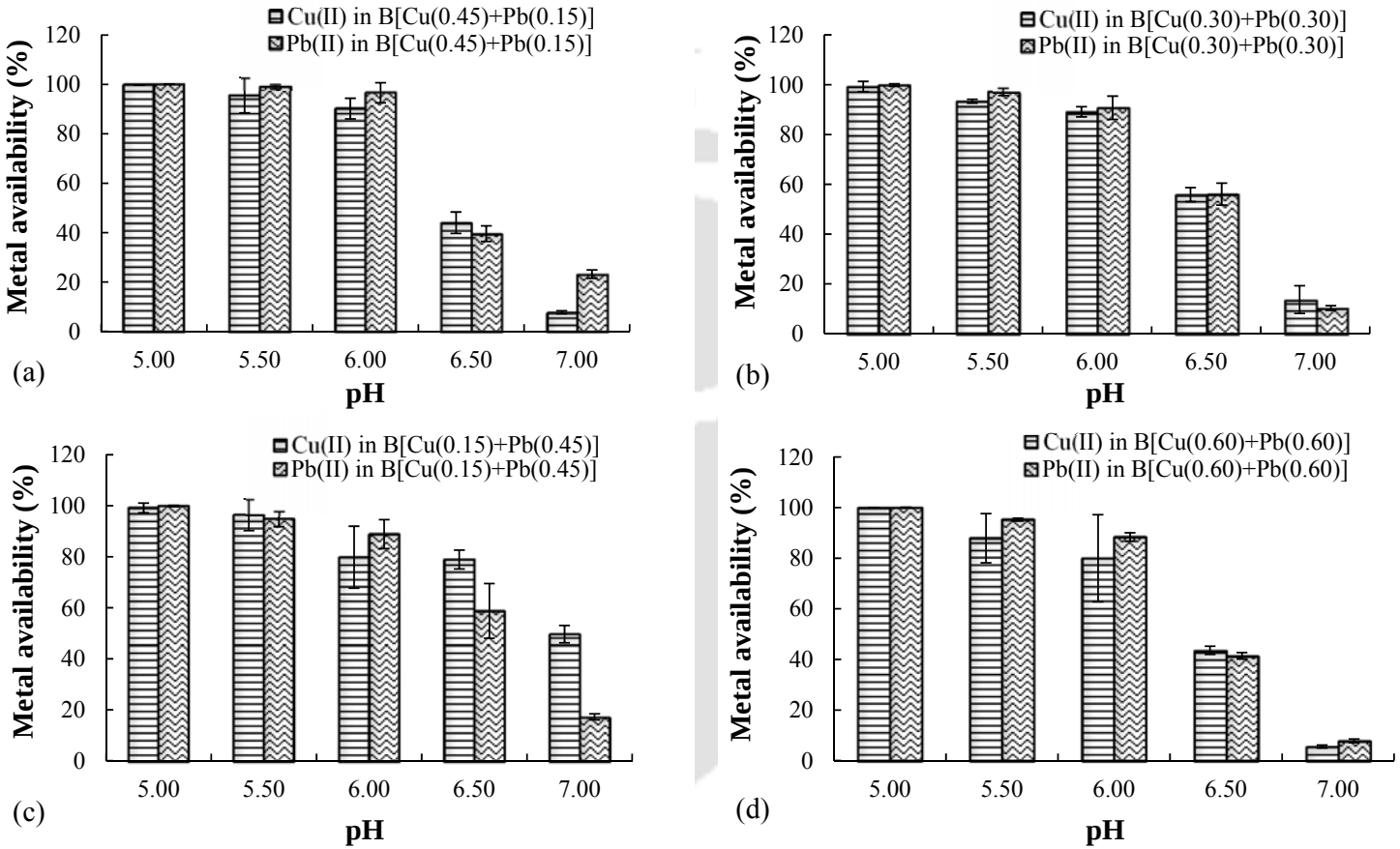

Fig. 5.2: Availability of Cu(II) and Pb(II) metal ions in aqueous phase with variation in solution pH from binary-metal ion system combinations (a) B[Cu(0.45)+Pb(0.15)], (b) B[Cu(0.30)+Pb(0.30)], (c) B[Cu(0.15)+Pb(0.45)] and (d) B[Cu(0.60)+Pb(0.60)] {Initial metal conc. in combinations B[Cu(0.45)+Pb(0.15)] = 0.44±0.00 meq/L of Cu(II) + 0.15±0.00 meq/L of Pb(II), B[Cu(0.30)+Pb(0.30)] = 0.30±0.00 meq/L of Cu(II) + 0.29±0.00 meq/L of Pb(II), B[Cu(0.15)+Pb(0.45)] = 0.15±0.00 meq/L of Cu(II) + 0.45±0.00 meq/L of Pb(II), B[Cu(0.60)+Pb(0.60)] = 0.61±0.00 meq/L of Cu(II) + 0.58±0.01 meq/L of Pb(II)} (Each data represents an average of two independent experimental values with vertical bars at each data points representing 95% confidence interval).

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observed approximately to 99%, 97%, 95% and 95% in B[Cu(0.45)+Pb(0.15)], B[Cu(0.30)+Pb(0.30)], B[Cu(0.15)+Pb(0.45)] and B[Cu(0.60)+Pb(0.60)] combinations respectively at solution pH 5.50. At solution pH 6.00, Cu(II) availability in aqueous phase reduced approximately to 90%, 89%, 80% and 80% while Pb(II) availability in aqueous phase reduced approximately to 96%, 91%, 89% and 88% in B[Cu(0.45)+Pb(0.15)], B[Cu(0.30)+Pb(0.30)], B[Cu(0.15)+Pb(0.45)] and B[Cu(0.60)+Pb(0.60)] combinations respectively. Further, the availability of Cu(II) and Pb(II) in aqueous phase decreased rapidly between pH 6.00 and 7.00. The Cu(II) metal ion availability in aqueous phase at pH 7.00 reduced to 8%, 13%, 49% and 5% while for Pb(II) metal ion, it reduced to 23%, 10%, 17% and 8% respectively in B[Cu(0.45)+Pb(0.15)], B[Cu(0.30)+Pb(0.30)], B[Cu(0.15)+Pb(0.45)] and B[Cu(0.60)+Pb(0.60)] combinations. Therefore, availability in aqueous phase of close to or more than 80% of Cu(II) and Pb(II) metal ions were up to solution pH of 6.00 and has been considered accordingly in the present study.

The variation in trend of availability of metal ions in aqueous phase from four different combinations of binary-metal ion systems comprising of Cr(III)+Pb(II) is represented in Fig. 5.3. Both the metal ions were 100% available in aqueous phase till pH 5.00 in B[Cr(0.45)+Pb(0.15)], B[Cr(0.30)+Pb(0.30)], B[Cr(0.15)+Pb(0.45)] and B[Cr(0.60)+Pb(0.60)] combinations. The Cr(III) metal ions availability in aqueous phase were observed approximately 99%, 97%, 91% and 99% respectively in B[Cr(0.45)+Pb(0.15)], B[Cr(0.30)+Pb(0.30)], B[Cr(0.15)+Pb(0.45)] and B[Cr(0.60)+Pb(0.60)] combinations at solution pH 5.50. The Pb(II) metal ions availability in aqueous phase at pH 5.50 were observed approximately 94%, 100%, 95% and 96% respectively in B[Cr(0.45)+Pb(0.15)], B[Cr(0.30)+Pb(0.30)], B[Cr(0.15)+Pb(0.45)] and B[Cr(0.60)+Pb(0.60)] combinations. At pH 6.00, Cr(III) availability in aqueous phase reduced approximately to 95%, 73%, 60% and 85% while Pb(II) availability in aqueous phase were reduced approximately to 87%, 83%, 88% and 85% respectively in B[Cr(0.45)+Pb(0.15)], B[Cr(0.30)+Pb(0.30)], B[Cr(0.15)+Pb(0.45)] and B[Cr(0.60)+Pb(0.60)] combinations. Further, the availability of Cr(III) and Pb(II) in aqueous phase decreased rapidly between pH 6.00 and 7.00. Therefore, availability of more than 80% of Cr(III) and Pb(II) metal ions in aqueous phase were up to solution pH of 6.00 except for Cr(III) metal ions in B[Cr(0.30)+Pb(0.30)] and B[Cr(0.15)+Pb(0.45)] combinations.

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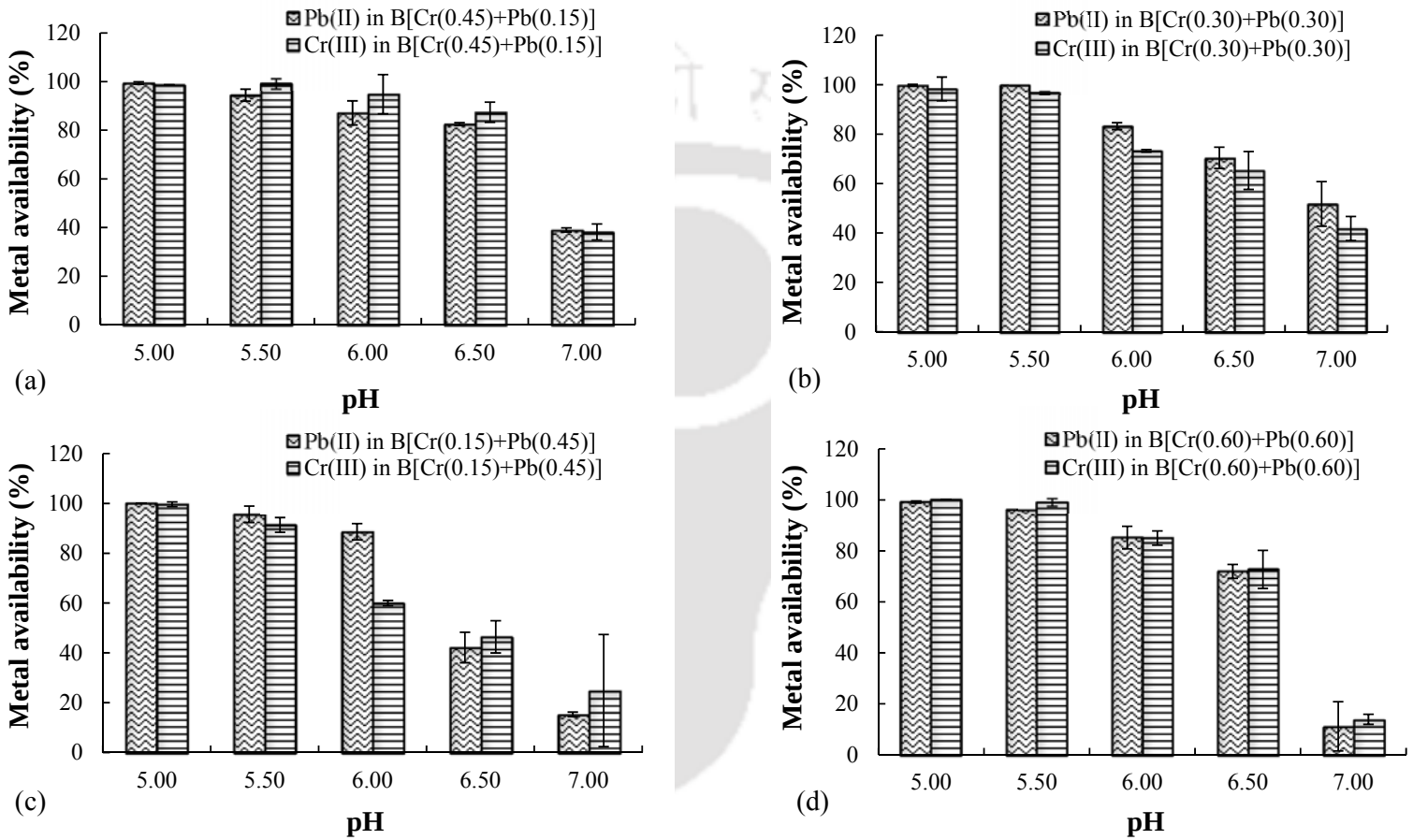

Fig. 5.3: Availability of Cr(III) and Pb(II) metal ions in aqueous phase with variation in solution pH from binary-metal ion system combinations (a) B[Cr(0.45)+Pb(0.15)], (b) B[Cr(0.30)+Pb(0.30)], (c) B[Cr(0.15)+Pb(0.45)] and (d) B[Cr(0.60)+Pb(0.60)] {Initial metal conc. in combinations B[Cr(0.45)+Pb(0.15)] = 0.41±0.00 meq/L of Cr(III) + 0.15±0.00 meq/L of Pb(II), B[Cr(0.30)+Pb(0.30)] = 0.29±0.00 meq/L of Cr(III) + 0.30±0.00 meq/L of Pb(II), B[Cr(0.15)+Pb(0.45)] = 0.15±0.00 meq/L of Cr(III) + 0.45±0.00 meq/L of Pb(II), B[Cr(0.60)+Pb(0.60)] = 0.58±0.00 meq/L of Cr(III) + 0.60±0.00 meq/L of Pb(II)} (Each data represents an average of two independent experimental values with vertical bars at each data points representing 95% confidence interval).

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The metal ions availability in aqueous phase from four different combinations of binary-metal ion systems comprising of Cu(II)+Cr(III) were also investigated with variation in solution pH and results are shown in Fig. 5.4. The study revealed precipitation of Cu(II) and Cr(III) metal ions at pH 5.00 in B[Cu(0.30)+Cr(0.30)], B[Cu(0.45)+Cr(0.15)] and B[Cu(0.60)+Cr(0.60)] combinations except in B[Cu(0.15)+Cr(0.45)] combination. At pH 5.00, Cu(II) metal ions availability in aqueous phase reduced to 48%, 29% and 11% respectively in B[Cu(0.45)+Cr(0.15)], B[Cu(0.30)+Cr(0.30)] and B[Cu(0.60)+Cr(0.60)] combinations while it was available in aqueous phase up to 98% in B[Cu(0.15)+Cr(0.45)] combination. Similarly for Cr(III) metal ion, the availability in aqueous phase at pH 5.00 reduced to 1%, 40% and 33% respectively in B[Cu(0.45)+Cr(0.15)], B[Cu(0.30)+Cr(0.30)] and B[Cu(0.60)+Cr(0.60)] combinations while it was available in aqueous phase up onto 97% in B[Cu(0.15)+Cr(0.45)] combination. These observations indicated that the presence of Cu(II) and Cr(III) metal ions together in the solution has had profound effect on their availability in aqueous phase around solution pH of 5.00.

5.1.3 Availability of metal ions in aqueous phase with variation in solution pH from ternary-metal ion system comprising of Cu(II), Pb(II) and Cr(III) ions

The Cu(II), Pb(II) and Cr(III) metal ions availability in aqueous phase were also investigated from two different combinations of ternary-metal ion systems viz. T[Cu(0.20)+Pb(0.20)+Cr(0.20)] and T[Cu(0.60)+Pb(0.60)+Cr(0.60)]. Fig. 5.5 depicts availability of metal ions in aqueous phase with variation in solution pH. At pH 5.00, the availability of Cu(II), Pb(II) and Cr(III) metal ions in aqueous phase were observed approximately 100%, 97% and 98% respectively in T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination, which further reduced approximately to 17%, 82% and 10% respectively at solution pH 5.50. It indicated substantial precipitation of Cu(II) and Cr(III) metal ions compared to Pb(II) metal ions when these metals were present together in solution. In the case of T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combination, the availability of Cu(II) and Cr(III) metal ions in aqueous phase at solution pH 5.00 reduced approximately to 17% and 37% respectively compared to Pb(II) metal ions which was 99%. Further, the availability of Cu(II), Pb(II) and Cr(III) metal ions in aqueous phase reduced approximately to 2%, 82% and 5% respectively at pH 5.50. In this combination also, the observed precipitation of Cu(II) and Cr(III) metal ions were higher compared to Pb(II) metal ions. The inclusion of Cu(II) in ternary-metal ion system of Cu(II)+Pb(II)+Cr(III) (Fig. 5.5) has had marked effect on availability of all the metal ions in aqueous phase at solution pH of 5.00 or more.

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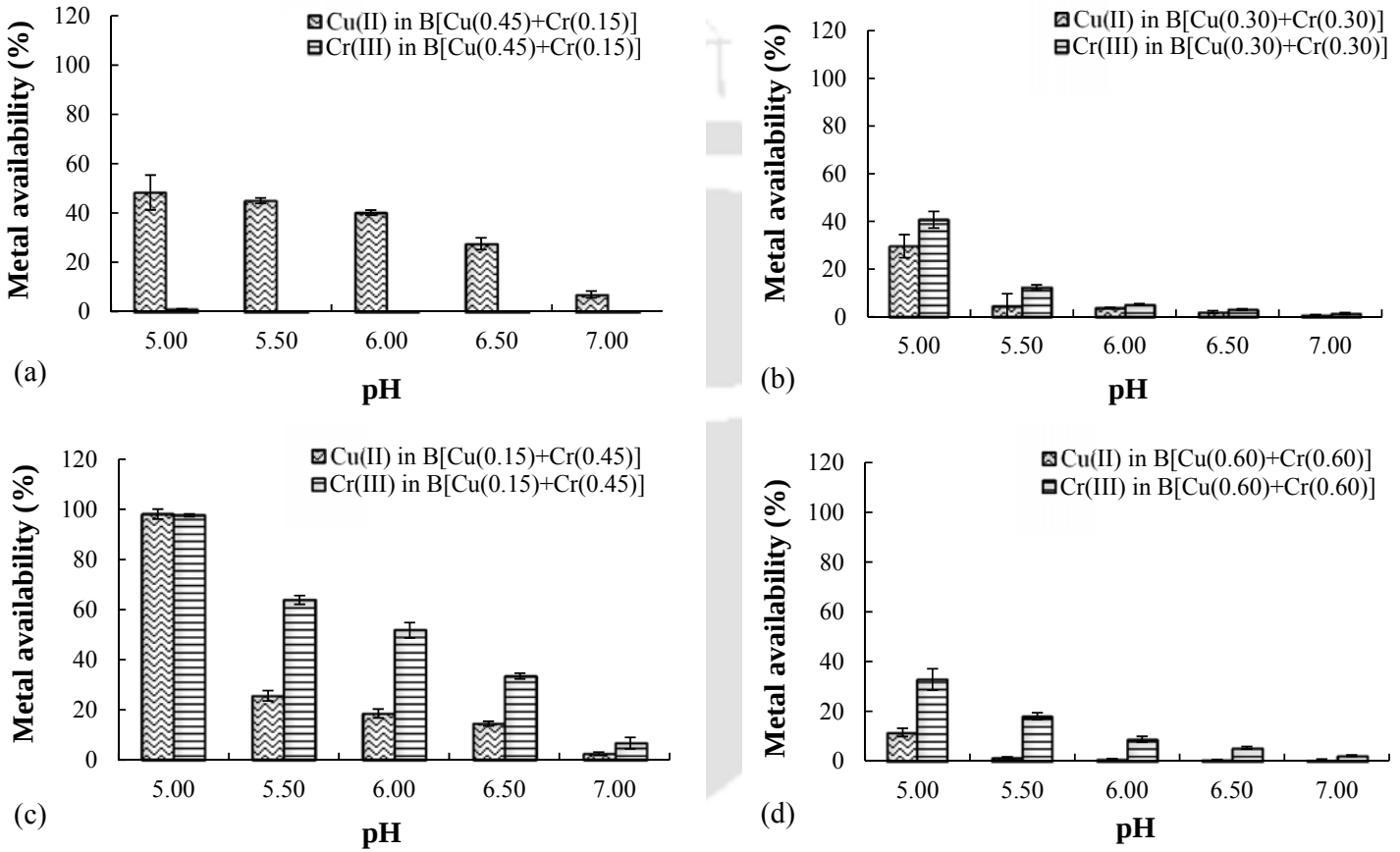

Fig. 5.4: Availability of Cu(II) and Cr(III) metal ions in aqueous phase with variation in solution pH from binary-metal ion system combinations (a) B[Cu(0.45)+Cr(0.15)], (b) B[Cu(0.30)+Cr(0.30)], (c) B[Cu(0.15)+Cr(0.45)] and (d) B[Cu(0.60)+Cr(0.60)] {Initial metal conc. in combinations B[Cu(0.45)+Cr(0.15)] = 0.44±0.00 meq/L of Cu(II) + 0.16±0.00 meq/L of Cr(III), B[Cu(0.30)+Cr(0.30)] = 0.30±0.00 meq/L of Cu(II) + 0.27±0.00 meq/L of Cr(III), B[Cu(0.15)+Cr(0.45)] = 0.15±0.00 meq/L of Cu(II) + 0.41±0.00 meq/L of Cr(III), B[Cu(0.60)+Cr(0.60)] = 0.60±0.00 meq/L of Cu(II) + 0.59±0.01 meq/L of Cr(III)} (Each data represents an average of two independent experimental values with vertical bars at each data points representing 95% confidence interval).

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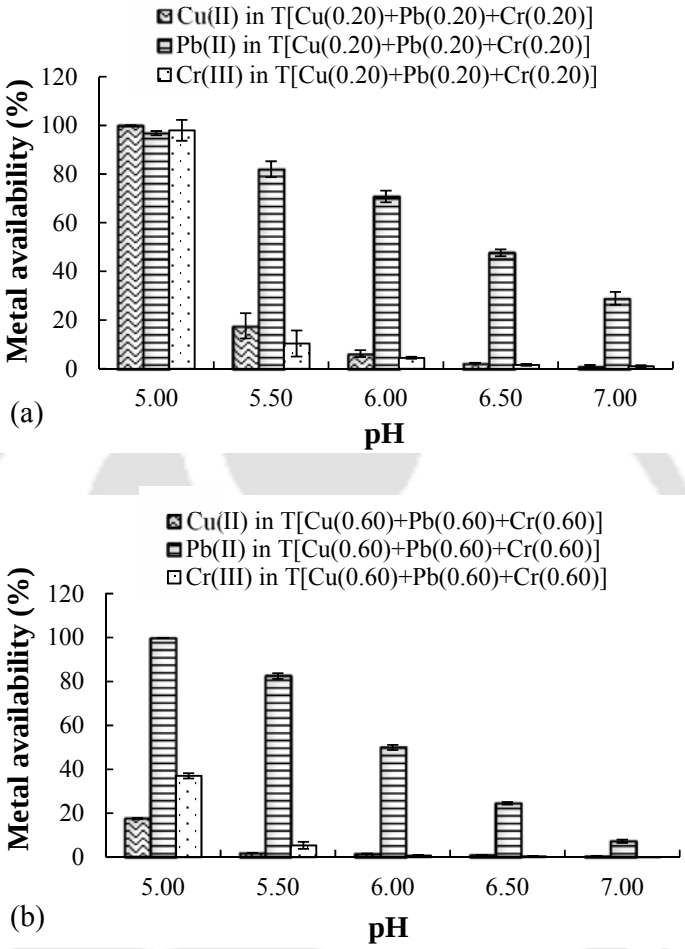

Fig. 5.5: Availability of Cu(II), Pb(II) and Cr(III) metal ions in aqueous phase with variation in solution pH from ternary-metal ion system combinations (a) T[Cu(0.20)+Pb(0.20)+Cr(0.20)] and (b) T[Cu(0.60)+Pb(0.60)+Cr(0.60)] {Initial metal conc. in combinations T[Cu(0.20)+Pb(0.20)+Cr(0.20)] = 0.20±0.00 meq/L of Cu(II) + 0.21±0.00 meq/L of Pb(II) + 0.20±0.00 meq/L of Cr(III); T[Cu(0.60)+Pb(0.60)+Cr(0.60)] = 0.60±0.00 meq/L of Cu(II) + 0.59±0.00 meq/L of Pb(II) + 0.60±0.00 meq/L of Cr(III)} (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

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5.1.4 Availability of metal ions in aqueous phase with variation in solution pH from mono-, binary- and ternary-metal ions systems comprising of Cu(II), Pb(II) and Cr(III) ions estimated using MINEQL+ software

The speciation of metal ions in all the combinations of mono-, binary- and ternary metal ion systems comprising of Cu(II), Pb(II) and Cr(III) were also investigated under uncontrolled and controlled pH conditions using MINEQL+ software (Schecher & McAvoy, 1998). The input parameters such as initial concentrations of different components [viz., Cu(II), Pb(II), Cr(III), SO_4^{2-}, NO_3^-, CH_3COO^-, Na^+, etc.] present in aqueous phase were estimated based on the initial experimental conditions adopted in section 4.3. The speciation of metal ions under uncontrolled pH conditions was estimated for pH range of 5.00 to 7.00. All the concentrations of metal species present in ionic form were added together to estimate the percentage of metal availability in the aqueous phase.

The availability of Cu(II), Pb(II) and Cr(III) metal ions in aqueous phase from mono-, binary- and ternary-metal ion systems with variation in solution pH are shown in Fig. 5.6 to 5.8. The estimated availability of Cu(II), Pb(II) and Cr(III) metal ions in aqueous phase from mono-metal ions systems at solution pH 5.50 were approximately 98%, 98% and 21% respectively. The estimated availability of Cr(III) metal ion in aqueous phase was much lower than the approximately 100% availability estimated experimentally as presented in section 5.1.1. The estimated availability of metal ions in aqueous phase from combinations of binary-metal ion systems indicated much higher reduction beyond pH 5.50 for Cu(II)+Pb(II) and

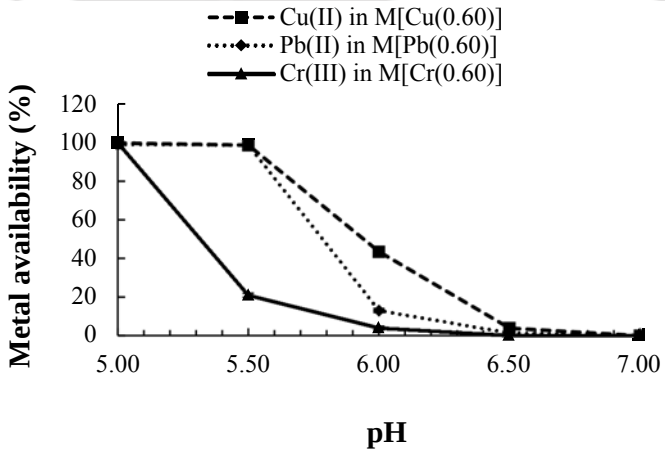

Fig. 5.6: Availability of Cu(II), Pb(II) and Cr(III) metal ions in aqueous phase with variation in solution pH estimated using MINEQL+ software from mono-metal ion systems.

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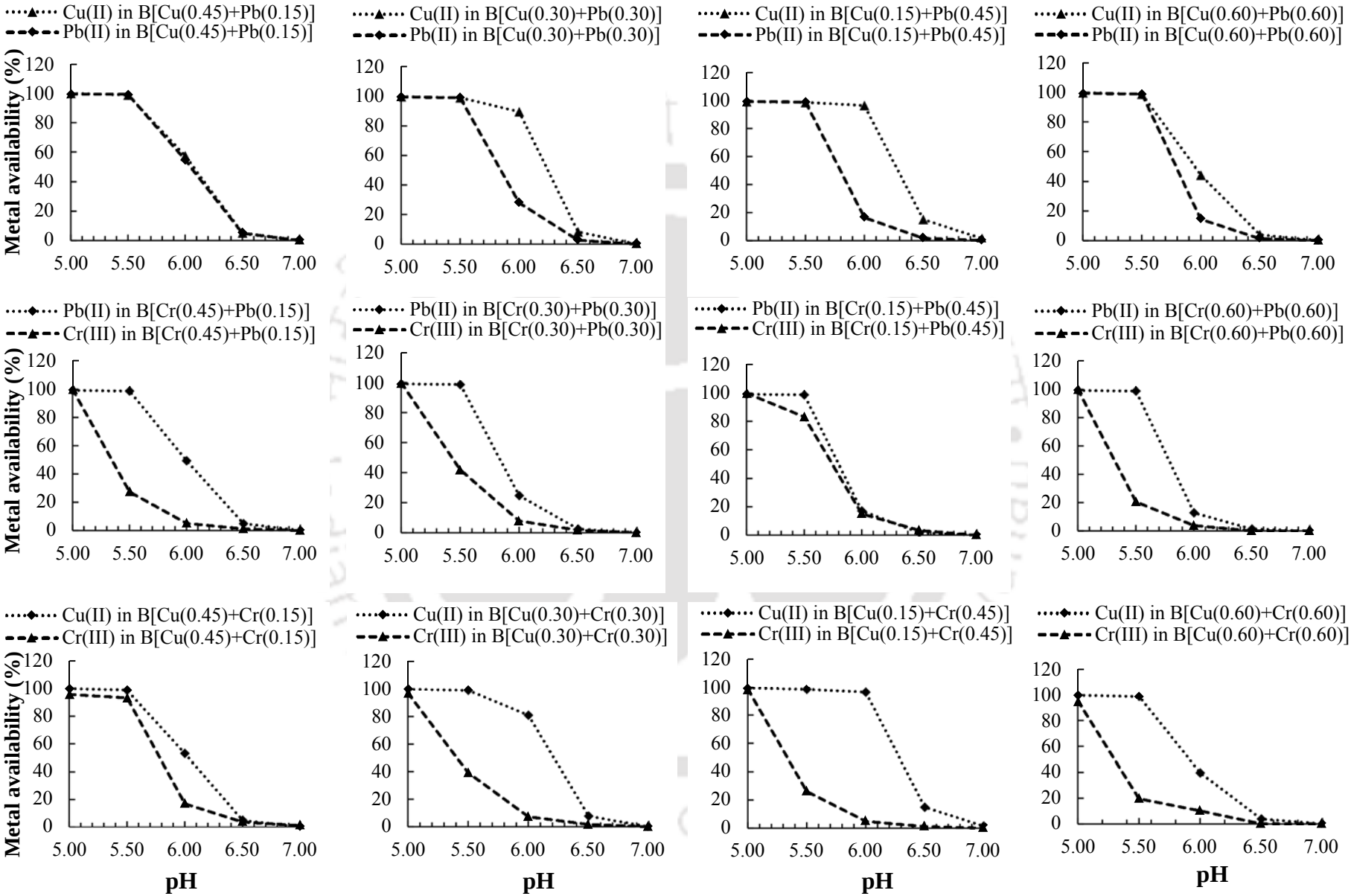

Fig. 5.7: Availability of Cu(II), Pb(II) and Cr(III) metal ions in aqueous phase with variation in solution pH estimated using MINEQL+ software from combinations of binary-metal ion systems.

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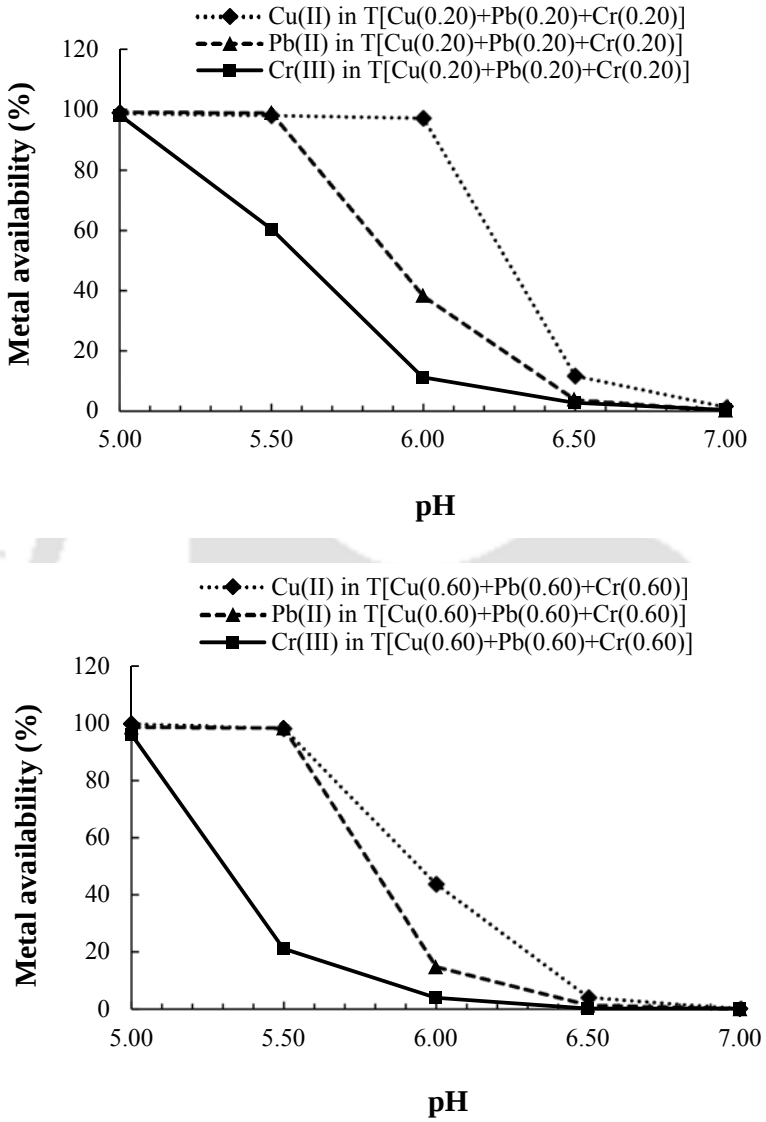

Fig. 5.8: Availability of Cu(II), Pb(II) and Cr(III) metal ions in aqueous phase with variation in solution pH estimated using MINEQL+ software from combinations of ternary-metal ion systems.

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Pb(II)+Cr(III) combinations and beyond pH 5.00 for Cu(II)+Cr(III) combinations. These observations were not in consonance with the experimentally observed reduction in metal availability in aqueous phase. Similarly, the estimated metal availability in aqueous phase was much off the track compared to experimental results obtained for ternary-metal ion systems.

The solution pH was fixed at 5.00 under controlled pH conditions and hence the availability of different species of metal ions was estimated at pH 5.00 using MINEQL+ software. The results are presented in Table 5.1. It appeared that more than 80% of Cu(II), Pb(II) and Cr(III) metal ions were available in aqueous phase in the form of metal-acetate complex.

5.1.5 Summary

The availability of metal ions in aqueous phase with variation in solution pH from mono-, binary- and ternary-metal ion systems was experimentally investigated. The availability of Cu(II) and Cr(III) metal ions in aqueous phase from mono-metal ion system was ≥ 80% up to solution pH 6.00, while for Pb(II) metal ion it was ≥ 70%. Similarly the availability of ≥ 80% of metal ions in aqueous phase were observed up to solution pH of 6.00 from all the four combinations of binary-metal ion systems of Cu(II)+Pb(II), Cr(III)+Pb(II) except Cr(III) metal ions availability in B[Cr(0.30)+Pb(0.30)] and B[Cr(0.15)+Pb(0.45)] combinations which was ≤ 73%. However metal availability in aqueous phase drastically reduced in all four combinations of Cu(II)+Cr(III) and two combinations of ternary-metal ion systems even at solution pH of 5.00 or higher due to precipitation or co-precipitation of metal ions. The metal availability in aqueous phase at different solution pH estimated using MINEQL+ software were not in agreement with the experimental results obtained. The metal availability in aqueous phase at controlled pH 5.00 from mono-, binary- and ternary-metal ion systems using MINEQL+ software estimated more than 80% for Cu(II), Pb(II) and Cr(III) metal ions in the form of metal-acetate complex. The results of these investigations are likely to help in understanding metal removal from aqueous phase during subsequent investigations.

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Table 5.1: Speciation of Cu(II), Pb(II) and Cr(III) metal ions from mono-, binary- and ternary-metal ions systems under controlled pH conditions.

Metal ion systems	Metal ion combinations	Cu speciation (%)				Pb speciation (%)			Cr speciation (%)	
		Cu^{2+}	$Cu(CH_3COO)_3^-$	$Cu(CH_3COO)^+$	$Cu(CH_3COO)_2$	Pb^{2+}	$Pb(CH_3COO)_2$	$Pb(CH_3COO)^+$	$Cr(CH_3COO)_3$	$Cr(CH_3COO)_2^+$
Mono	M[Cu(0.60)]	10.9	2.1	45.2	41.2	-	-	-	-	-
	M[Pb(0.60)]	-	-	-	-	3.4	35.8	60.1	-	-
	M[Cr(0.60)]	-	-	-	-	-	-	-	91.8	7.2
Binary	B[Cu(0.45)+Pb(0.15)]	8.9	2.2	44.8	43.9	2.7	37.9	58.9	-	-
	B[Cu(0.30)+Pb(0.30)]	8.9	2.2	44.8	44.0	2.7	38.0	58.5	-	-
	B[Cu(0.15)+Pb(0.45)]	8.9	2.2	44.8	44.0	2.7	38.0	58.5	-	-
	B[Cu(0.60)+Pb(0.60)]	9.2	2.1	45.1	43.3	2.8	37.4	58.9	-	-
	B[Cr(0.45)+Pb(0.15)]	-	-	-	-	2.8	37.2	59.3	91.9	7.2
	B[Cr(0.30)+Pb(0.30)]	-	-	-	-	2.8	37.5	59.0	92.0	7.1
	B[Cr(0.15)+Pb(0.45)]	-	-	-	-	2.8	37.7	58.8	92.1	7.0
	B[Cr(0.60)+Pb(0.60)]	-	-	-	-	3.0	36.4	60.0	91.6	7.4
	B[Cu(0.45)+Cr(0.15)]	9.0	2.1	45.0	43.7	-	-	-	92.1	7.0
	B[Cu(0.30)+Cr(0.30)]	9.2	2.1	45.2	43.4	-	-	-	92.0	7.1
	B[Cu(0.15)+Cr(0.45)]	9.3	2.0	45.5	43.1	-	-	-	91.9	7.2
	B[Cu(0.60)+Cr(0.60)]	9.8	1.9	46.0	42	-	-	-	91.5	7.4
Ternary	T[Cu(0.20)+Pb(0.20)+Cr(0.20)]	9.1	2.1	45.1	43.6	2.8	37.6	58.9	92.0	7.1
	T[Cu(0.60)+Pb(0.60)+Cr(0.60)]	10.0	1.9	46.3	41.5	3.1	35.7	60.4	91.4	7.6

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5.2 Effect of contact time on metal ion concentration remaining in aqueous phase under uncontrolled and controlled pH conditions from mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions

The effect of contact time on the metal ion concentration remaining in aqueous phase from mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions have been investigated under uncontrolled and controlled pH conditions. The experiments were carried out with three different fixed total initial metal ion concentration of approximately 0.60, 1.20 and 1.80 meq/L in solution. The adsorbent doses used in all the experiments were kept fixed at 12 g GAA/L (i.e. 0.6 g GAA/50 mL solution volume).

5.2.1 Effect of contact time on metal ion concentration remaining in aqueous phase under uncontrolled and controlled pH conditions from mono-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions

The effect of contact time on metal ion concentration remaining in aqueous phase from mono-metal ion systems of M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] were investigated under uncontrolled as well as controlled pH conditions. In all the systems, initial solution pH was adjusted to 5.00±0.02 while keeping an initial metal ion concentration close to 0.60 meq/L. The concentration of Cu(II), Pb(II) and Cr(III) metal ions remaining in solution along with variation in pH obtained under uncontrolled and controlled pH conditions are depicted in Fig. 5.9 and 5.10 respectively.

The variations in solution pH with time under uncontrolled pH conditions was recorded and presented in Fig. 5.9(a). The solution pH for M[Cu(0.60)] system was observed to increase in the range of 5.80-5.97 (average solution pH 5.90) from initially adjusted pH of 5.00 within first 5 min., which further increased in the range of 5.93-6.21 (average solution pH 6.04) at the end of 90 min. of experimentation. Towards the end of experiments at 240 min., the solution pH varied in the range of 6.35-6.57 (average solution pH 6.44). It is evident from experimental results presented in section 5.1.1 and metal speciation results presented in section 5.1.4 that Cu(II) ions were available in aqueous phase close to 100% up to solution pH of 5.50, whereas the availability of Cu(II) ions in aqueous phase decreased drastically at higher pH values. Since the solution pH increased beyond 5.50 within first 5 min. of the experimentation, the reduction in Cu(II) metal ions might be attributed to combined effects of adsorption and precipitation.

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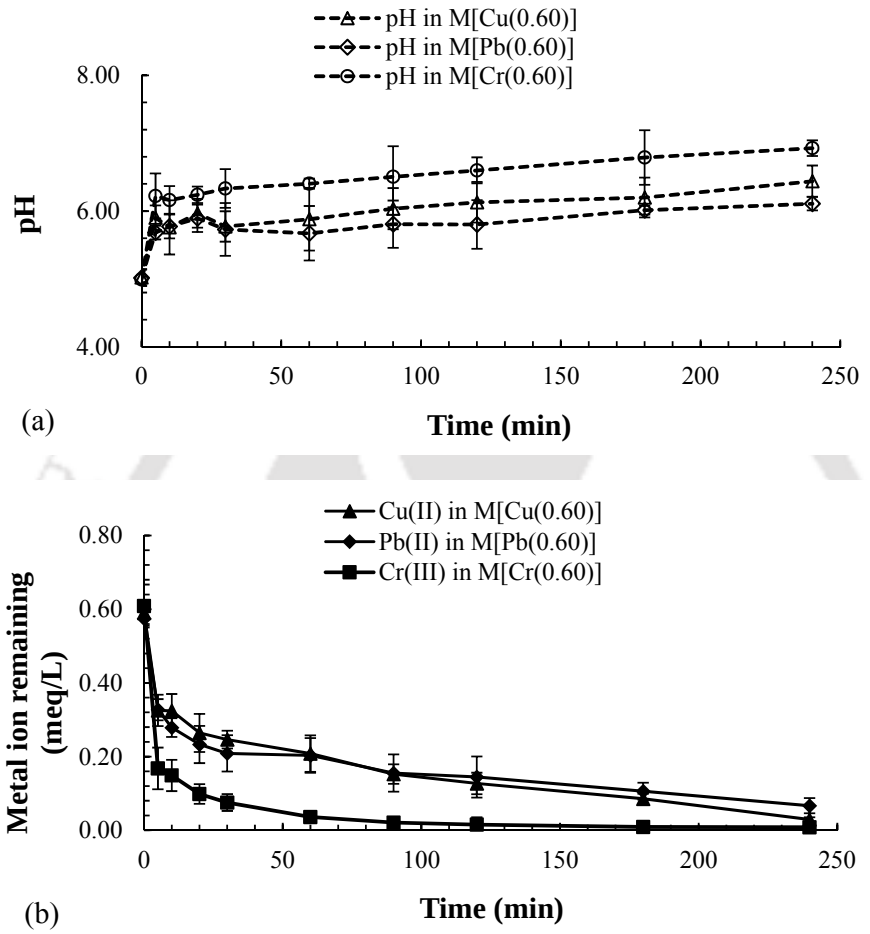

Fig. 5.9: Variation in (a) solution pH and (b) metal ion concentration remaining in aqueous phase from mono-metal ion systems of M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] with contact time under uncontrolled pH conditions {Initial metal conc. in M[Cu(0.60)] = 0.59±0.01 meq/L, M[Pb(0.60)] = 0.57±0.02 meq/L, M[Cr(0.60)] = 0.61±0.06 meq/L, Temp. = 30±2 °C, Initial adjusted pH = 5.00±0.02, GAA dose =12 g/L, Mixing speed = 66 rpm} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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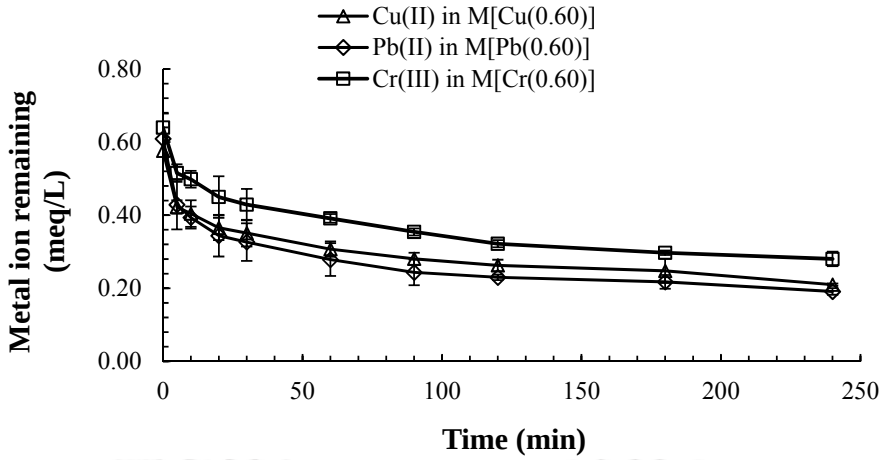

Fig. 5.10: Variation in metal ion concentration remaining in aqueous phase from mono-metal ion systems of M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] with contact time under controlled pH conditions {Initial metal conc. in M[Cu(0.60)] = 0.58±0.01 meq/L, M[Pb(0.60)] = 0.61±0.01 meq/L, M[Cr(0.60)] = 0.64±0.04 meq/L, Temp. = 30±2 °C, Buffered pH = 5.00±0.02, GAA dose =12 g/L, Mixing speed = 66 rpm} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

The solution pH for M[Pb(0.60)] system was observed to increase in the range of 5.63-5.73 (average solution pH 5.68) from initially adjusted pH of 5.00 within first 5 min., which further increased to 5.99-6.05 (average solution pH 6.01) at the end of 180 min. of experimentation. The solution pH varied in the range of 6.06-6.16 (average solution pH 6.11) towards the end of experiments. The Pb(II) ions were available 100% in aqueous phase up to solution pH 5.50 and availability decreased with increase in solution pH (refer sections 5.1.1 and 5.1.4). It indicated that precipitation of Pb(II) metal ions might have started within 5 min. of experimentation. Hence the reduction in Pb(II) ion concentration from the solution might be attributed to adsorption as well as precipitation.

The solution pH for M[Cr(0.60)] system was observed to rise rapidly in the range of 6.05-6.38 (average solution pH 6.20) from initially adjusted pH of 5.00 within first 5 min. Thereafter, the solution pH showed a steady rising trend throughout the experiment and the solution pH recorded towards the end of experiments was in the range of 6.86-6.96 (average solution pH 6.93). Almost entire Cr(III) ions were expected to be in aqueous phase up to solution pH of 6.00, which, however decreased to approximately 84% at pH 6.50 and 55% at pH 7.00 (Fig. 5.1). The estimated Cr(III) availability in aqueous phase started to decrease

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with increase in initially adjusted pH (refer section 5.1.4). Hence, the precipitation of Cr(III) ions from the solution was very much expected.

Under controlled pH conditions (Fig. 5.10), pH of the solution in M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] systems remained unchanged to the initially buffered pH of 5.00 during the course of experimentation. Hence most of Cu(II), Pb(II) and Cr(III) metal ions remained in aqueous phase under controlled pH conditions. The reduction in concentration of metal ions from aqueous phase might be attributed only to accumulation of the metal ions onto GAA surface instead of reduction by precipitation and/or adsorption as seen under uncontrolled pH conditions. The reduction in residual concentrations of metal ions was observed to be higher during first 10-20 min. and thereafter it became slow and steady.

The metal ion concentrations remaining in solution was observed to decrease rapidly for all mono-metal ion systems in the beginning as could be seen in Fig. 5.9(b) and 5.10. The decrease in metal ion concentrations were relatively more in systems with uncontrolled pH conditions compared to systems with controlled pH conditions. After a period of initial 20 min., the concentration of metal ions remaining in solution decreased rather slowly under uncontrolled and controlled pH conditions. By the end of 180 min., the concentration of metal ion remaining in solution appeared to have reached to a fixed level and further decrease in metal ion concentration was observed to be very slow. At the end of the contact period of 240 min., the percentage metal ion remaining in aqueous phase under uncontrolled pH conditions was observed as 5% for Cu(II), 12% for Pb(II) and 1% for Cr(III) whereas 36% for Cu(II), 31% for Pb(II) and 44% for Cr(III) was observed under controlled pH conditions. The lower values of concentrations of metal ions remaining in aqueous phase for uncontrolled pH conditions might be attributed to precipitation of metal ions due to rise in pH value along with its migration from aqueous phase to GAA surface. Whereas, the reduction in metal ions concentrations under controlled pH conditions were most likely due to migration of metal ions from aqueous phase to GAA surfaces. The difference in concentrations of metal ions remaining in aqueous phase might be attributed to (i) precipitation of metal ions under uncontrolled pH conditions but absence of metal reduction due to precipitation under controlled pH conditions and (ii) formation of metal-acetate complex under controlled pH conditions thereby making a part of the metal ions less available for adsorption.

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5.2.2 Effect of contact time on metal ion concentration remaining in aqueous phase under uncontrolled and controlled pH conditions from binary-metal ion systems comprising of Cu(II) and Pb(II) ions

The effect of contact time on concentrations of metal ions remaining in aqueous phase from binary-metal ion systems comprising of Cu(II)+Pb(II) were investigated under uncontrolled as well as controlled pH conditions. The solution pH was adjusted to 5.00±0.02 in all the binary-metal ion systems. The reduction in concentrations of Cu(II) and Pb(II) metals from binary-metal ion systems comprising of Cu(II)+Pb(II) were investigated for four selected combinations viz. B[Cu(0.45)+Pb(0.15)], B[Cu(0.30)+Pb(0.30)], B[Cu(0.15)+Pb(0.45)] and B[Cu(0.60)+Pb(0.60)]. The total initial metal ion concentrations in the first three combinations were fixed close to 0.60 meq/L, while in the fourth combination the total initial metal ion concentration was near to 1.20 meq/L – just double of other three combinations. In each of these combinations of binary-metal ion systems, the metal ion of interest was designated as the target metal while the other metal ion was termed as non-target metal for the purpose of presentation of experimental results. The variation in solution pH with contact time for each of the binary-metal ion system combinations is shown in Fig. 5.11, while the time profiles of target Cu(II), target Pb(II) and total metal ions remaining in aqueous phase investigated under uncontrolled and controlled pH conditions are shown in Fig. 5.12 and 5.13 respectively.

The solution pH of B[Cu(0.45)+Pb(0.15)] combination was observed in the range of 5.52-5.92 (average solution pH 5.69) up to first 30 min. from the initially adjusted pH of 5.00. The pH of the solution was observed to increase further in the range of 5.87-6.28 (average solution pH 6.09) at 60 min., while at the end of experimentation it was in the range of 6.35-6.64 (average solution pH 6.47) as seen in Fig. 5.11. The solution pH of B[Cu(0.30)+Pb(0.30)] combination was observed in the range of 5.63-5.93 (average solution pH 5.76) up to first 10 min. from the initially adjusted pH of 5.00. The pH of the solution was observed to increase further in the range of 5.56-6.32 (average solution pH 5.87) at 20 min., while it was in the range of 6.22-6.85 (average solution pH 6.64) at the end of experimentation. In B[Cu(0.15)+Pb(0.45)] combination, pH of the solution was observed in the range of 5.86-5.94 (average solution pH 5.89) up to first 30 min. from the initially adjusted pH of 5.00. The pH of the solution was observed to increase in the range of 6.05-6.16 (average solution pH 6.13) at 90 min., while it was in the range of 6.30-6.41 (average

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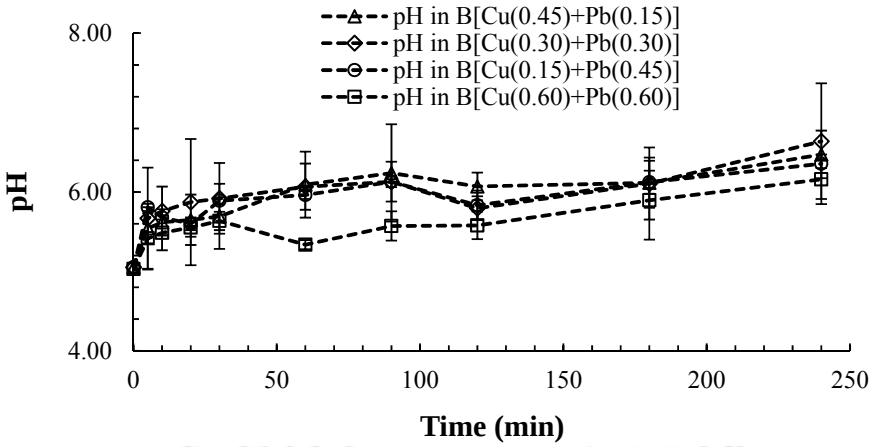

Fig. 5.11: Variation in solution pH with contact time for binary-metal ion systems comprising of Cu(II)+Pb(II) under uncontrolled pH conditions {Temp. = 30±2 °C, Initial adjusted pH = 5.00±0.02, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combinations B[Cu(0.45)+Pb(0.15)] = 0.44±0.01 meq/L of Cu(II) + 0.15±0.01 meq/L of Pb(II), B[Cu(0.30)+Pb(0.30)] = 0.29±0.00 meq/L of Cu(II) + 0.28±0.01 meq/L of Pb(II), B[Cu(0.15)+Pb(0.45)] = 0.15±0.00 meq/L of Cu(II) + 0.44±0.00 meq/L of Pb(II), B[Cu(0.60)+Pb(0.60)] = 0.59±0.03 meq/L of Cu(II) + 0.60±0.02 meq/L of Pb(II)} (Each data represents an average of three independent experimental values with vertical bars at each data points representing 95% confidence interval).

solution pH 6.36) at the end of experimentation. The solution pH of B[Cu(0.60)+Pb(0.60)] combination was observed in the range of 5.48-5.63 (average solution pH 5.58) up to first 120 min. from the initially adjusted pH of 5.00. It further increased in the range of 5.61-6.04 (average solution pH 5.90) at 180 min. and at the end of experimentation it was in the range of 5.98-6.25 (average solution pH 6.16). Considering the experimental results presented in Fig. 5.2 and metal speciation results presented in Fig. 5.7, 100% availability of Cu(II) and Pb(II) metal ions in aqueous phase was assured only up to solution pH of 5.50. The reduction in residual metal concentrations in the solution in all the combinations of Cu(II)+Pb(II) binary-metal ion system may be due to combined effects of precipitation and adsorption as the solution pH increased beyond 5.50.

Under controlled pH conditions (Fig. 5.13), pH of the solution in B[Cu(0.45)+Pb(0.15)], B[Cu(0.30)+Pb(0.30)], B[Cu(0.15)+Pb(0.45)] and B[Cu(0.60)+Pb(0.60)] combinations remained unchanged to initially buffered pH of 5.00 during the course of experimentation. Hence most of Cu(II) and Pb(II) metal ions remained in aqueous phase under controlled pH conditions. The reduction in concentration of metal ions

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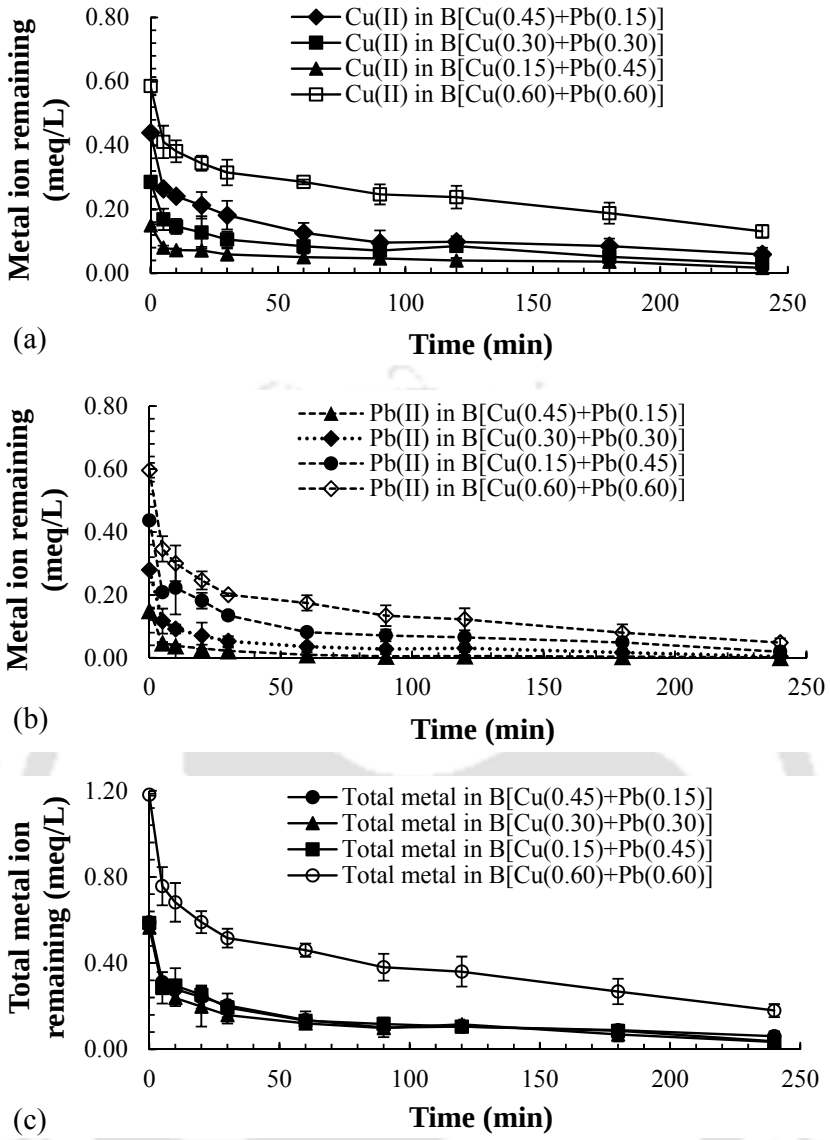

Fig. 5.12: Variation in (a) target Cu(II) metal (b) target Pb(II) metal and (c) total metal ion concentration remaining in aqueous phase from binary-metal ion systems comprising of Cu(II)+Pb(II) under uncontrolled pH conditions {Temp. = 30±2 °C, Initial adjusted pH = 5.00±0.02, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combinations B[Cu(0.45)+Pb(0.15)] = 0.44±0.01 meq/L of Cu(II) + 0.15±0.01 meq/L of Pb(II), B[Cu(0.30)+Pb(0.30)] = 0.29±0.00 meq/L of Cu(II) + 0.28±0.01 meq/L of Pb(II), B[Cu(0.15)+Pb(0.45)] = 0.15±0.00 meq/L of Cu(II) + 0.44±0.00 meq/L of Pb(II), B[Cu(0.60)+Pb(0.60)] = 0.59±0.03 meq/L of Cu(II) + 0.60±0.02 meq/L of Pb(II)} (Each data represents an average of three independent experimental values with vertical bars at each data points representing 95% confidence interval).

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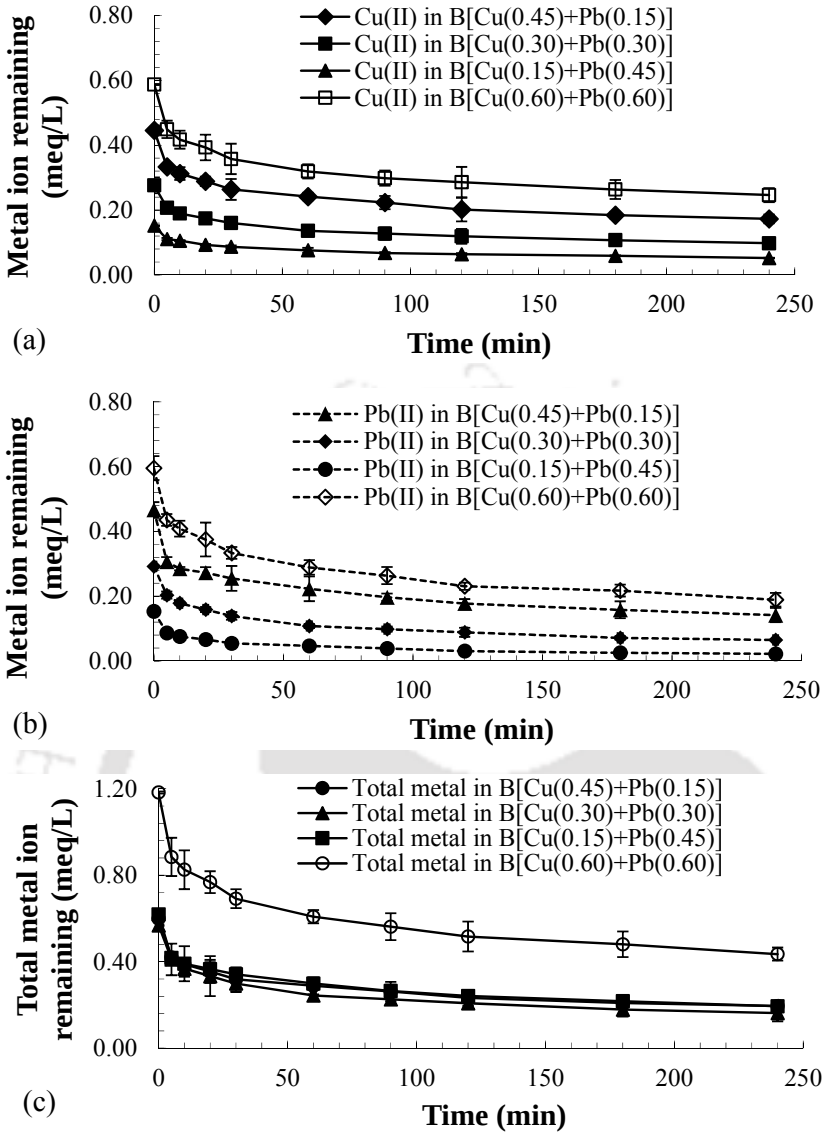

Fig. 5.13: Variation in (a) target Cu(II) metal (b) target Pb(II) metal and (c) total metal ion concentration remaining in aqueous phase from binary-metal ion systems comprising of Cu(II)+Pb(II) under controlled pH conditions {Temp. = 30±2 °C, Buffered pH = 5.00±0.02, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combinations B[Cu(0.45)+Pb(0.15)] = 0.45±0.02 meq/L of Cu(II) + 0.15±0.00 meq/L of Pb(II), B[Cu(0.30)+Pb(0.30)] = 0.28±0.02 meq/L of Cu(II) + 0.29±0.00 meq/L of Pb(II), B[Cu(0.15)+Pb(0.45)] = 0.15±0.00 meq/L of Cu(II) + 0.47±0.02 meq/L of Pb(II), B[Cu(0.60)+Pb(0.60)] = 0.59±0.02 meq/L of Cu(II) + 0.60±0.04 meq/L of Pb(II)} (Each data represents an average of three independent experimental values with vertical bars at each data points representing 95% confidence interval).

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from aqueous phase might be attributed only to accumulation of the metal ions onto GAA surface instead of reduction by precipitation and/or adsorption as seen under uncontrolled pH conditions. The reduction in residual concentrations of metal ions was observed to be higher during first 15-30 min. and thereafter it became slow and steady.

A careful inspection of Fig. 5.12 and 5.13 revealed that under uncontrolled pH conditions, the concentration of target Cu(II) remaining in aqueous phase was significantly lower as compared to concentration of target Cu(II) remaining under controlled pH conditions [Fig. 5.12(a) and 5.13(a)]. The data points for target Cu(II) metal obtained under uncontrolled pH conditions overlapped at 95% confidence interval after a contact period of 60 min. for B[Cu(0.45)+Pb(0.15)], B[Cu(0.30)+Pb(0.30)] and B[Cu(0.15)+Pb(0.45)] combinations as seen in Fig. 5.12(a). However, under controlled pH conditions, the concentration of target Cu(II) remaining in aqueous phase was observed to follow a decreasing trend with no overlap of experimental data points at 95% confidence intervals in any of the combinations as seen from Fig. 5.13(a). Under uncontrolled pH conditions, the concentration of target Pb(II) remaining in aqueous phase was significantly lower as compared to concentration of target Pb(II) remaining in aqueous phase under controlled pH conditions [Fig. 5.12(b) and 5.12(b)]. The data points for target Pb(II) under uncontrolled pH conditions overlapped at 95% confidence interval after a contact period of 20 min. for B[Cu(0.45)+Pb(0.15)] and B[Cu(0.30)+Pb(0.30)] combinations as seen in Fig. 5.12(b). However, under controlled pH conditions, the concentration of target Pb(II) remaining in aqueous phase was observed to follow a decreasing trend with no overlap of experimental data points at 95% confidence intervals throughout the contact period as could be seen in Fig. 5.13(b). The difference in concentrations of metal ions remaining in aqueous phase might be attributed to (i) precipitation of metal ions under uncontrolled pH conditions but absence of metal reduction due to precipitation under controlled pH conditions and (ii) formation of metal-acetate complex under controlled pH conditions thereby making a part of the metal ions less available for adsorption.

The inspection of Fig. 5.12 and 5.13 further revealed that concentrations of metal ions remaining in aqueous phase were decreasing simultaneously from binary-metal ion systems under uncontrolled and controlled pH conditions. Hence it was interesting to ascertain how much concentration of total metal ions were remaining in aqueous phase with variation in

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contact time. Therefore, the data obtained for individual metal ions had been re-plotted in Fig. 5.12(c) and 5.13(c) respectively for uncontrolled and controlled pH conditions by taking into account the total concentration of metal ions remaining in aqueous phase for all the combinations. The concentration of metal ion remaining in aqueous phase have been expressed in meq/L – a common term for expressing concentrations of different metal ions having difference in atomic weights and valence (Peavy et al., 1985). The concentrations expressed in common term of meq/L have the advantage to arrive at the total concentration of metal ions of different atomic weights and valence by simple algebraic summation. The concentrations of total metal ions remaining in solution phase under uncontrolled pH conditions were observed to decrease with contact time and overlapped at 95% confidence interval for B[Cu(0.45)+Pb(0.15)], B[Cu(0.30)+Pb(0.30)] and B[Cu(0.15)+Pb(0.45)] combinations throughout the contact period except for the B[Cu(0.60)+Pb(0.60)] combination as could be seen in Fig. 5.12(c). On the other hand, when total initial metal ion concentration was doubled to 1.20 meq/L in B[Cu(0.60)+Pb(0.60)] combination, the total metal ion concentration remaining in solution was observed to have decreasing trend but it did not overlap at 95% confidence intervals with combinations having total initial metal ion concentration near to 0.60 meq/L. The concentration of total metal ion remaining in B[Cu(0.60)+Pb(0.60)] combination was approximately twice above the concentration of total metal ion remaining in B[Cu(0.45)+Pb(0.15)], B[Cu(0.30)+Pb(0.30)] and B[Cu(0.15)+Pb(0.45)] combinations. Similarly, overlap of experimental data points at 95% confidence levels were also observed for B[Cu(0.45)+Pb(0.15)], B[Cu(0.30)+Pb(0.30)] and B[Cu(0.15)+Pb(0.45)] combinations under controlled pH conditions throughout the contact period [Fig. 5.13(c)]. Hence, it clearly indicated that the concentration of total metal ion remaining in aqueous phase was fairly independent of proportion of initial metal ion concentrations present in different combinations of binary-metal ion systems as long as total initial metal ion concentration was approximately the same.

5.2.3 Effect of contact time on metal ion concentration remaining in aqueous phase under uncontrolled and controlled pH conditions from binary-metal ion systems comprising of Cr(III) and Pb(II) ions

The effect of contact time on concentrations of metal ions remaining in aqueous phase from binary-metal ion systems comprising of Cr(III)+Pb(II) were investigated under uncontrolled as well as controlled pH conditions. The solution pH was initially adjusted to

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5.00±0.05 in all the binary-metal ion systems. The reduction in concentration of Cr(III) and Pb(II) metals from binary-metal ion systems comprising of Cr(III)+Pb(II) were investigated for four selected combinations viz. B[Cr(0.45)+Pb(0.15)], B[Cr(0.30)+Pb(0.30)], B[Cr(0.15)+Pb(0.45)] and B[Cr(0.60)+Pb(0.60)]. The total initial metal ion concentrations in the first three combinations were fixed close to 0.60 meq/L while in the fourth combination the total initial metal ion concentration was near to 1.20 meq/L – just double of other three combinations. In each of these combinations of binary-metal ion systems, the metal ion of interest was designated as the target metal while the other metal ion was termed as non-target metal for the purpose of presentation of experimental results. Fig. 5.14 depicts the variation in solution pH with contact time for each of the binary-metal ion system combinations investigated. The time profiles of target Cr(III), target Pb(II) and total metal ions remaining in aqueous phase investigated under uncontrolled and controlled pH conditions are shown in Fig. 5.15 and 5.16 respectively.

The solution pH of B[Cr(0.45)+Pb(0.15)] combination was observed in the range of 5.10-5.36 (average solution pH 5.26) up to first 60 min. from the initially adjusted pH of 5.00±0.05 (Fig. 5.14). The solution pH further increased in the range of 5.59-5.64 (average solution pH 5.62) towards the end of experimentation. Similarly for B[Cr(0.30)+Pb(0.30)] combination, the solution pH was observed in the range of 5.22-5.49 (average solution pH 5.40) up to first 60 min. from the initially adjusted pH of 5.00±0.05 which further increased in the range of 5.41-5.49 (average solution pH 5.45) towards the end of experimentation. In B[Cr(0.15)+Pb(0.45)] combination, the solution pH was observed in the range of 5.17-5.25 (average solution pH 5.22) up to first 60 min. from the initially adjusted pH of 5.00±0.05 which further increased in the range of 6.01-6.23 (average solution pH 6.11) at 120 min. and eventually fluctuated in the same pH range till the end of experimentation. The solution pH in B[Cr(0.60)+Pb(0.60)] combination was observed in the range of 5.70-5.90 (average solution pH 5.82) up to first 20 min. from the initially adjusted pH of 5.00±0.05 which further increased in the range of 6.01-6.20 (average solution pH 6.09) at 60 min. and eventually fluctuated in the range of 6.25-6.30 (average solution pH 6.27) towards the end of experimentation. Considering the experimental results presented in Fig. 5.3 and metal speciation results presented in Fig. 5.7, 100% availability in aqueous phase of Cr(III) beyond pH 5.00 and Pb(II) beyond pH 5.50 were not assured and both adsorption as well as precipitation might have contributed in reduction of concentrations of both the metal ions in

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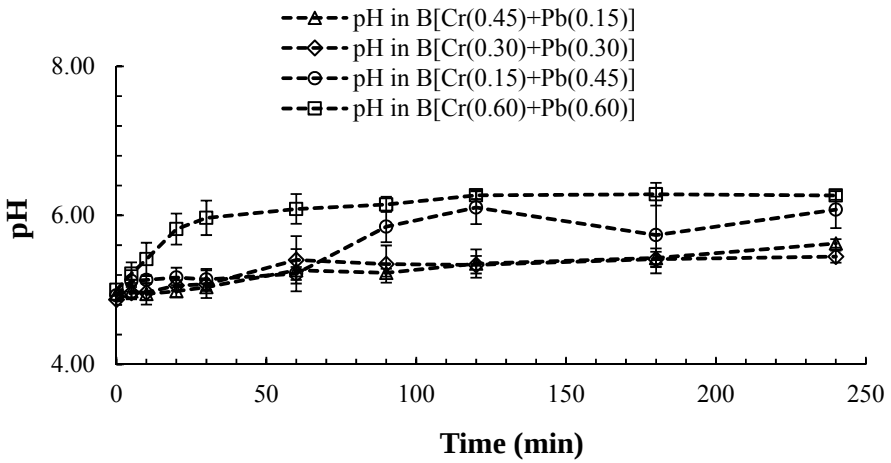

Fig. 5.14: Variation in solution pH with contact time for binary-metal ion systems comprising of Cr(III)+Pb(II) under uncontrolled pH conditions {Temp. = 30±2 °C, Initial adjusted pH = 5.00±0.05, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combinations B[Cr(0.45)+Pb(0.15)] = 0.50±0.05 meq/L of Cr(III) + 0.15±0.00 meq/L of Pb(II), B[Cr(0.30)+Pb(0.30)] = 0.32±0.00 meq/L of Cr(III) + 0.31±0.01 meq/L of Pb(II), B[Cr(0.15)+Pb(0.45)] = 0.15±0.05 meq/L of Cr(III) + 0.43±0.00 meq/L of Pb(II), B[Cr(0.60)+Pb(0.60)] = 0.57±0.04 meq/L of Cr(III) + 0.55±0.01 meq/L of Pb(II)} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

the solution.

Under controlled pH conditions (Fig. 5.16), the solution pH of B[Cr(0.45)+Pb(0.15)], B[Cr(0.30)+Pb(0.30)], B[Cr(0.15)+Pb(0.45)] and B[Cr(0.60)+Pb(0.60)] combinations remained unchanged to initially buffered pH of 5.00 during the course of experimentation. Hence most of Cr(III) and Pb(II) metal ions remained in aqueous phase under controlled pH conditions. The reduction in concentration of metal ions from the solution might be attributed only to accumulation of the metal ions onto GAA surface instead of reduction by precipitation and/or adsorption as seen under uncontrolled pH conditions. The reduction in residual concentrations of metal ions was observed to be higher during first 10 min. and afterwards it became slow and steady.

An inspection of time profiles of target Cr(III), target Pb(II) and total metal ions remaining in aqueous phase revealed that under uncontrolled pH conditions, the concentration of target Cr(III) metal remaining in aqueous phase was significantly lower

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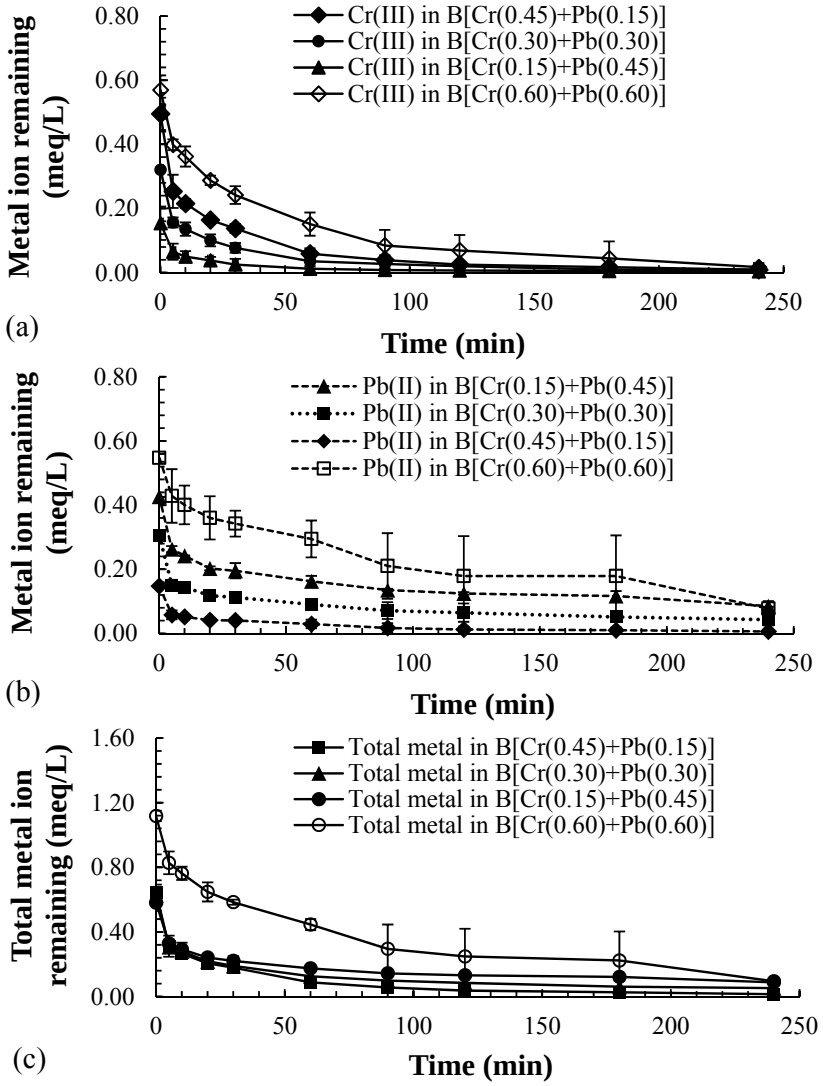

Fig. 5.15: Variation in (a) target Cr(III) metal, (b) target Pb(II) metal and (c) total metal ion concentration remaining in aqueous phase from binary-metal ion systems comprising of Cr(III)+Pb(II) under uncontrolled pH conditions {Temp. = 30±2 °C, Initial adjusted pH = 5.00±0.05, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combinations B[Cr(0.45)+Pb(0.15)] = 0.50±0.05 meq/L of Cr(III) + 0.15±0.00 meq/L of Pb(II), B[Cr(0.30)+Pb(0.30)] = 0.32±0.00 meq/L of Cr(III) + 0.31±0.01 meq/L of Pb(II), B[Cr(0.15)+Pb(0.45)] = 0.15±0.05 meq/L of Cr(III) + 0.43±0.00 meq/L of Pb(II), B[Cr(0.60)+Pb(0.60)] = 0.57±0.04 meq/L of Cr(III) + 0.55±0.01 meq/L of Pb(II)} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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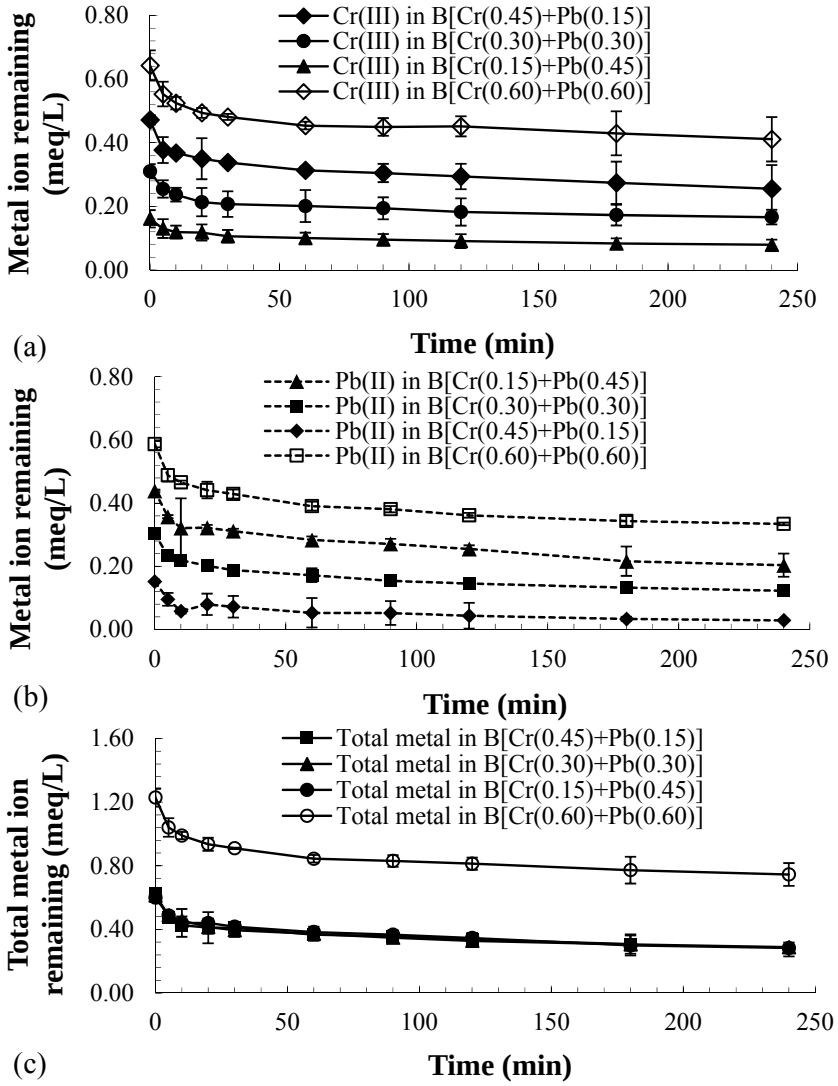

Fig. 5.16: Variation in (a) target Cr(III) metal, (b) target Pb(II) metal and (c) total metal ion concentration remaining in aqueous phase from binary-metal ion systems comprising of Cr(III)+Pb(II) under controlled pH conditions {Temp. = 30±2 °C, Buffered pH = 5.00±0.05, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combinations B[Cr(0.45)+Pb(0.15)] = 0.47±0.02 meq/L of Cr(III) + 0.15±0.00 meq/L of Pb(II), B[Cr(0.30)+Pb(0.30)] = 0.31±0.02 meq/L of Cr(III) + 0.30±0.01 meq/L of Pb(II), B[Cr(0.15)+Pb(0.45)] = 0.16±0.03 meq/L of Cr(III) + 0.44±0.00 meq/L of Pb(II), B[Cr(0.60)+Pb(0.60)] = 0.64±0.05 meq/L of Cr(III) + 0.59±0.01 meq/L of Pb(II)} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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[Fig. 5.15(a)] as compared to concentration of target Cr(III) metal remaining under controlled pH conditions [Fig. 5.16(a)]. The data points for target Cr(III) metal obtained under uncontrolled pH conditions overlapped at 95% confidence interval after a contact period of 60 min. for B[Cr(0.45)+Pb(0.15)], B[Cr(0.30)+Pb(0.30)] and B[Cr(0.15)+Pb(0.45)] combinations as seen in Fig. 5.15(a). However, under controlled pH conditions, the concentrations of target Cr(III) metal remaining in aqueous phase was observed to follow a decreasing trend with no overlap of experimental data points at 95% confidence intervals in any of the combinations investigated as seen from Fig. 5.16(a). Under uncontrolled pH conditions, the concentration of target Pb(II) metal remaining in aqueous phase was significantly lower [Fig. 5.15(b)] as compared to concentration of target Pb(II) metal remaining under controlled pH conditions [Fig. 5.16(b)]. No overlap of data points for target Pb(II) concentration remaining in solution at 95% confidence intervals were observed for any of the combinations investigated under uncontrolled [Fig. 5.15(b)] and controlled [Fig. 5.16(b)] pH conditions. The difference in concentrations of metal ions remaining in aqueous phase might be attributed to (i) precipitation of metal ions under uncontrolled pH conditions but absence of metal reduction due to precipitation under controlled pH conditions and (ii) formation of metal-acetate complex under controlled pH conditions thereby making a part of the metal ions less available for adsorption.

The residual concentrations of both−the target as well as non-target metal ions were simultaneously decreasing in the solution with increase in contact time. Therefore, the data obtained for individual metal ions have been re-plotted in Fig. 5.15(c) and 5.16(c) respectively for uncontrolled and controlled pH conditions by taking into account total concentration of metal ions remaining in aqueous phase for all the combinations. The concentration of total metal ions remaining in aqueous phase under uncontrolled pH conditions was observed to decrease with contact time and data points overlapped at 95% confidence interval for B[Cr(0.45)+Pb(0.15)], B[Cr(0.30)+Pb(0.30)] and B[Cr(0.15)+Pb(0.45)] combinations throughout the contact period, but more pronounced in the initial 30 min. except for B[Cr(0.60)+Pb(0.60)] combination as seen in Fig. 5.15(c). On the other hand, when total initial metal ion concentration in solution increased to 1.20 meq/L in B[Cr(0.60)+Pb(0.60)] combination, the concentration of total metal ion remaining was observed to have decreasing trend but it did not overlap at 95% confidence intervals with any of the other combinations of binary-metal ion systems. Similarly, overlap of experimental

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data points at 95% confidence intervals were also observed for all the combinations except B[Cr(0.60)+Pb(0.60)] combination under controlled pH conditions throughout the contact period [Fig. 5.16(c)]. Further, higher extent of overlap was observed under controlled pH conditions than that under uncontrolled pH conditions as seen in Fig. 5.15(c) and 5.16(c). Hence, it clearly indicated that the concentration of total metal ion remaining in aqueous phase was fairly independent of proportion of initial metal ion concentrations in binary-metal ion systems as long as total initial metal ion concentration was approximately the same.

5.2.4 Effect of contact time on metal ion concentration remaining in aqueous phase under uncontrolled and controlled pH conditions from binary-metal ion systems comprising of Cu(II) and Cr(III) ions

The presence of Cu(II) and Cr(III) metal ions together in the solution has had profound effect on its availability in aqueous phase around solution pH 5.00 and at higher pH levels as observed in Fig. 5.4. The metal speciation results presented in Fig. 5.7 also indicated lower availability of Cu(II) and Cr(III) metal ions in aqueous phase with increase in solution pH. Hence, a few additional preliminary studies were carried out at lower initial solution pH values of 3.50 and 4.30 under uncontrolled pH conditions with an aim to keep most of the metal ions in aqueous phase. However quick rise in solution pH levels above 5.00 were observed in the beginning of experiments. On the other hand, no metal precipitation was observed under controlled pH conditions with initial solution pH values buffered to 3.50 and 4.30, but it did not show any reduction in metal ion concentration. Therefore, in order to maintain uniformity in experimental investigations of metal ions concentrations remaining in aqueous phase from mono- [i.e. Cu(II) or Pb(II) or Cr(III)] and binary-[i.e. Cu(II)+Pb(II) and Cr(III)+Pb(II)] metal ions systems investigated, the concentration of metal ions remaining in aqueous phase from the binary-metal ion systems comprising of Cu(II)+Cr(III) were also investigated under uncontrolled and controlled pH conditions by adjusting the initial solution pH to 5.00. Even though considerably higher precipitation of Cu(II) and Cr(III) metal ions were observed and likely to lead to much lower availability of metal ions in aqueous phase with further rise in solution pH with increase in contact time.

The effect of contact time on metal ion concentration remaining in aqueous phase from binary-metal ion systems comprising of Cu(II)+Cr(III) were investigated under uncontrolled as well as controlled pH conditions. The solution pH was initially adjusted to

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5.00±0.05 in all the binary-metal ion systems. The reduction in concentrations of Cu(II) and Cr(III) metals from binary-metal ion systems comprising of Cu(II)+Cr(III) were investigated for four selected combinations viz. B[Cu(0.45)+Cr(0.15)], B[Cu(0.30)+Cr(0.30)], B[Cu(0.15)+Cr(0.45)] and B[Cu(0.60)+Cr(0.60)]. The total initial metal ion concentrations in the first three combinations were fixed close to 0.60 meq/L while in the fourth combination the total initial metal ion concentration was near to 1.20 meq/L – just double of other three combinations. In each of these combinations of binary-metal ion systems, the metal ion of interest was designated as the target metal while the other metal ion was termed as non-target metal for the purpose of presentation of experimental results. The variation in solution pH with contact time for each of the binary-metal ion system combinations under uncontrolled pH conditions are presented in Fig. 5.17. The time profiles of target Cu(II) and target Cr(III) metal ions remaining in aqueous phase investigated under uncontrolled and controlled pH conditions are shown in Fig. 5.18 and 5.19 respectively.

In the case of binary-metal ion systems of Cu(II)+Cr(III) under uncontrolled pH conditions (Fig. 5.4), considerable precipitation of both Cu(II) and Cr(III) metal ions [51-79% for Cu(II) and 63-93% for Cr(III) of the initial individual metal ion concentration] were observed at initial solution pH 5.00 in B[Cu(0.45)+Cr(0.15)], B[Cu(0.30)+Cr(0.30)] and B[Cu(0.60)+Cr(0.60)] combinations at time t = 0, whereas combination B[Cu(0.15)+Cr(0.45)] did not show any reduction in metal concentration at t = 0. Further, the solution pH for all the combinations increased rapidly above 6.00 from the initially adjusted solution pH of 5.00 within first 5 min. under uncontrolled pH conditions (Fig. 5.17). This might have caused further precipitation of the metal ions from the solution and thereby making availability of metal ions in aqueous phase much lower restricting the metal reduction by adsorption (Fig. 5.18). Therefore, it was decided not to investigate combinations of binary-metal ion systems of Cu(II)+Cr(III) under uncontrolled pH conditions any further. Under controlled pH conditions 100% availability of both Cu(II) and Cr(III) metal ions in aqueous phase were observed at buffered solution pH of 5.00 from binary-metal ion system combinations (Fig. 5.19) in the beginning (when t = 0), and no precipitation was observed in any of the combinations. This might be due to complex formation of metal ions with acetate which kept metal ions in aqueous phase (Table 5.1).

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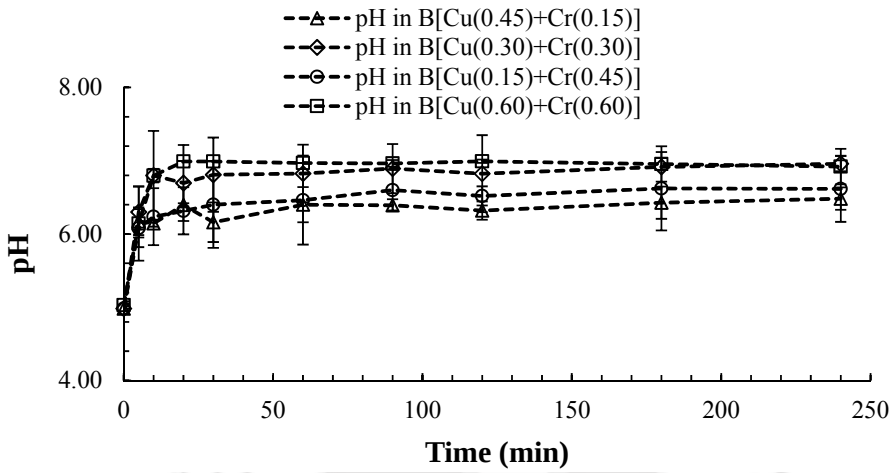

Fig. 5.17: Variation in solution pH with contact time from binary-metal ion systems comprising of Cu(II)+Cr(III) under uncontrolled pH conditions {Temp. = 30±2 °C, Initial adjusted pH = 5.00±0.05, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combinations B[Cu(0.45)+Cr(0.15)] = 0.22±0.03 meq/L of Cu(II) + 0.01±0.00 meq/L of Cr(III), B[Cu(0.30)+Cr(0.30)] = 0.11±0.01 meq/L of Cu(II) + 0.16±0.06 meq/L of Cr(III), B[Cu(0.15)+Cr(0.45)] = 0.15±0.00 meq/L of Cu(II) + 0.47±0.03 meq/L of Cr(III), B[Cu(0.60)+Cr(0.60)] = 0.12±0.02 meq/L of Cu(II) + 0.23±0.02 meq/L of Cr(III)} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

The concentration of target Cu(II) and target Cr(III) metal ions remaining in aqueous phase obtained under controlled pH conditions was observed to follow decreasing trend up to first 20-30 min. and thereafter decrease appeared to be much lower. The experimental data points did not overlap at 95% confidence interval for any of the combinations. The reduction in metal ion concentrations in aqueous phase might be attributed to migration of metal ions to GAA surfaces. Higher concentration of metal ions remaining in aqueous phase under controlled pH conditions might be attributed to complex formation with buffering reagent used thereby making a part of metal ions non-available for migration to GAA surfaces. This was further supported by estimating speciation of Cu(II) and Cr(III) metal ions in presence of acetate. The maximum percentage of both the metal ions was observed in the form of metal-acetate complex as could be seen in Table 5.1.

The residual concentrations of both Cu(II) and Cr(III) metal ions remaining in aqueous phase were decreasing simultaneously from binary-metal ion systems under uncontrolled and controlled pH conditions. Therefore, the data obtained for individual metal ions as presented

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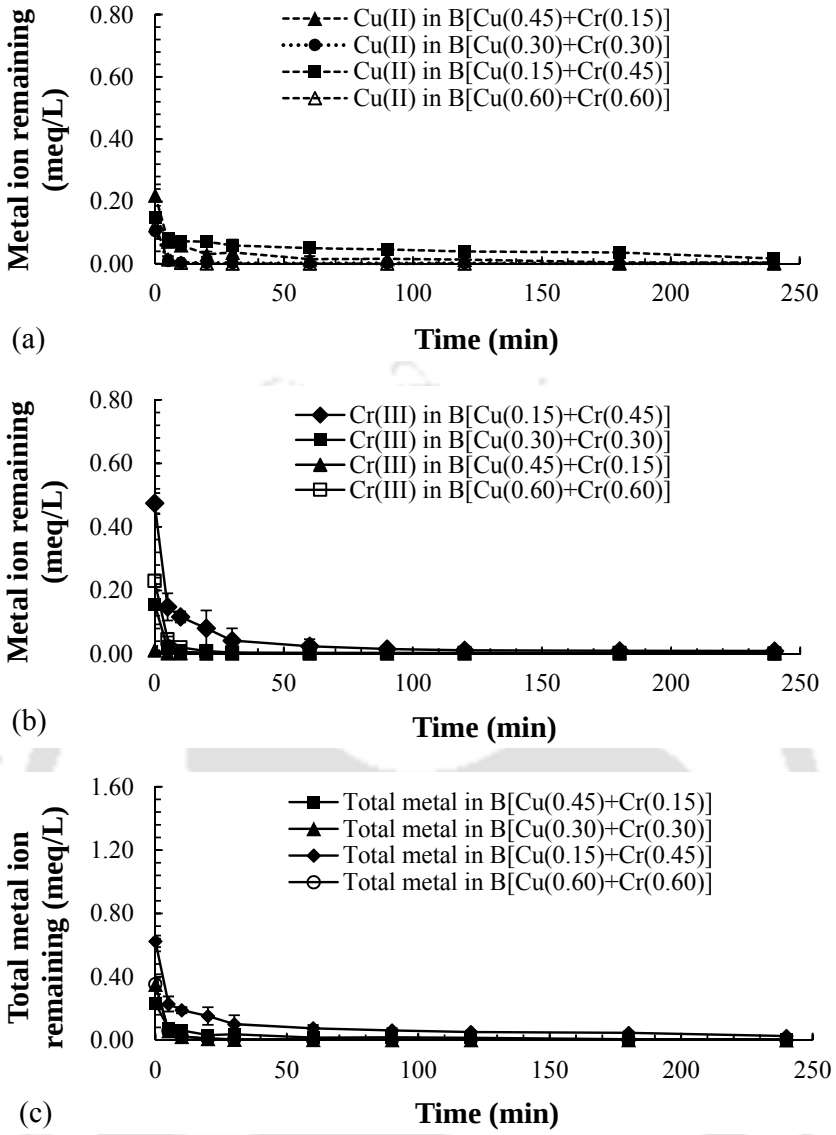

Fig. 5.18: Variation in (a) target Cu(II) metal, (b) target Cr(III) metal and (c) total metal ion concentration remaining in aqueous phase from binary-metal ion systems comprising of Cu(II)+Cr(III) under uncontrolled pH conditions {Temp. = 30±2 °C, Initial adjusted pH = 5.00±0.05, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combinations B[Cu(0.45)+Cr(0.15)] = 0.22±0.03 meq/L of Cu(II) + 0.01±0.00 meq/L of Cr(III), B[Cu(0.30)+Cr(0.30)] = 0.11±0.01 meq/L of Cu(II) + 0.16±0.06 meq/L of Cr(III), B[Cu(0.15)+Cr(0.45)] = 0.15±0.00 meq/L of Cu(II) + 0.47±0.03 meq/L of Cr(III), B[Cu(0.60)+Cr(0.60)] = 0.12±0.02 meq/L of Cu(II) + 0.23±0.02 meq/L of Cr(III)} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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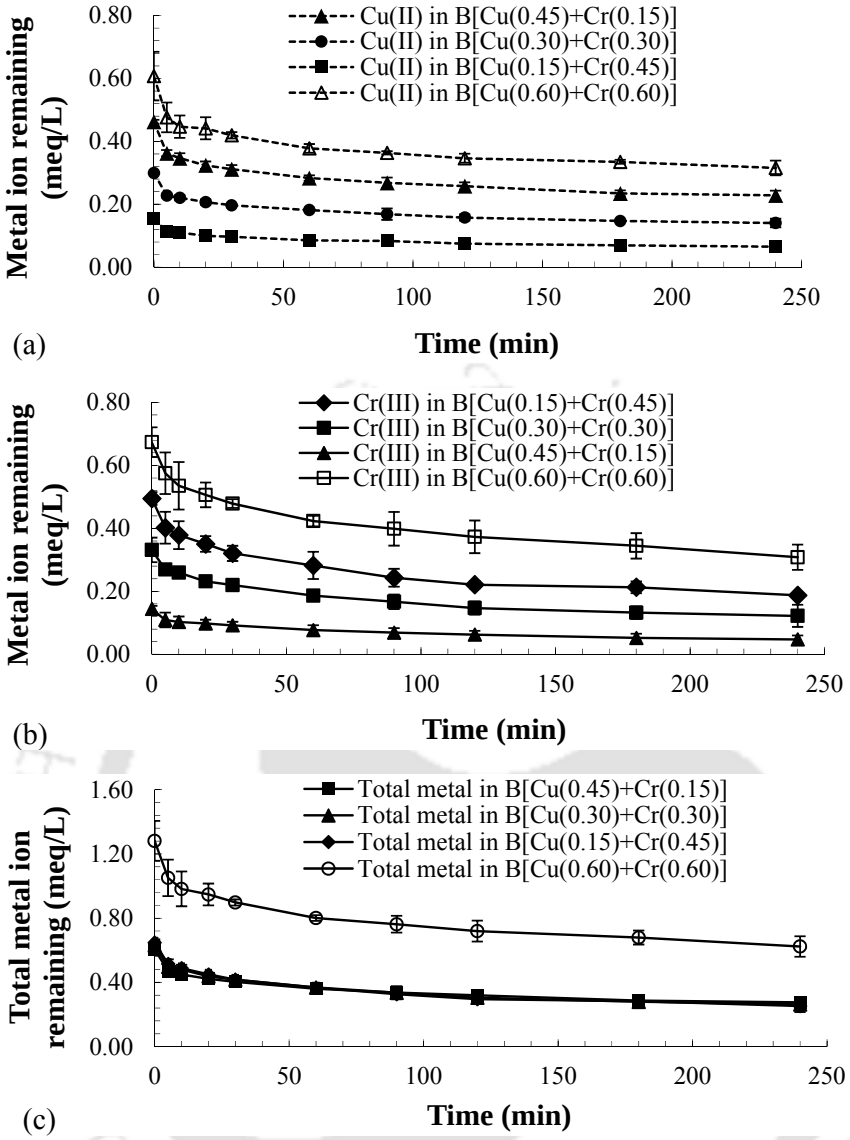

Fig. 5.19: Variation in (a) target Cu(II) metal (b) target Cr(III) metal and (c) total metal ion concentration remaining in aqueous phase from binary-metal ion systems comprising of Cu(II)+Cr(III) under controlled pH conditions {Temp. = 30±2 °C, Buffered pH = 5.00±0.05, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combinations B[Cu(0.45)+Cr(0.15)] = 0.46±0.01 meq/L of Cu(II) + 0.14±0.01meq/L of Cr(III), B[Cu(0.30)+Cr(0.30)] = 0.30±0.00 meq/L of Cu(II) + 0.33±0.04 meq/L of Cr(III), B[Cu(0.15)+Cr(0.45)] = 0.15±0.00 meq/L of Cu(II) + 0.49±0.02 meq/L of Cr(III), B[Cu(0.60)+Cr(0.60)] = 0.61±0.08 meq/L of Cu(II) + 0.67±0.05 meq/L of Cr(III)} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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in Fig. 5.18(a & b) and 5.19(a & b) have been re-plotted in Fig. 5.18(c) and 5.19(c) respectively for uncontrolled and controlled pH conditions taking into account the total concentration of metal ions remaining in aqueous phase for all the combinations. Under uncontrolled pH conditions, since the removal of both the metal ions by precipitation started around pH 5.00, the total metal ion concentrations remaining in solution from B[Cu(0.60)+Cr(0.60)] combination overlapped within 95% confidence interval with the total metal ion concentrations remaining in solution from B[Cu(0.45)+Cr(0.15)], B[Cu(0.30)+Cr(0.30)] and B[Cu(0.15)+Cr(0.45)] combinations. Further, under controlled pH conditions, the overlap of experimental data points at 95% confidence levels were observed for all the combinations of binary-metal ion systems having total initial metal ion concentrations close to 0.60 meq/L throughout the contact period [Fig. 5.19(c)]. However, as the concentration was doubled in B[Cu(0.60)+Cr(0.60)] combination, the total metal ion concentration remaining in aqueous phase was higher contradicting the results obtained under uncontrolled pH conditions. Hence, the results obtained under controlled pH conditions clearly indicated that the concentration of total metal remaining in aqueous phase was fairly independent of proportion of initial metal ion concentrations in binary-metal ion systems as long as total initial metal ion concentration was approximately the same.

5.2.5 Effect of contact time on metal ion concentration remaining in aqueous phase under uncontrolled and controlled pH conditions from ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions

The higher precipitation of Cu(II) and Cr(III) metal ions in T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combination was observed at pH 5.00 as seen in Fig. 5.5. With rise in solution pH to higher levels from the initially adjusted pH of 5.00, the availability of individual metal ions in aqueous phase was likely to be much lower. The metal speciation results also indicated lower availability of metal ions in aqueous phase at higher pH levels (Fig. 5.8). Therefore, a few additional preliminary studies were carried out at lower initial solution pH values of 3.50 and 4.30 for T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combination under uncontrolled pH conditions so as to keep the metal ions in aqueous phase. However, quick rise in solution pH levels above 5.00 was observed during the course of experiments. On the other hand, the reduction in residual metal concentrations under controlled pH conditions at buffered pH values of 3.50 and 4.30 were negligible. Therefore, in order to maintain uniformity in experimental investigations of metal ion concentrations remaining in

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aqueous phase from mono- [i.e. Cu(II), Pb(II) and Cr(III)] and binary-[i.e. Cu(II)+Pb(II), Cr(III)+Pb(II) and Cu(II)+Cr(III)] metal ions systems investigated, the concentration of metal ions remaining in aqueous phase from ternary-metal ion systems comprising of Cu(II)+Pb(II)+Cr(III) were also investigated under uncontrolled and controlled pH conditions by adjusting the initial solution pH to 5.00. Even though precipitation of Cu(II) and Cr(III) metal ions was observed and likely to impact adversely availability of metal ions in aqueous phase with further rise in solution pH with increase in contact time.

The effect of contact time on metal ion concentration remaining in aqueous phase from ternary-metal ion systems comprising of Cu(II)+Pb(II)+Cr(III) were investigated under uncontrolled as well as controlled pH conditions at adjusted initial solution pH of 5.00±0.02. The combinations of ternary-metal ion systems were T[Cu(0.20)+Pb(0.20)+Cr(0.20)] and T[Cu(0.60)+Pb(0.60)+Cr(0.60)]. The total initial metal ion concentrations in the first combination was fixed close to 0.60 meq/L while in the second combination the total initial metal ion concentration was near to 1.80 meq/L – just thrice of the first combination. In each of these combinations of ternary-metal ion systems, the metal ion of interest was designated as the target metal while the other two metal ions were termed as non-target metals for the purpose of presentation of experimental results.

In case of T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combination investigated under uncontrolled pH condition, substantial reduction in concentrations of Cu(II) and Cr(III) metal ions were observed by precipitation at initially adjusted pH 5.00 (Fig. 5.5). Hence it was decided not to investigate this combination any further. The time profiles of metal ion concentration remaining in aqueous phase from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination along with variation in pH have been developed and presented in Fig. 5.20 for all the three metal ions. In T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination, pH of the solution was observed in the range of 6.00-6.23 (average solution pH 6.08) within first 5 min. and it was recorded in the range of 6.40-6.85 (average solution pH 6.52) towards the end of experimentation [Fig. 5.20(a)]. Therefore in T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination, the reduction in concentrations of all the three metal ions might have been due to precipitation. The concentrations of metal ion remaining in aqueous phase from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] and T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combinations investigated under controlled pH conditions are presented in Fig. 5.21. The concentrations of

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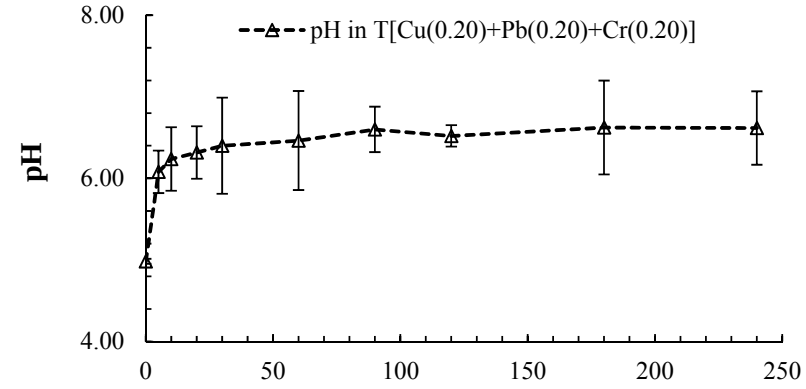
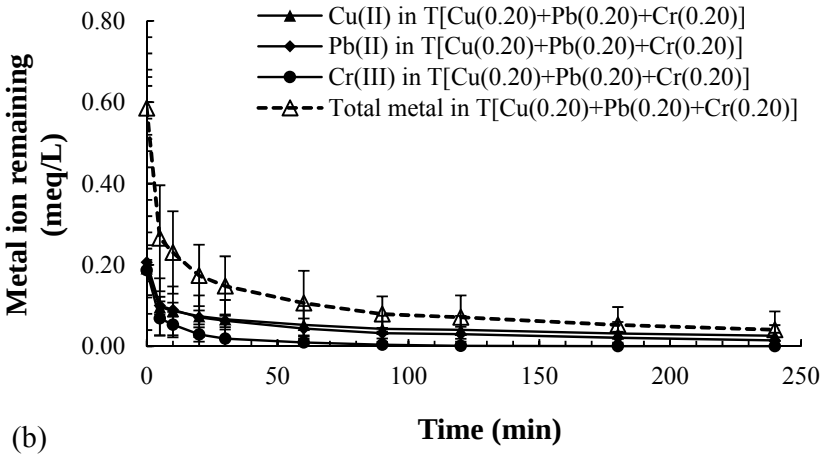


(a)



(b)

Fig. 5.20: Variation in (a) solution pH (b) target Cu(II), target Pb(II), target Cr(III) and total metal ion concentration remaining in aqueous phase from ternary-metal ion system comprising of Cu(II)+Pb(II)+Cr(III) under uncontrolled pH conditions {Temp. = 30±2 °C, Initial adjusted pH = 5.00±0.02, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combination T[Cu(0.20)+Pb(0.20)+Cr(0.20)] = 0.19±0.01 meq/L of Cu(II) + 0.21±0.01 meq/L of Pb(II) + 0.19±0.06 meq/L of Cr(III)} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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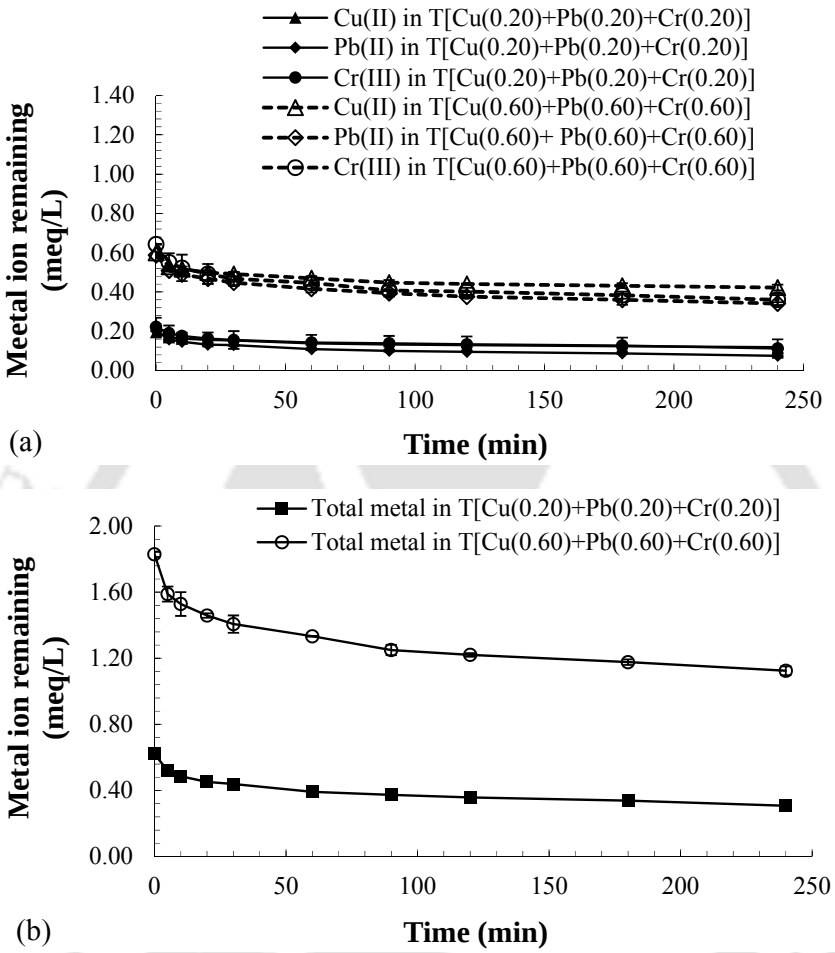

Fig. 5.21: Variation in (a) target Cu(II), target Pb(II) and target Cr(III) metal and (b) total metal ion concentration remaining in aqueous phase from ternary-metal ion systems comprising of Cu(II)+Pb(II)+Cr(III) under controlled pH conditions {Temp. = 30±2 °C, Buffered pH = 5.00±0.02, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combinations T[Cu(0.20)+Pb(0.20)+Cr(0.20)] = 0.20±0.01 meq/L of Cu(II) + 0.20±0.01 meq/L of Pb(II) + 0.22±0.05 meq/L of Cr(III), T[Cu(0.60)+Pb(0.60)+Cr(0.60)] = 0.60±0.00 meq/L of Cu(II) + 0.59±0.02 meq/L of Pb(II) + 0.64±0.00 meq/L of Cr(III)} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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all the three metal ions decreased with time under controlled pH conditions as could be seen in Fig. 5.21(a). The reduction in residual metal ion concentrations might be attributed to migration of metal ions to GAA surfaces. However, the residual concentration of metal ions from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination were lower compared to T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combination. The metal ion concentration remaining in solution for Cu(II), Pb(II) and Cr(III) metal ions overlapped within 95% confidence interval as could be seen in Fig. 5.21(a).

Further, all the three metal ion concentrations remaining in solution were decreasing simultaneously from ternary-metal ion systems. Therefore, the data obtained for individual metal ions as presented in Fig. 5.20 and 5.21 have been re-plotted in Fig. 5.20(b) and 5.21(b) respectively by taking into account the total concentration of metal ion remaining in aqueous phase. The total metal ion concentration remaining in solution from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination under uncontrolled pH condition overlapped within 95% confidence interval after 60 min. with the individual metal ions concentrations remaining in aqueous phase [Fig. 5.20(b)]. Further, the total metal ion concentration remaining in solution from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] and T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combinations under controlled pH conditions did not overlap within 95% confidence interval as the total initial metal ion concentration was much higher in second combination. The difference in concentrations of metal ions remaining in aqueous phase might be attributed to (i) precipitation of metal ions under uncontrolled pH conditions but absence of metal reduction due to precipitation under controlled pH conditions and (ii) formation of metal-acetate complex under controlled pH conditions thereby making a part of the metal ions less available for adsorption.

5.2.6 Summary

The metal ion concentration remaining in aqueous phase were investigated from selected combinations of mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) metals under uncontrolled and controlled pH conditions. The total initial metal ion concentrations were fixed approximately at 0.60 meq/L for all mono-metal ion systems and most of the combinations of binary- and ternary-metal ion systems while three combinations of binary-metal ion systems and one combination of ternary-metal ion system were investigated at total initial metal ion concentration approximately of 1.20 meq/L and

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1.80 meq/L respectively. The increase in average solution pH had significantly impacted the metal removal mechanisms from the solution. In all the selected combinations of mono-, binary- and ternary-metal ion systems investigated under uncontrolled pH conditions, the solution pH increased with contact time leading to removal of metal ions due to combined effects of precipitation and adsorption. In mono-, binary-, and ternary-metal ion systems investigated under controlled pH conditions, solution pH remained unchanged throughout the contact time and hence the removal of all the three metal ions were due to adsorption only. The metal ion concentrations remaining in aqueous phase from all mono-, binary- and ternary-metal ion systems were higher under controlled pH conditions compared to uncontrolled pH conditions. This was attributed to metal-complex formation with acetate buffer components thereby making a part of metal ions unavailable for adsorption. Further, the total metal ion concentrations remaining in aqueous phase from selected combinations of Cu(II)+Pb(II), Cr(III)+Pb(II) and Cu(II)+Cr(III) binary-metal ion systems overlapped within 95% confidence interval when the total initial metal ion concentration was kept fixed approximately 0.60 meq/L. It clearly indicated that the concentration of total metal ion remaining in aqueous phase was fairly independent of proportion of initial metal ion concentrations in binary-metal ion systems as long as total initial metal ion concentration was approximately the same. As the total initial metal ion concentrations increased in solution, the total metal ion concentration remaining also increased except for Cu(II)+Cr(III) binary-metal ion system combinations investigated under uncontrolled pH conditions.

5.3 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from mono-, binary- and ternary-metal ions systems comprising of Cu(II), Pb(II) and Cr(III) ions

The published literature presented in Chapter 2 highlighted lack of monitored data on variation in solution pH from initially adjusted pH level during the course of experimentations on adsorption kinetics (Liu et al., 2013; Olanipekun et al., 2014; Srivastava et al., 2006). In fact, Tien (2008) in his editorial note made the following observations: "Metal ion adsorption is well known to be pH dependent. However, pH effect was invariably examined only in terms of the initial pH of the aqueous solution used in experiments. Not in a single case have we seen data demonstrating the changes of the solution pH during the course of an adsorption experiment." Therefore the possibility of rise in solution pH during the course of experiments and consequently metal removal due to combined effects of

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precipitation and adsorption could not be completely ruled out. All the metal ions removed from the solution, be it through precipitation and/or adsorption was attributed to the metal uptake by the adsorbent in most of the published literatures. These experimental data were also fitted to adsorption kinetic models namely (a) pseudo-first-order kinetic model, (b) pseudo-second-order kinetic model and (c) intra-particle diffusion model. To our understanding, the estimated kinetic constants were most likely represented the metal removal through precipitation and/or through adsorption rather than solely representing the metal uptake by adsorbent through adsorption.

The kinetics of metal uptake under controlled pH conditions and metal removal (or reduction) under uncontrolled pH conditions have been studied from mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) metal ions in the present work. The kinetic studies were carried out with a fixed total initial metal ion concentrations of approximately 0.60, 1.20 and 1.80 meq/L in solution using a fixed dose of adsorbent at initially adjusted pH of 5.00. The experimental data obtained in the investigation of effect of contact time on metal ion concentration remaining in aqueous phase from mono-, binary- and ternary-metal ion systems as presented in section 5.2 were used to elucidate the mechanism of metal uptake by GAA and metal removal (or reduction) from the aqueous phase. The experimental data of concentration of metal ions remaining in aqueous phase with contact time obtained under controlled pH conditions were analyzed applying three widely used kinetic models as discussed in Chapter 2.

However, the reduction in concentration of metal ions from mono-, binary- and ternary-metal ion systems investigated under uncontrolled pH conditions were attributed to combined effects of precipitation along with adsorption as presented in section 5.2. It was not possible to quantify exact fraction of metal ions getting precipitated out of solution and/or adsorbed onto GAA with rise in solution pH in the present investigation. However, the rise in solution pH and subsequent reduction in metal ion concentration (be it through precipitation or through adsorption or both) is mainly caused by the mass of adsorbent (i.e. GAA) used. Therefore, the amount of metal ion removed (or reduced) from the aqueous phase might be expressed as milliequivalents (meq) of metal ion removed (or reduced) from the solution per gram (g) of adsorbent used (i.e. meq/g – a similar unit normally used for the metal uptake through adsorption). In published literature, the kinetics of metal removal (or reduction) data

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have been inadvertently analyzed using pseudo-first-order and pseudo-second-order kinetic models. Therefore, there is a need to re-designate the metal uptake and rate constants in these rate equations to reflect the combined effects of precipitation and adsorption in this study. The re-designated pseudo-first-order rate model is expressed as

$$Q_t = Q_e (1 - e^{-K_1 t}) \tag{5.1}$$

and pseudo-second-order rate model is expressed in linearized form as

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{K_2 Q_e^2} \tag{5.2}$$

where Q_t is amount of metal removed (or reduced) from the aqueous phase at time '*t*' (meq/g), Q_e is amount of metal removed (or reduced) from the aqueous phase at equilibrium (meq/g), K_1 is first-order rate constant (1/min), K_2 is second-order rate constant (g/meq.min) and '*t*' is time (min). As a note of caution, these equations only attempt to distinguish the kinetic constants for metal removal (or reduction) from the aqueous phase through combined effects of precipitation and adsorption.

5.3.1 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from mono-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions

The data obtained for metal ion concentrations remaining in aqueous phase from mono-metal ion systems (refer section 5.2.1) were utilized to investigate the kinetics of Cu(II), Pb(II) and Cr(III) metal ions removal under uncontrolled pH conditions and metal uptake under controlled pH conditions. The amount of Cu(II), Pb(II) and Cr(III) metal ions removed from solution under uncontrolled pH conditions is estimated using

$$Q_t = \frac{V(C_o - C_t)}{1000m} \tag{5.3}$$

and metal uptake by GAA under controlled pH conditions is estimated using

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$$q_t = \frac{V(C_o - C_t)}{1000m} \tag{5.4}$$

where Q_t is amount of metal removed (meq/g) from the aqueous phase at time '*t*', q_t is metal uptake (meq/g) at time '*t*', V is solution volume (mL), C_o is initial metal ion concentration (meq/L), C_t is metal ion concentration remaining in aqueous phase at time '*t*' (meq/L) and m is mass of adsorbent (g).

The kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from mono-metal ion systems of M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] are presented in Fig. 5.22 and 5.23 respectively. The metal removals and metal uptakes with time are plotted with 95% confidence intervals (i.e. mean of the data added with two times the standard deviation). The metal removal under uncontrolled pH conditions appeared to be very fast during first 20 min. with Cr(III) removal comparatively higher than Cu(II) and Pb(II) removals. This might be due to quick rise in solution pH above 6.00 within first 5 min. in the case of Cr(III) metal ions which eventually might have caused removal of higher fraction of Cr(III) metal ions by precipitation in the beginning and then possibly followed by adsorption compared to Cu(II) and Pb(II) metal ions. After a period of first 60 min., the metal removals were observed to be very slow – leading towards equilibrium condition. The Cu(II) and Pb(II) metal removal data obtained under uncontrolled pH conditions overlapped at 95% confidence interval up to 120 min. while Cr(III) metal removal data didn't overlap at 95% confidence interval either with Cu(II) or Pb(II) metal ions removal data throughout the experimentation. However, the metal uptakes under controlled pH conditions were observed to be moderately fast up to a time period of 30 min. and became slow and steady after first 60 min. of experimentation.

The kinetic data for metal removals under uncontrolled pH conditions and metal uptakes under controlled pH conditions were fitted into pseudo-first- and second-order rate or kinetic models. All the estimated kinetic parameters are presented in Table 5.2. Higher values of coefficient of determination (R^2) indicated appropriateness of pseudo-second-order rate or kinetic model to describe experimental kinetic data as compared to pseudo-first-order rate or kinetic model. The experimental amount of metal removed at equilibrium ($Q_{e,exp}$) under uncontrolled pH conditions were 0.0467 meq/g for Cu(II), 0.0423 meq/g for Pb(II) and 0.0500 meq/g for Cr(III) while under controlled pH conditions, the experimental amount

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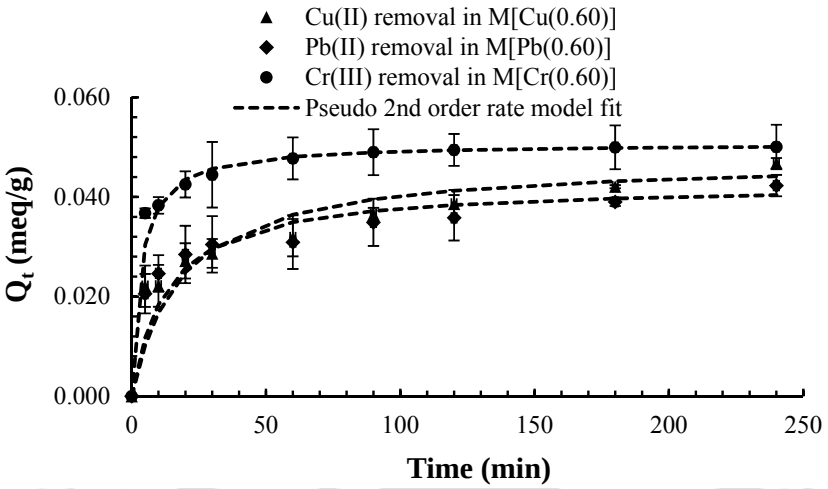

Fig. 5.22: Variation in Cu(II), Pb(II) and Cr(III) metal removal from mono-metal ion systems investigated under uncontrolled pH conditions {Initial metal conc. in M[Cu(0.60)] = 0.59±0.01 meq/L, M[Pb(0.60)] = 0.57±0.02 meq/L, M[Cr(0.60)] = 0.61±0.06 meq/L, Temp. = 30±2 °C, Initial adjusted pH = 5.00±0.02, GAA dose =12 g/L, Mixing speed = 66 rpm} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

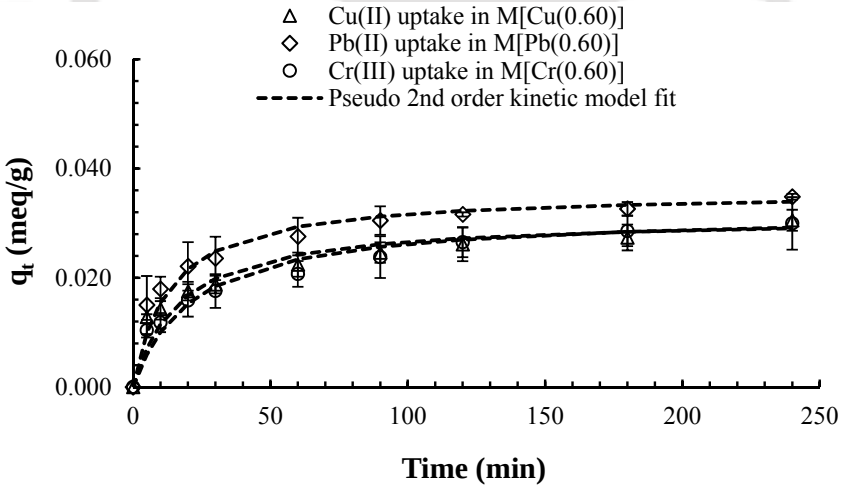

Fig. 5.23: Variation in Cu(II), Pb(II) and Cr(III) metal uptake from mono-metal ion systems investigated under controlled pH conditions {Initial metal conc. in M[Cu(0.60)] = 0.58±0.01 meq/L, M[Pb(0.60)] = 0.60±0.01 meq/L, M[Cr(0.60)] = 0.64±0.04 meq/L, Temp. = 30±2 °C, Buffered pH = 5.00±0.02, GAA dose =12 g/L, Mixing speed = 66 rpm} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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Table 5.2: Summary of estimated kinetic parameters for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from mono-metal ion systems investigated.

Metal system	Initial conc. (meq/L)	Uncontrolled pH conditions			Controlled pH conditions		
		Parameters	Pseudo-first-order rate model	Pseudo-second-order rate model	Parameters	Pseudo-first-order kinetic model	Pseudo-second-order kinetic model
M[Cu(0.60)]	0.59±0.01	$Q_{e,exp}$ (meq/g)	0.0467±0.0010		$q_{e,exp}$ (meq/g)	0.0305±0.0019	
		Q_{em} (meq/g)	0.0376	0.0475	q_{em} (meq/g)	0.0251	0.0311
		K_1 (1/min)	0.0585	-	k_1 (1/min)	0.0621	-
		K_2 (g/meq.min)	-	1.1555	k_2 (g/meq.min)	-	1.8941
		R^2	0.851	0.986	R^2	0.900	0.991
M[Pb(0.60)]	0.57±0.02	$Q_{e,exp}$ (meq/g)	0.0423±0.0021		$q_{e,exp}$ (meq/g)	0.0348±0.0005	
		Q_{em} (meq/g)	0.0348	0.0426	q_{em} (meq/g)	0.0301	0.0358
		K_1 (1/min)	0.1064	-	k_1 (1/min)	0.0724	-
		K_2 (g/meq.min)	-	1.7979	k_2 (g/meq.min)	-	2.1356
		R^2	0.900	0.991	R^2	0.929	0.997
M[Cr(0.60)]	0.61±0.06	$Q_{e,exp}$ (meq/g)	0.0500±0.005		$q_{e,exp}$ (meq/g)	0.0300±0.0048	
		Q_{em} (meq/g)	0.0478	0.0508	q_{em} (meq/g)	0.0253	0.0319
		K_1 (1/min)	0.1798	-	k_1 (1/min)	0.0434	-
		K_2 (g/meq.min)	-	5.9115	k_2 (g/meq.min)	-	1.4470
		R^2	0.950	0.999	R^2	0.923	0.992

$Q_{e,exp}$ = experimental metal removal at equilibrium, Q_{em} = metal removal at equilibrium calculated using rate models, $q_{e,exp}$ = experimental metal uptake capacity at equilibrium, q_{em} = metal uptake capacity at equilibrium calculated using kinetic models. Data presented in xx±yy format represents average value as xx and standard deviation as yy estimated with three independent data points.

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of metal uptake at equilibrium ($q_{e,exp}$) were 0.0305 meq/g for Cu(II), 0.0348 meq/g for Pb(II) and 0.0300 meq/g for Cr(III). The estimated K_2 values were higher for Cr(III) compared to Cu(II) and Pb(II) metal ions under uncontrolled pH conditions while Pb(II) metal ions had higher k_2 value compared to Cu(II) and Cr(III) metal ions under controlled pH conditions.

The adsorption of metal ions might have taken place on the external surface of the GAA as well as in pores via intra-particle diffusion. The possibility of transport of metal ions through pores of GAA was tested with intra-particle diffusion model using the kinetic data obtained from mono-metal ion systems under controlled pH conditions only. The existence of intra-particle diffusion in the adsorption system was tested through a graphical relationship between metal ion uptake and square root of time (Li et al., 2011; Mohan et al., 2006) using the relation

$$q_t = K_p\, t^{0.5} \tag{5.5}$$

where K_p is intra-particle diffusion rate constant (meq/g.min$^{0.5}$). The plots of q_t versus $t^{0.5}$ are shown in Fig. 5.24 for M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] systems. The plots showed initial curved portions reflecting film (or boundary layer) diffusion effect and the subsequent linear portions reflecting the intra-particle diffusion effect (Singh & Pant, 2004; Yadav et al., 2006). The linear portions did not pass through origin of the plot suggesting

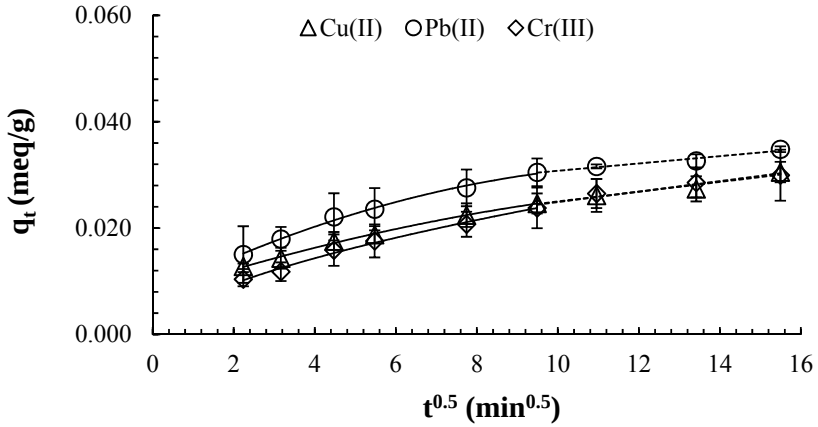

Fig. 5.24: Intra-particle diffusion model for mono-metal ion system of M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] investigated under controlled pH conditions.

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adsorption of metal ions on GAA to be a complex process involving surface adsorption as well as intra-particle diffusion contributing to rate controlling steps (Mahramanlioglu et al., 2002).

5.3.2 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from binary-metal ion systems comprising of Cu(II) and Pb(II) ions

The data represented in section 5.2.2 for metal ion concentrations remaining in aqueous phase with contact time obtained for selected combinations of binary-metal ion systems comprising of Cu(II)+Pb(II) have been utilized to investigate Cu(II) and Pb(II) metal removal rate under uncontrolled pH conditions and metal uptake kinetics under controlled pH conditions. The variation in metal removal from aqueous phase under uncontrolled pH conditions and metal uptake by GAA under controlled pH conditions considering Cu(II) as target metal ion in presence of corresponding Pb(II) as non-target metal ion and vice-versa are shown in Fig. 5.25 and 5.26 respectively. The variation in Cu(II) metal removal from binary combinations investigated under uncontrolled pH conditions didn't overlap at 95% confidence interval except for a few data points for B[Cu(0.45)+Pb(0.15)] and B[Cu(0.60)+Pb(0.60)] combinations [Fig. 5.25(a)]. The Pb(II) metal ions removal from binary combinations investigated under uncontrolled pH conditions didn't overlap at 95% confidence interval [Fig. 5.25(b)]. The Cu(II) and Pb(II) metal ions uptake data under controlled pH conditions from all the combinations were distinct and didn't overlap at 95% confidence interval as shown in Fig. 5.26.

The kinetic data obtained under uncontrolled pH conditions were fitted into pseudo-first- and pseudo-second-order rate models while data obtained under controlled pH conditions were fitted to pseudo-first- and pseudo-second-order kinetic models. The estimated kinetic parameters are presented in Table 5.3 for uncontrolled pH conditions and Table 5.4 for controlled pH conditions. Higher values of coefficient of determination (R^2) indicated suitability of pseudo-second-order rate model to describe experimental kinetic data as compared to pseudo-first-order rate model under uncontrolled pH conditions. Similarly higher R^2 indicated applicability of pseudo-second-order kinetic model to describe experimental kinetic data obtained under controlled pH conditions. From Table 5.3 and 5.4, it

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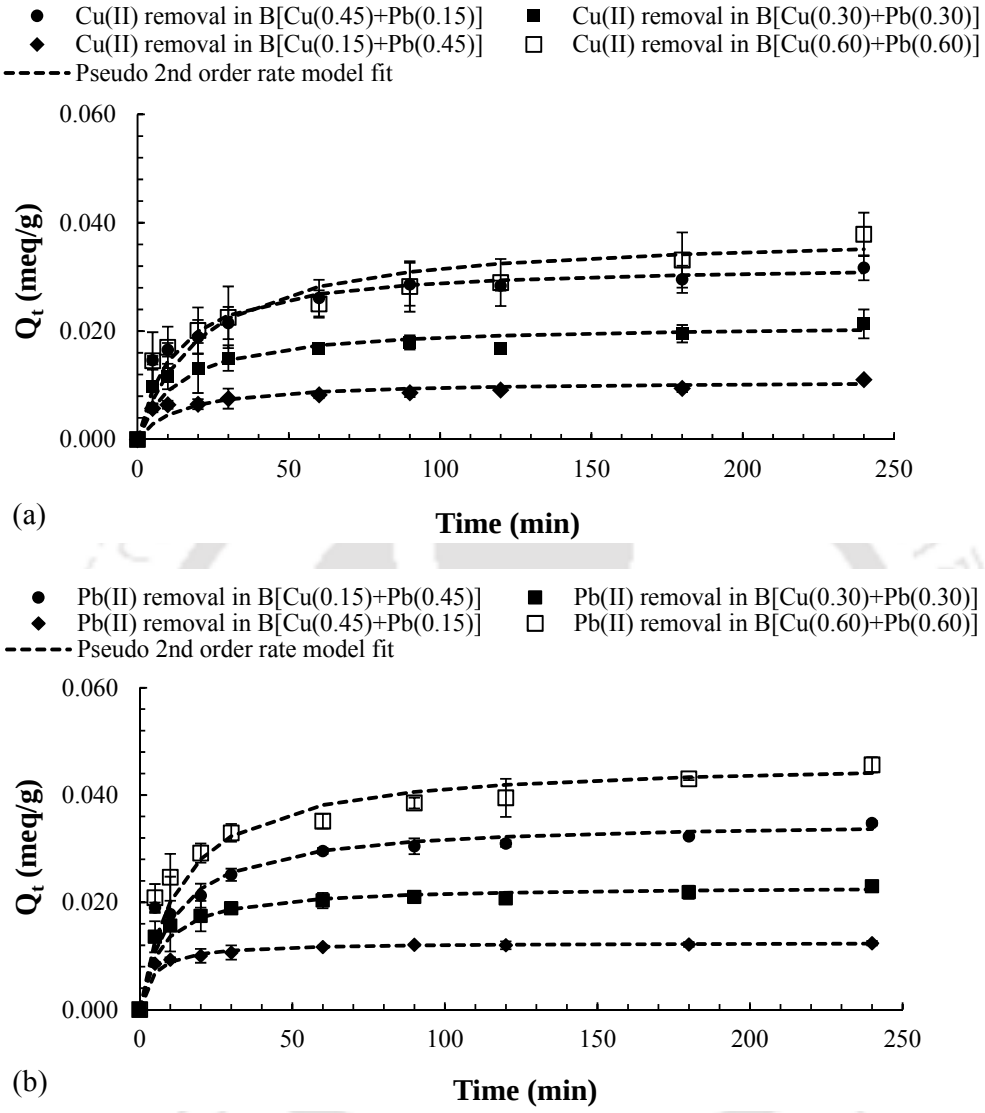

Fig. 5.25: Variation in (a) target Cu(II) and (b) target Pb(II) metal removal from binary-metal ion systems comprising of Cu(II)+Pb(II) under uncontrolled pH conditions {Temp. = 30±2 °C, Initial adjusted pH = 5.00±0.02, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combinations B[Cu(0.45)+Pb(0.15)] = 0.44±0.01 meq/L of Cu(II) + 0.15±0.01 meq/L of Pb(II), B[Cu(0.30)+Pb(0.30)] = 0.29±0.00 meq/L of Cu(II) + 0.28±0.01 meq/L of Pb(II), B[Cu(0.15)+Pb(0.45)] = 0.15±0.00 meq/L of Cu(II) + 0.44±0.00 meq/L of Pb(II), B[Cu(0.60)+Pb(0.60)] = 0.59±0.03 meq/L of Cu(II) + 0.60±0.02 meq/L of Pb(II)} (Each data represents an average of three independent experimental values with vertical bars at each data points representing 95% confidence interval).

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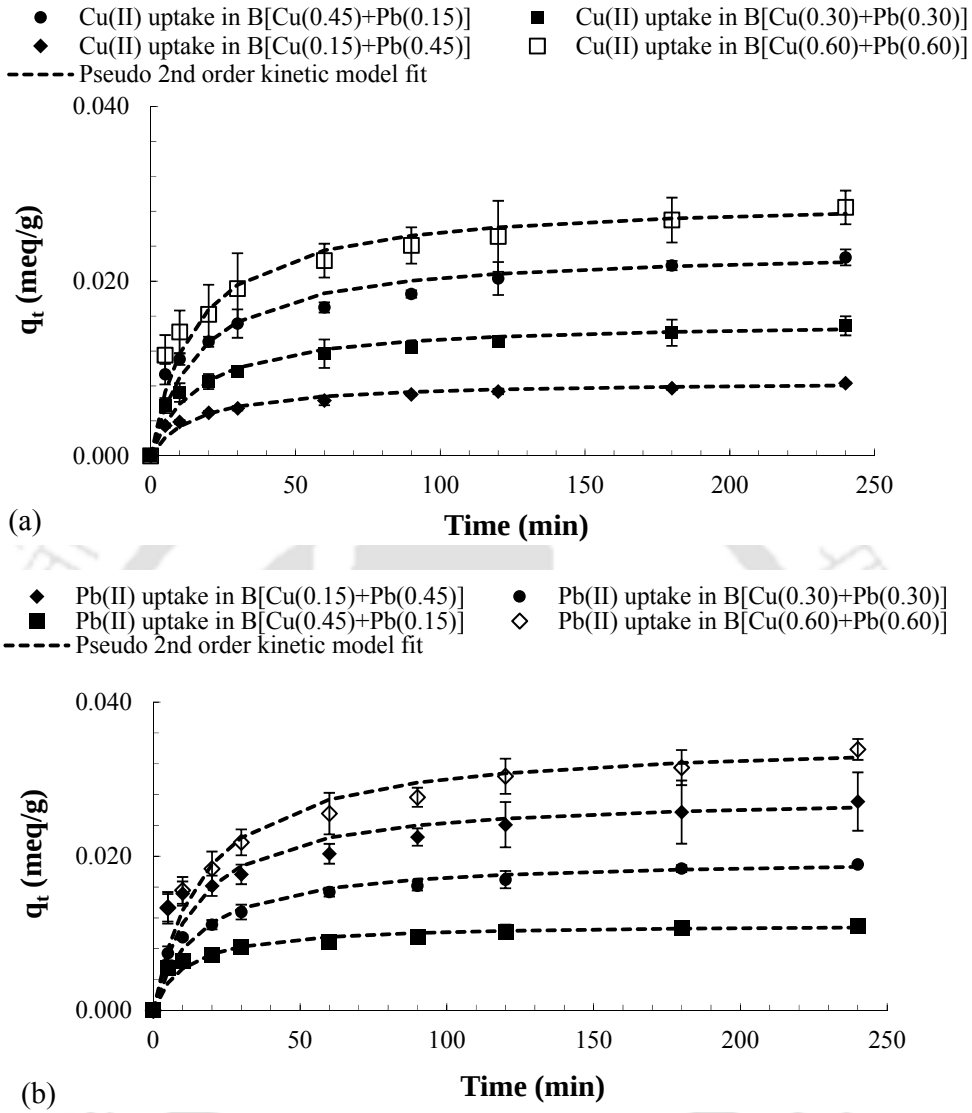

Fig. 5.26: Variation in (a) target Cu(II) and (b) target Pb(II) metal uptake from binary-metal ion systems comprising of Cu(II)+Pb(II) under controlled pH conditions {Temp. = 30±2 °C, Buffered pH = 5.00±0.02, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combinations B[Cu(0.45)+Pb(0.15)] = 0.45±0.02 meq/L of Cu(II) + 0.15±0.00 meq/L of Pb(II), B[Cu(0.30)+Pb(0.30)] = 0.28±0.02 meq/L of Cu(II) + 0.29±0.00 meq/L of Pb(II), B[Cu(0.15)+Pb(0.45)] = 0.15±0.00 meq/L of Cu(II) + 0.47±0.02 meq/L of Pb(II), B[Cu(0.60)+Pb(0.60)] = 0.59±0.02 meq/L of Cu(II) + 0.60±0.04 meq/L of Pb(II)} (Each data represents an average of three independent experimental values with vertical bars at each data points representing 95% confidence interval).

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Table 5.3: Summary of estimated kinetic parameters for target metal removal in presence of non-target metal under uncontrolled pH conditions from binary-metal ion systems comprising of Cu(II) and Pb(II) ions.

Target Metal	Combinations	$Q_{e,exp}$ (meq/g)	Pseudo-first-order rate model			Pseudo-second-order rate model		
			Q_{em} (meq/g)	K_1 (1/min)	R^2	Q_{em} (meq/g)	K_2 (g/meq.min)	R^2
Cu(II) removal in presence of Pb(II)	B[Cu(0.45)+Pb(0.15)]	0.0317±0.0023	0.0285	0.0666	0.921	0.0296	3.2812	0.973
	B[Cu(0.30)+Pb(0.30)]	0.0213±0.0027	0.0178	0.0899	0.906	0.0214	3.4263	0.987
	B[Cu(0.15)+Pb(0.45)]	0.0111±0.0003	0.0087	0.1030	0.856	0.0109	6.6298	0.985
	B[Cu(0.60)+Pb(0.60)]	0.0379±0.0040	0.0286	0.0629	0.865	0.0382	1.2290	0.978
Pb(II) removal in presence of Cu(II)	B[Cu(0.15)+Pb(0.45)]	0.0347±0.0004	0.0312	0.0609	0.900	0.0353	2.5048	0.996
	B[Cu(0.30)+Pb(0.30)]	0.0230±0.0008	0.0208	0.1493	0.949	0.0231	6.29504	0.998
	B[Cu(0.45)+Pb(0.15)]	0.0124±0.0004	0.0116	0.1645	0.945	0.0124	19.6604	0.967
	B[Cu(0.60)+Pb(0.60)]	0.0456±0.0014	0.0390	0.0847	0.919	0.0465	1.6369	0.994

$Q_{e,exp}$ = experimental metal removal at equilibrium, Q_{em} = metal removal at equilibrium calculated using rate models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with three independent data points.

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Table 5.4: Summary of estimated kinetic parameters for target metal uptake in presence of non-target metal under controlled pH conditions from binary-metal ion systems comprising of Cu(II) and Pb(II) ions.

Target Metal	Combinations	$q_{e,exp}$ (meq/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
			q_{em} (meq/g)	k_1 (1/min)	R^2	q_{em} (meq/g)	k_2 (g/meq.min)	R^2
Cu(II) uptake in presence of Pb(II)	B[Cu(0.45)+Pb(0.15)]	0.0227±0.0009	0.0196	0.0613	0.912	0.0236	2.5917	0.974
	B[Cu(0.30)+Pb(0.30)]	0.0149±0.0011	0.0127	0.0624	0.928	0.0154	4.0823	0.983
	B[Cu(0.15)+Pb(0.45)]	0.0083±0.0001	0.0065	0.0617	0.924	0.0086	7.5147	0.979
	B[Cu(0.60)+Pb(0.60)]	0.0284±0.0005	0.0245	0.0645	0.924	0.0295	2.2490	0.996
Pb(II) uptake in presence of Cu(II)	B[Cu(0.15)+Pb(0.45)]	0.0271±0.0038	0.0228	0.0701	0.850	0.0279	2.4343	0.946
	B[Cu(0.30)+Pb(0.30)]	0.0189±0.0001	0.0165	0.0640	0.936	0.0198	3.4427	0.986
	B[Cu(0.45)+Pb(0.15)]	0.0109±0.0003	0.0092	0.0872	0.890	0.0112	8.2670	0.972
	B[Cu(0.60)+Pb(0.60)]	0.0339±0.0014	0.0288	0.0555	0.927	0.0352	1.6674	0.995

$q_{e,exp}$ = experimental metal uptake capacity at equilibrium, q_{em} = metal uptake capacity at equilibrium calculated using kinetic models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with three independent data points.

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was apparent that as the initial concentration of target metal ions had increased, the experimental target metal removal under uncontrolled pH conditions ($Q_{e,exp}$) and metal uptake under controlled pH conditions ($q_{e,exp}$) at equilibrium had also increased even though the corresponding initial concentration of non-target metal had decreased. The target metal $Q_{e,exp}$ values were relatively higher for binary-metal ion systems under uncontrolled pH conditions compared to $q_{e,exp}$ values under controlled pH conditions. It might be due to metal removal by precipitation because of rise in solution pH under uncontrolled pH conditions. Further, K_2 and k_2 values for Cu(II) and Pb(II) metal ions from combinations of binary-metal ion systems investigated had increased as their initial metal ion concentrations in the combinations had decreased.

An inspection of Fig. 5.25 and 5.26 revealed simultaneous metal removals under uncontrolled pH conditions and metal uptakes under controlled pH conditions from combinations of binary-metal ion systems investigated. Hence it was felt appropriate to ascertain how much removal and uptake of both the metals have taken place with variation in contact time. Therefore, data of Fig. 5.25 and 5.26 have been re-plotted in Fig. 5.27 by taking into account the total metal removal (TQ_t) under uncontrolled pH conditions and total metal uptake (Tq_t) under controlled pH conditions. The metal removal and metal uptake estimated in meq/g have advantage to arrive at the total removal and total uptake of metal ions of different atomic weights and valence by simple algebraic summation. The total metal uptake (Tq_t) under controlled pH conditions was observed to increase with contact time and overlapped at 95% confidence interval for B[Cu(0.45)+Pb(0.15)], B[Cu(0.30)+Pb(0.30)] and B[Cu(0.15)+Pb(0.45)] combinations throughout the contact period as seen in Fig. 5.27(b). Hence, it clearly indicated that the total metal uptake (Tq_t) was similar and fairly independent of proportion of initial metal ion concentrations present in selected combinations of binary-metal ion systems comprising of Cu(II)+Pb(II) under controlled pH conditions as long as total initial metal ion concentration was approximately the same, i.e. 0.60 meq/L even though ionic radius as well as atomic weight of the metal ions were different from each other. On the other hand, when total initial metal ion concentration was doubled to 1.20 meq/L in B[Cu(0.60)+Pb(0.60)] combination without increasing GAA dose, the total metal uptake (Tq_t) increased and did not overlap at 95% confidence intervals with the total metal uptake (Tq_t) from combinations having total initial metal ions concentration near to 0.60 meq/L. The total metal uptake (Tq_t) from B[Cu(0.60)+Pb(0.60)] combination was approximately twice

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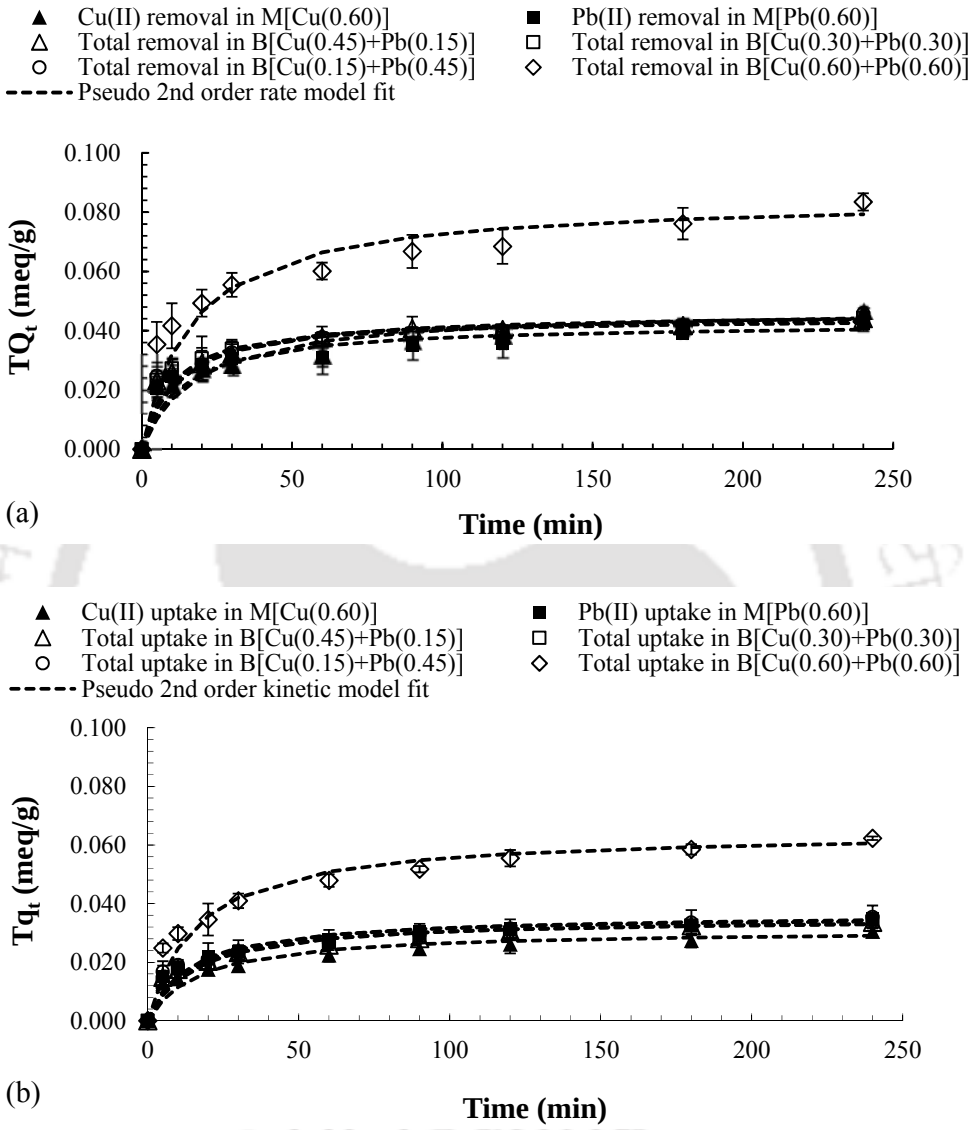

Fig. 5.27: Variation in (a) total metal removal under uncontrolled pH conditions and (b) total metal uptake under controlled pH conditions with contact time from mono- and binary-metal ion systems comprising of Cu(II) and Pb(II) ions.

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above the total metal uptake (Tq_t) from B[Cu(0.45)+Pb(0.15)], B[Cu(0.30)+Pb(0.30)] and B[Cu(0.15)+Pb(0.45)] combinations even though the adsorbent dose was the same in all the combinations. The GAA has shown to have additional metal uptake capacity due to increase in total initial metal ion concentration. Similarly, total metal removal (TQ_t) under uncontrolled pH conditions obtained from B[Cu(0.45)+Pb(0.15)], B[Cu(0.30)+Pb(0.30)] and B[Cu(0.15)+Pb(0.45)] combinations also overlapped within 95% confidence interval amongst them as seen in Fig. 5.27(a). As the total initial metal ion concentration was increased to 1.20 meq/L, total metal removal (TQ_t) also increased under uncontrolled pH conditions. The experimental total metal removal (TQ_t) under uncontrolled pH conditions and experimental total metal uptake (Tq_t) under controlled pH conditions from three combinations of binary-metal ion systems with fixed total initial metal ion concentration of 0.60 meq/L are presented in Table 5.5. The total metal removal (TQ_t) under uncontrolled pH conditions and total metal uptake (Tq_t) under controlled pH conditions were very close to each other in the range of 0.0441-0.0458 meq/g and 0.0336-0.0354 meq/g respectively. The GAA used has shown to have additional metal removal capability even with doubling of total initial metal ion concentration. Further, pseudo-first- and pseudo-second-order rate models were also used to describe the total metal removal under uncontrolled pH conditions and pseudo-first- and pseudo-second-order kinetic models were used to describe the total metal uptake under controlled pH conditions while estimated kinetic parameters are shown in Table 5.5. Higher R^2 values for pseudo-second-order rate and kinetic models indicated its appropriateness to describe total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions. The best fit plots of pseudo-second-order rate and kinetic models to experimental total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions are also shown in Fig. 5.27.

The variation in total metal removal (TQ_t) under uncontrolled pH conditions and total metal uptake (Tq_t) under controlled pH conditions from binary-metal ion systems having total initial metal ions concentration near to 0.60 meq/L have also been compared with variation in metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from M[Cu(0.60)] and M[Pb(0.60)] systems. The Cu(II) and Pb(II) metal removal under uncontrolled pH conditions and Cu(II) and Pb(II) metal uptake under controlled pH conditions from M[Cu(0.60)] and M[Pb(0.60)] systems have also been plotted in Fig. 5.27. The variation in Cu(II) and Pb(II) metal removal under uncontrolled pH conditions and

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Table 5.5: Summary of estimated kinetic parameters for total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions from binary-metal ion systems comprising of Cu(II) and Pb(II) ions.

			Pseudo-first-order rate model			Pseudo-second-order rate model		
Uncontrolled pH conditions	Binary-metal ion combinations	$TQ_{e,exp}$ (meq/g)	Q_{em} (meq/g)	K_1 (1/min)	R^2	Q_{em} (meq/g)	K_2 (g/meq.min)	R^2
	B[Cu(0.15)+Pb(0.45)]	0.0458±0.0006	0.0401	0.0698	0.889	0.0461	1.8239	0.994
	B[Cu(0.30)+Pb(0.30)]	0.0443±0.0034	0.0379	0.1186	0.927	0.0444	2.2834	0.994
	B[Cu(0.45)+Pb(0.15)]	0.0441±0.0020	0.0392	0.0842	0.916	0.0420	2.8783	0.971
	B[Cu(0.60)+Pb(0.60)]	0.0835±0.0029	0.0678	0.0752	0.895	0.0847	0.7152	0.989
			Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Controlled pH conditions	Binary-metal ion combinations	$Tq_{e,exp}$ (meq/g)	q_{em} (meq/g)	k_1 (1/min)	R^2	q_{em} (meq/g)	k_2 (g/meq.min)	R^2
	B[Cu(0.15)+Pb(0.45)]	0.0354±0.0039	0.0307	0.0684	0.870	0.0365	1.8442	0.956
	B[Cu(0.30)+Pb(0.30)]	0.0338±0.0010	0.0304	0.0652	0.934	0.0352	1.8675	0.985
	B[Cu(0.45)+Pb(0.15)]	0.0336±0.0006	0.0289	0.0691	0.900	0.0349	2.0005	0.973
	B[Cu(0.60)+Pb(0.60)]	0.0623±0.0006	0.0540	0.0593	0.923	0.0646	0.9584	0.995

$TQ_{e,exp}$ = experimental total metal removal at equilibrium, Q_{em} = total metal removal at equilibrium calculated using rate models, $Tq_{e,exp}$ = experimental total metal uptake capacity at equilibrium, q_{em} = total metal uptake capacity at equilibrium calculated using kinetic models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with three independent data points.

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Cu(II) and Pb(II) metal uptake under controlled pH conditions with contact time from mono-metal ion systems of M[Cu(0.60)] and M[Pb(0.60)] overlapped within 95% confidence interval respectively with the total metal removal (TQ_t) under uncontrolled pH conditions and total metal uptake (Tq_t) under controlled pH conditions from combinations of binary-metal ion systems comprising of Cu(II)+Pb(II) having total initial metal ions concentration of 0.60 meq/L in solution. The experimental equilibrium metal removal and experimental equilibrium metal uptake obtained from mono-metal ion systems [0.0467 meq/g for Cu(II) removal and 0.0423 meq/g for Pb(II) removal under uncontrolled pH conditions while 0.0305 meq/g for Cu(II) uptake and 0.0348 meq/g for Pb(II) uptake under controlled pH conditions] were comparable with the total metal removal (TQ_t) and total metal uptake (Tq_t) from combinations of binary-metal ion systems having total initial metal ions concentration of 0.60 meq/L in solution.

While investigating metal uptake from mono- and binary-metal ion systems, the initial concentrations of individual metal ions in mono- and binary-metal ions systems have been kept the same (Al-Rub et al., 2006; Li et al., 2011; Mohan et al., 2006; Srivastava et al., 2006). For example, if 'n' mg/L (or mmol/L or meq/L) of individual metal ions is used in mono-metal ion systems, the total metal ions concentration become n+n = '2n' mg/L (or mmol/L or meq/L) – just double of the mono-metal ion system in binary-metal ion system. This must have led to change in the experimental conditions in the two systems especially in terms of initial metal ion concentration gradient – recognized as an important factor affecting metal uptake by the adsorbent. In the present study, investigations were also carried out for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions under similar experimental conditions i.e. doubling the total initial metal ion concentration in binary-metal ion system compared to mono-metal ion system comprising of Cu(II) and Pb(II). The variations in individual as well as total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions from M[Cu(0.60)], M[Pb(0.60)] and B[Cu(0.60)+Pb(0.60)] combinations are presented in Fig. 5.28. It revealed that the experimental metal removal and experimental metal uptake from B[Cu(0.60)+Pb(0.60)] combination had reduced in the case of target metal Cu(II) ion [observed Cu(II) removal of 0.0379 meq/g under uncontrolled pH conditions and Cu(II) uptake of 0.0284 meq/g under controlled pH conditions] in presence of 0.60 meq/L of non-target metal Pb(II) ion compared to Cu(II) removal and Cu(II) uptake from M[Cu(0.60)]

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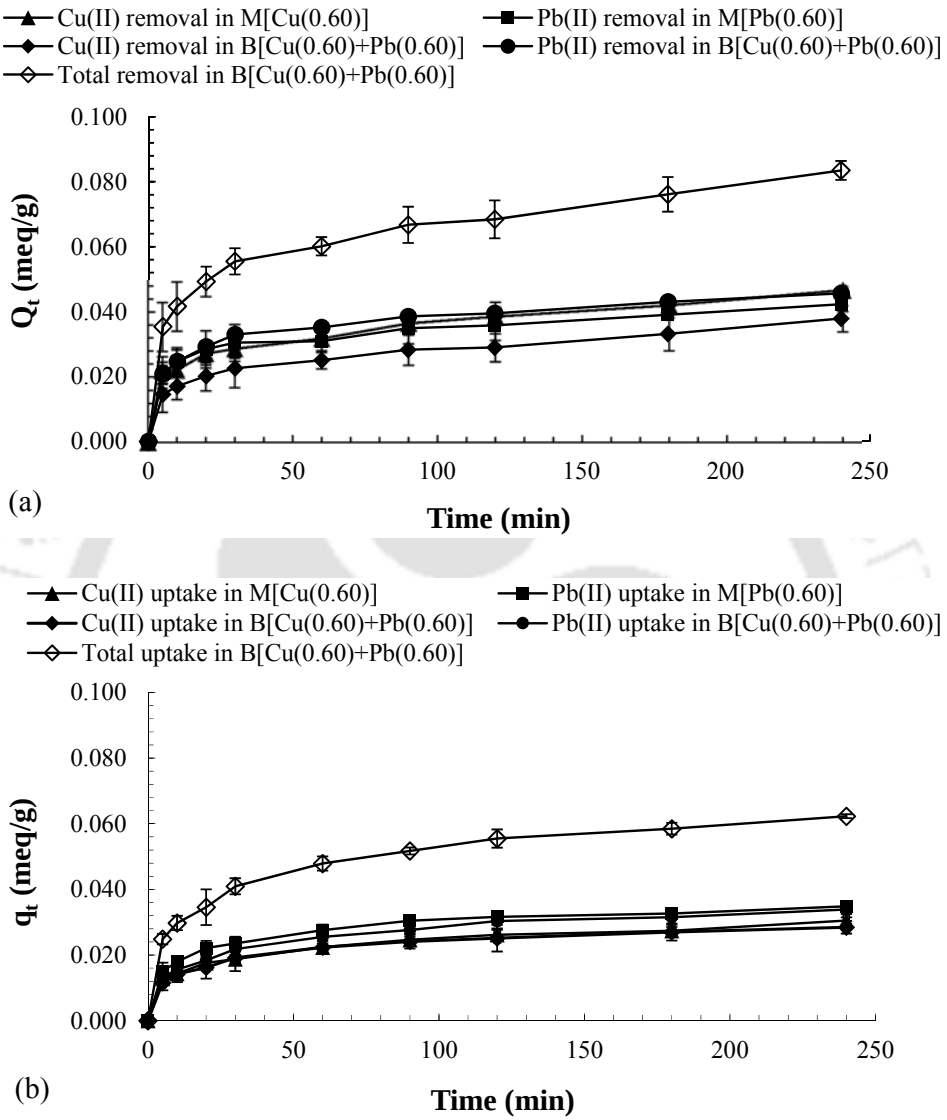

Fig. 5.28: Variation in (a) total metal removal under uncontrolled pH conditions and (b) total metal uptake under controlled pH conditions from mono- and binary-metal ion systems comprising of Cu(II) and Pb(II) metal ions investigated at an initial concentration of 0.60 meq/L for individual metal ions.

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[Cu(II) removal of 0.0467 meq/g under uncontrolled pH conditions and Cu(II) uptake of 0.0305 meq/g under controlled pH condition] system. However, in the case of Pb(II) metal ions, the experimental Pb(II) removal had increased under uncontrolled pH conditions but experimental Pb(II) uptake had decreased marginally under controlled pH conditions from B[Cu(0.60)+Pb(0.60)] combination [Pb(II) removal of 0.0456 meq/g under uncontrolled pH conditions and Pb(II) uptake of 0.0339 meq/g under controlled pH conditions] in presence of 0.60 meq/L of non-target Cu(II) metal ion compared to Pb(II) removal and Pb(II) uptake from M[Pb(0.60)] system [observed Pb(II) removal of 0.0423 meq/g under uncontrolled pH conditions and Pb(II) uptake of 0.0348 meq/g under controlled pH conditions]. Also, the Cu(II) and Pb(II) removals under uncontrolled pH conditions and Cu(II) and Pb(II) uptakes under controlled pH conditions from B[Cu(0.60)+Pb(0.60)] combination appeared to have overlapped at 95% confidence intervals with Cu(II) and Pb(II) metal removals under uncontrolled pH conditions and Cu(II) and Pb(II) metal uptakes under controlled pH conditions from M[Cu(0.60)] and M[Pb(0.60)] systems. These observations appeared to contradict the published findings (Li et al., 2011; Mohan et al., 2006; Srivastava et al., 2006) wherein target metal uptake from binary-metal ion systems was reported to decrease due to competition of non-target metals for available adsorption sites. In the present investigation, no effect on the removal and uptake of target metal ions from mono- and binary-metal ion systems comprising of Cu(II)+Pb(II) having similar initial concentration of target and non-target metal ions in the solution was observed. It indirectly indicated adequacy of GAA to alter solution pH for target and non-target metal removals under uncontrolled pH conditions and availability of adsorption sites for target and non-target metal uptakes under controlled pH conditions. Further, the most striking feature noted in this investigation was the simultaneous metal removals under uncontrolled pH conditions and metal uptakes under controlled pH conditions of both the metal ions (Fig. 5.28) from the binary-metal ion systems comprising of Cu(II)+Pb(II) yielding increased experimental total metal removal and experimental total metal uptake (observed total metal removal of 0.0835 meq/g under uncontrolled pH conditions and observed total metal uptake of 0.0623 meq/g under controlled pH conditions) compared to metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from M[Cu(0.60)] and M[Pb(0.60)] systems investigated.

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The existence of intra-particle diffusion in combinations of binary-metal ion systems was tested using intra-particle diffusion model. The plots of q_t versus $t^{0.5}$ are shown in Fig. 5.29 for all the combinations of binary-metal ion systems investigated under controlled pH conditions only. The plots showed initial curved portions and subsequent linear portions reflecting both external as well as intra-particle diffusion effect (Mahramanlioglu et al., 2002; Yadav et al., 2006). The initial curved and subsequent linear portions were predominantly visible for initial concentrations of 0.30, 0.45 and 0.60 meq/L of target metals while the same was difficult to distinguish for initial concentration of 0.15 meq/L of target metal. Also, the linear portions didn't pass through origin of the plot confirming the adsorption of target metal ions on GAA to be a complex process involving surface adsorption as well as intra-particle diffusion contributing to rate controlling steps (Hawari & Mulligan, 2007).

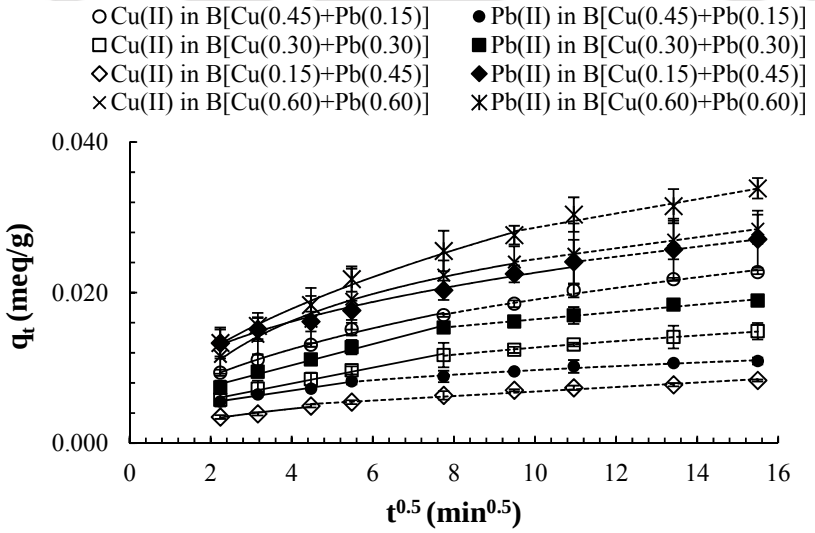

Fig. 5.29: Intra-particle diffusion model for target Cu(II) and target Pb(II) metal ions in presence of respective non-target Pb(II) and non-target Cu(II) metal ions from binary-metal ion systems comprising of Cu(II) and Pb(II) ions investigated under controlled pH conditions.

5.3.3 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from binary-metal ion systems comprising of Cr(III) and Pb(II) ions

The data represented in section 5.2.3 for metal ion concentrations remaining in aqueous phase with contact time obtained for selected combinations of binary-metal ion

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systems comprising of Cr(III)+Pb(II) have been utilized to investigate metal removal rate under uncontrolled pH conditions and metal uptake kinetics under controlled pH conditions.

The variation in metal removal from aqueous phase under uncontrolled pH conditions and metal uptake under controlled pH conditions considering Cr(III) as target metal ions in presence of corresponding Pb(II) as non-target metal and vice-versa are shown in Fig. 5.30 and 5.31 respectively. The variation in Cr(III) metal removal from B[Cr(0.45)+Pb(0.15)], B[Cr(0.30)+Pb(0.30)] and B[Cr(0.15)+Pb(0.45)] combinations investigated under uncontrolled pH conditions didn't overlap at 95% confidence interval while Cr(III) metal removal from B[Cr(0.60)+Pb(0.60)] combination overlapped with B[Cr(0.45)+Pb(0.15)] combination at 95% confidence interval as seen in Fig. 5.30(a). The Pb(II) metal removal from B[Cr(0.45)+Pb(0.15)], B[Cr(0.30)+Pb(0.30)] and B[Cr(0.15)+Pb(0.45)] combinations investigated under uncontrolled pH conditions didn't overlap at 95% confidence interval while Pb(II) metal removal from B[Cr(0.60)+Pb(0.60)] combination overlapped at 95% confidence interval with few data points of B[Cr(0.15)+Pb(0.45)] and B[Cr(0.30)+Pb(0.30)] combinations as seen in Fig. 5.30(b). The Cr(III) and Pb(II) metal uptake from B[Cr(0.45)+Pb(0.15)], B[Cr(0.30)+Pb(0.30)] and B[Cr(0.15)+Pb(0.45)] combinations investigated under controlled pH conditions didn't overlap at 95% confidence interval as seen in Fig. 5.31. However most of Cr(III) metal uptake data points of B[Cr(0.45)+Pb(0.15)] and B[Cr(0.60)+Pb(0.60)] combinations investigated under controlled pH conditions overlapped at 95% confidence interval as seen in Fig. 5.31(a). Similar observations were made for Pb(II) metal for which the uptake data from B[Cr(0.15)+Pb(0.45)] and B[Cr(0.60)+Pb(0.60)] combinations investigated under controlled pH conditions overlapped at 95% confidence interval as shown in Fig. 5.31(b).

The kinetic data obtained under uncontrolled pH conditions were fitted into pseudo-first- and pseudo-second-order rate models while data obtained under controlled pH conditions were fitted to pseudo-first- and pseudo-second-order kinetic models. The estimated kinetic parameters are presented in Table 5.6 for uncontrolled pH conditions and Table 5.7 for controlled pH conditions. Higher values of R^2 indicated suitability of pseudo-second-order rate model to describe experimental kinetic data as compared to pseudo-first-order rate model under uncontrolled pH conditions. Similarly higher values of R^2 indicated applicability of pseudo-second-order kinetic model to describe experimental kinetic data

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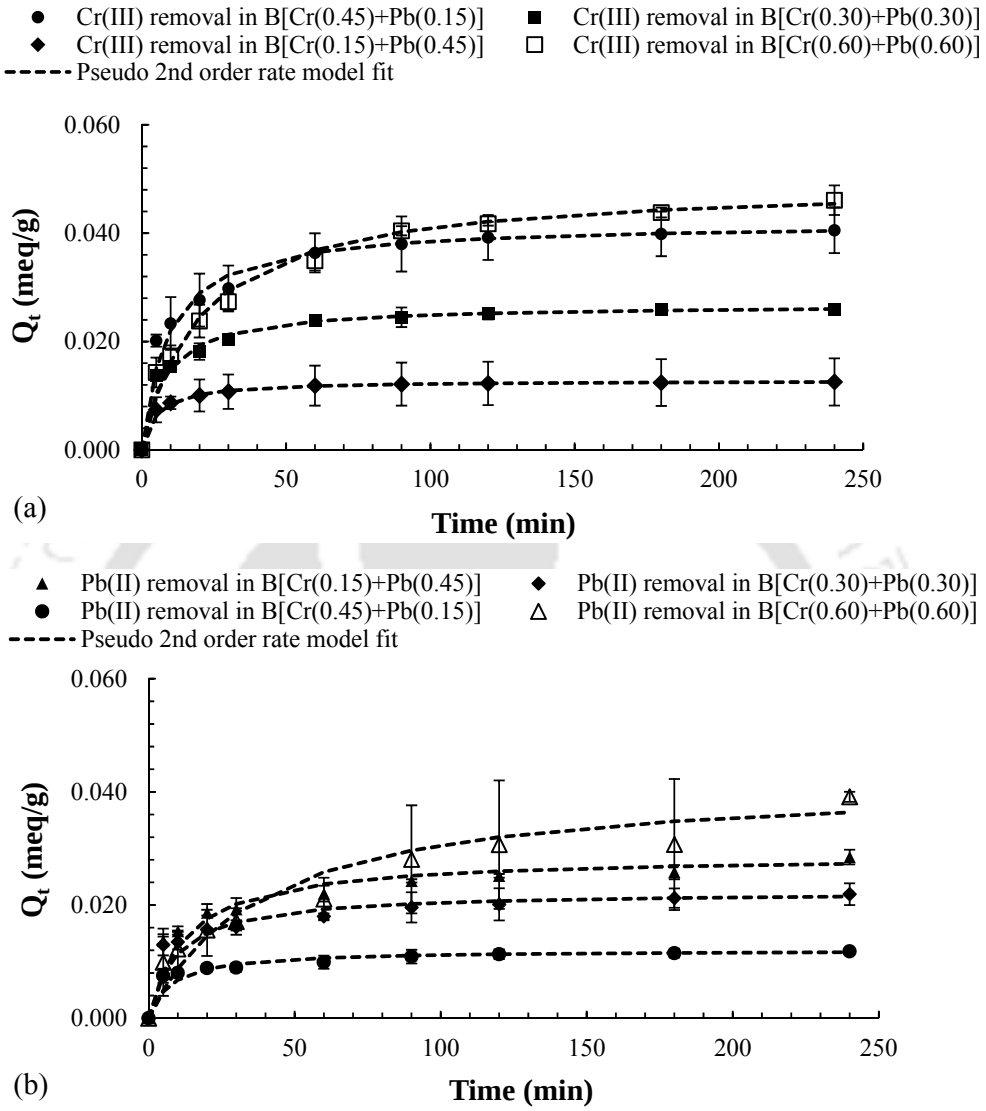

Fig. 5.30: Variation in (a) target Cr(III) and (b) target Pb(II) metal removal from binary-metal ion systems comprising of Cr(III)+Pb(II) under uncontrolled pH conditions {Temp. = 30±2 °C, Initial adjusted pH = 5.00±0.05, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combinations B[Cr(0.45)+Pb(0.15)] = 0.50±0.05 meq/L of Cr(III) + 0.15±0.00 meq/L of Pb(II), B[Cr(0.30)+Pb(0.30)] = 0.32±0.00 meq/L of Cr(III) + 0.31±0.01 meq/L of Pb(II), B[Cr(0.15)+Pb(0.45)] = 0.15±0.05 meq/L of Cr(III) + 0.43±0.00 meq/L of Pb(II), B[Cr(0.60)+Pb(0.60)] = 0.57±0.04 meq/L of Cr(III) + 0.55±0.01 meq/L of Pb(II)} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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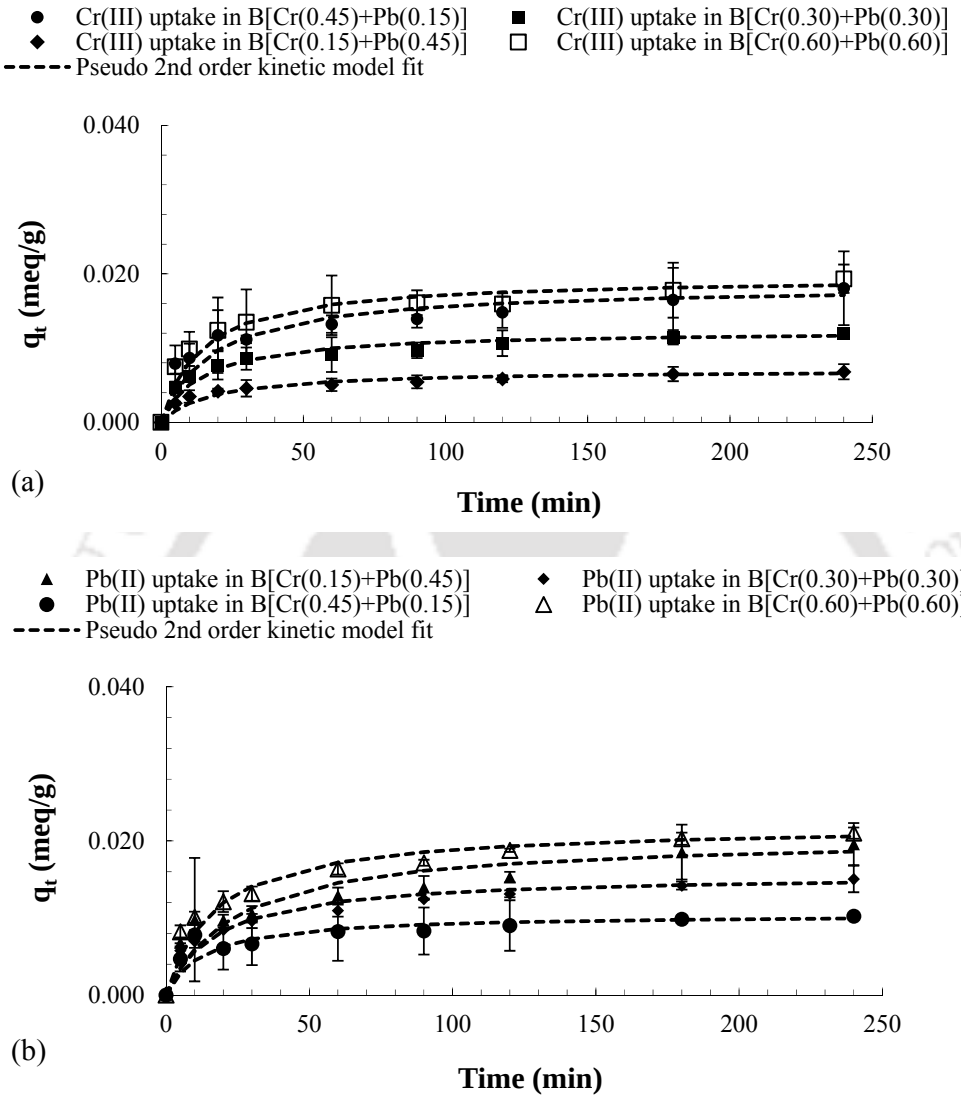

Fig. 5.31: Variation in (a) target Cr(III) and (b) target Pb(II) metal uptake from binary-metal ion systems comprising of Cr(III)+Pb(II) under controlled pH conditions {Temp. = 30±2 °C, Buffered pH = 5.00±0.05, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combinations B[Cr(0.45)+Pb(0.15)] = 0.47±0.02 meq/L of Cr(III) + 0.15±0.00 meq/L of Pb(II), B[Cr(0.30)+Pb(0.30)] = 0.31±0.02 meq/L of Cr(III) + 0.30±0.01 meq/L of Pb(II), B[Cr(0.15)+Pb(0.45)] = 0.16±0.03 meq/L of Cr(III) + 0.44±0.00 meq/L of Pb(II), B[Cr(0.60)+Pb(0.60)] = 0.64±0.05 meq/L of Cr(III) + 0.59±0.01 meq/L of Pb(II)} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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Table 5.6: Summary of estimated kinetic parameters for target metal removal in presence of non-target metal under uncontrolled pH conditions from binary-metal ion systems comprising of Cr(III) and Pb(II) ions.

Target metal	Combinations	$Q_{e,exp}$ (meq/g)	Pseudo-first-order rate model			Pseudo-second-order rate model		
			Q_{em} (meq/g)	K_1 (1/min)	R^2	Q_{em} (meq/g)	K_2 (g/meq.min)	R^2
Pb(II) removal in presence of Cr(III)	B[Cr(0.15)+Pb(0.45)]	0.0285±0.0013	0.0240	0.0850	0.906	0.0287	2.7509	0.994
	B[Cr(0.30)+Pb(0.30)]	0.0219±0.0019	0.0196	0.0957	0.889	0.0224	4.6697	0.997
	B[Cr(0.45)+Pb(0.15)]	0.0118±0.0005	0.0108	0.1128	0.889	0.0121	10.6526	0.998
	B[Cr(0.60)+Pb(0.60)]	0.0391±0.0009	0.0299	0.0329	0.893	0.0421	0.6277	0.960
Cr(III) removal in presence of Pb(II)	B[Cr(0.45)+Pb(0.15)]	0.0405±0.0042	0.0371	0.0782	0.937	0.0419	2.6618	0.999
	B[Cr(0.30)+Pb(0.30)]	0.0260±0.0004	0.0240	0.0860	0.941	0.0268	4.7704	0.999
	B[Cr(0.15)+Pb(0.45)]	0.0125±0.0043	0.0120	0.1274	0.954	0.0128	15.4597	0.999
	B[Cr(0.60)+Pb(0.60)]	0.0461±0.0027	0.0420	0.0410	0.965	0.0492	1.0094	0.997

$Q_{e,exp}$ = experimental metal removal at equilibrium, Q_{em} = metal removal at equilibrium calculated using rate models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with three independent data points.

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Table 5.7: Summary of estimated kinetic parameters for target metal uptake in presence of non-target metal under controlled pH conditions from binary-metal ion systems comprising of Cr(III) and Pb(II) ions.

Target metal	Combinations	$q_{e,exp}$ (meq/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
			q_{em} (meq/g)	k_1 (1/min)	R^2	q_{em} (meq/g)	k_2 (g/meq.min)	R^2
Pb(II) uptake in presence of Cr(III)	B[Cr(0.15)+Pb(0.45)]	0.0196±0.0027	0.0159	0.0565	0.834	0.0205	1.9834	0.976
	B[Cr(0.30)+Pb(0.30)]	0.0151±0.0020	0.0120	0.0583	0.918	0.0157	3.6254	0.994
	B[Cr(0.45)+Pb(0.15)]	0.0102±0.0001	0.0086	0.1046	0.823	0.0105	7.1179	0.993
	B[Cr(0.60)+Pb(0.60)]	0.0210±0.0007	0.0181	0.0584	0.920	0.0220	2.7129	0.995
Cr(III) uptake in presence of Pb(II)	B[Cr(0.45)+Pb(0.15)]	0.0181±0.0050	0.0096	0.0728	0.873	0.0184	3.0313	0.988
	B[Cr(0.30)+Pb(0.30)]	0.0120±0.0002	0.0098	0.0814	0.935	0.0124	5.6446	0.994
	B[Cr(0.15)+Pb(0.45)]	0.0068±0.0010	0.0065	0.0619	0.908	0.0071	8.0930	0.993
	B[Cr(0.60)+Pb(0.60)]	0.0193±0.0019	0.0161	0.0809	0.940	0.0196	3.6803	0.992

$q_{e,exp}$ = experimental metal uptake capacity at equilibrium, q_{em} = metal uptake capacity at equilibrium calculated using kinetic models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with three independent data points.

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obtained under controlled pH conditions. From Table 5.6 and 5.7, it is apparent that as the initial concentration of target metal ions had increased, the experimental target metal removal under uncontrolled pH conditions ($Q_{e,exp}$) and metal uptake under controlled pH conditions ($q_{e,exp}$) at equilibrium had also increased even though the corresponding initial concentration of non-target metal had decreased. The target metal $Q_{e,exp}$ values were relatively higher for binary-metal ion systems under uncontrolled pH conditions compared to $q_{e,exp}$ values under controlled pH conditions. It was probably due to metal removal by precipitation because of rise in solution pH under uncontrolled pH conditions. Further, K_2 and k_2 values for Cr(III) and Pb(II) metal ions from combinations of binary-metal ion systems investigated had generally increased as their initial concentrations in the combinations had decreased.

An inspection of Fig. 5.30 and 5.31 revealed simultaneous metal removals under uncontrolled pH conditions and metal uptakes under controlled pH conditions from combinations of binary-metal ion systems investigated. Hence it was felt appropriate to ascertain how much removal and uptake of both the metals have taken place with variation in contact time. Therefore, data of Fig. 5.30 and 5.31 have been re-plotted in Fig. 5.32 by taking into account the total metal removal (TQ_t) under uncontrolled pH conditions and total metal uptake (Tq_t) under controlled pH conditions. The variation in Tq_t data points under controlled pH conditions was observed to increase with contact time and overlapped at 95% confidence interval for B[Cr(0.45)+Pb(0.15)], B[Cr(0.30)+Pb(0.30)] and B[Cr(0.15)+Pb(0.45)] combinations throughout the contact period as seen in Fig. 5.32(b). Hence, it clearly indicated that the total metal uptake (Tq_t) was similar and fairly independent of proportion of initial metal ion concentrations present in selected combinations of binary-metal ion systems comprising of Cr(III)+Pb(II) under controlled pH conditions as long as total initial metal ion concentration was approximately the same, i.e. 0.60 meq/L even though ionic radius, valence as well as atomic weight of the metal ions were different from each other. On the other hand, when total initial metal ion concentration was doubled to 1.20 meq/L in B[Cr(0.60)+Pb(0.60)] combination without increasing GAA dose, total metal uptake (Tq_t) increased and did not overlap at 95% confidence interval with the total metal uptake (Tq_t) from combinations having total initial metal ions concentration near to 0.60 meq/L. The GAA used has shown to have additional metal uptake capacity due to increase in total initial metal ion concentration. Similarly, total metal removal (TQ_t) under uncontrolled pH conditions was observed to increase with contact time and overlapped at 95% confidence interval for

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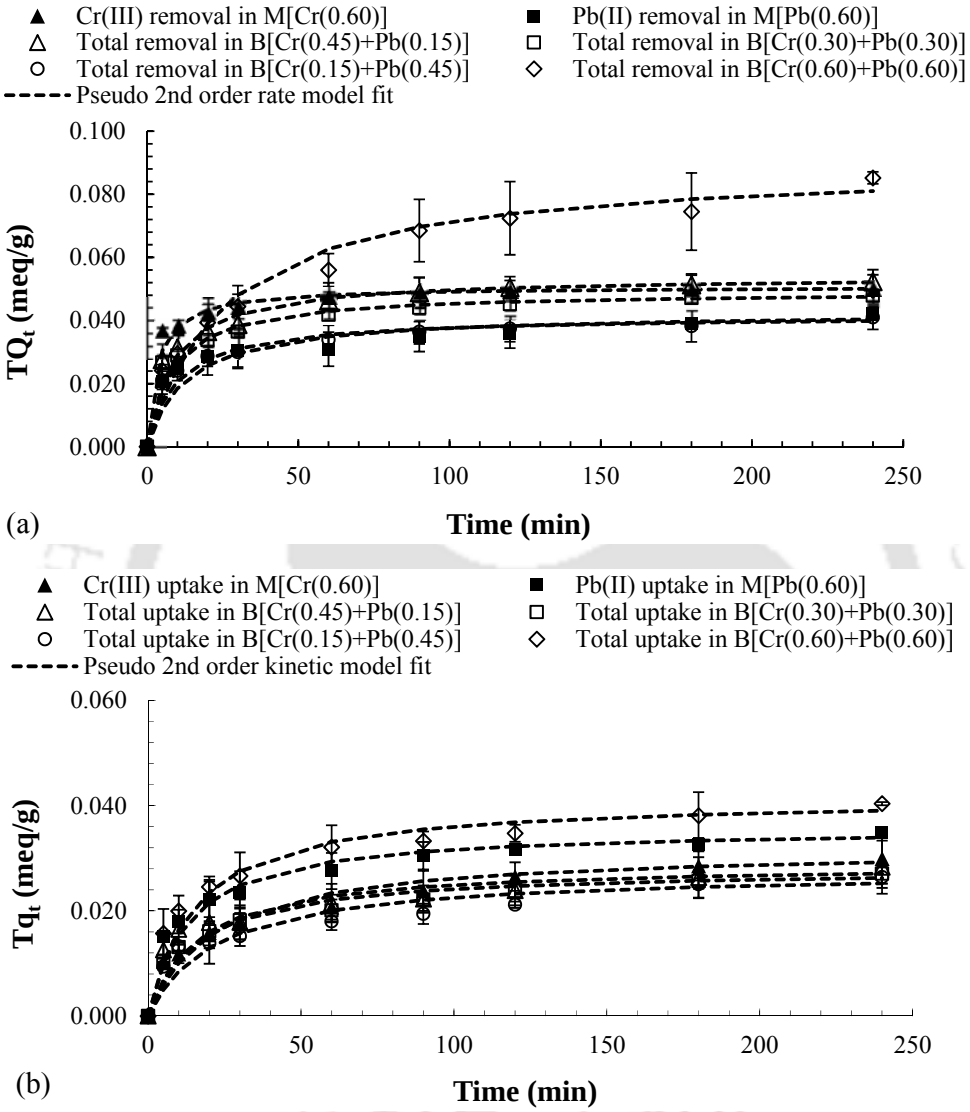

Fig. 5.32: Variation in (a) total metal removal under uncontrolled pH conditions and (b) total metal uptake under controlled pH conditions with contact time from mono- and binary-metal ion systems comprising of Cr(III) and Pb(II) ions.

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B[Cr(0.45)+Pb(0.15)] and B[Cr(0.30)+Pb(0.30)] combinations while total metal removal (TQ_t) from B[Cr(0.15)+Pb(0.45)] combination was slightly less than other combinations [Fig. 5.32(a)]. As the total initial metal ions concentration was increased to 1.20 meq/L in B[Cr(0.60)+Pb(0.60)] combination, the total metal removal also increased. The experimental total metal removal (TQ_t) under uncontrolled pH conditions and experimental total metal uptake (Tq_t) under controlled pH conditions from the three combinations of binary-metal ion systems with the fixed total metal ions concentration of 0.60 meq/L are presented in Table 5.8. The total metal removal (TQ_t) under uncontrolled pH conditions and total metal uptake (Tq_t) under controlled pH conditions were very close to each other in the range of 0.0410-0.0524 meq/g and 0.0264-0.0283 meq/g respectively. The GAA used has shown to have additional metal removal capability even with doubling of total initial metal ion concentration. Further, pseudo-first- and pseudo-second-order rate and kinetic models were also used to describe the total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions and estimated kinetic parameters are shown in Table 5.8. Higher R^2 values for pseudo-second-order rate and kinetic models indicated its appropriateness to describe total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions. The best fit plots of pseudo-second-order rate and kinetic models to experimental total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions are also shown in Fig. 5.32.

The variation in total metal removal (TQ_t) under uncontrolled pH conditions and total metal uptake (Tq_t) under controlled pH conditions from binary-metal ion systems having total initial metal ions concentration near to 0.60 meq/L have also been compared with variation in metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from M[Cr(0.60)] and M[Pb(0.60)] systems in Fig. 5.32. The variation in Cr(III) and Pb(II) metal uptake with contact time from mono-metal ion systems of M[Cr(0.60)] and M[Pb(0.60)] investigated under controlled pH conditions overlapped within 95% confidence interval with the total metal uptake (Tq_t) data from combinations of binary-metal ion system having total initial metal ions concentration of 0.60 meq/L in solution [Fig. 5.32(b)]. Similarly, the total metal removal (TQ_t) from B[Cr(0.15)+Pb(0.45)] combination investigated under uncontrolled pH conditions wherein the concentration of Pb(II) metal ions was relatively higher overlapped at 95% confidence interval with Pb(II) metal removal from M[Pb(0.60)] system [Fig. 5.32(a)]. Further, Cr(III) metal removal from M[Cr(0.60)] system

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Table 5.8: Summary of estimated kinetic parameters for total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions from binary-metal ion systems comprising of Cr(III) and Pb(II) ions.

			Pseudo-first-order rate model			Pseudo-second-order rate model		
Uncontrolled pH conditions	Binary-metal ion combinations	$TQ_{e,exp}$ (meq/g)	Q_{em} (meq/g)	K_1 (1/min)	R^2	Q_{em} (meq/g)	K_2 (g/meq.min)	R^2
	B[Cr(0.15)+Pb(0.45)]	0.0410±0.0039	0.0357	0.0969	0.924	0.0414	2.4078	0.998
	B[Cr(0.30)+Pb(0.30)]	0.0479±0.0016	0.0438	0.0910	0.920	0.0492	2.3728	0.999
	B[Cr(0.45)+Pb(0.15)]	0.0524±0.0037	0.0480	0.0850	0.926	0.0540	2.1482	0.999
	B[Cr(0.60)+Pb(0.60)]	0.0852±0.0019	0.0708	0.0377	0.939	0.0897	0.4299	0.988
			Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Controlled pH conditions	Binary-metal ion combinations	$Tq_{e,exp}$ (meq/g)	q_{em} (meq/g)	k_1 (1/min)	R^2	q_{em} (meq/g)	k_2 (g/meq.min)	R^2
	B[Cr(0.15)+Pb(0.45)]	0.0264±0.0020	0.0212	0.0591	0.855	0.0276	1.6097	0.982
	B[Cr(0.30)+Pb(0.30)]	0.0271±0.0019	0.0235	0.0681	0.924	0.0280	2.2270	0.994
	B[Cr(0.45)+Pb(0.15)]	0.0283±0.0050	0.0230	0.0819	0.863	0.0289	2.1610	0.990
	B[Cr(0.60)+Pb(0.60)]	0.0404±0.0012	0.0340	0.0712	0.929	0.0415	1.5798	0.995

$TQ_{e,exp}$ = experimental total metal removal at equilibrium, Q_{em} = total metal removal at equilibrium calculated using rate models, $Tq_{e,exp}$ = experimental total metal uptake capacity at equilibrium, q_{em} = total metal uptake capacity at equilibrium calculated using kinetic models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with three independent data points.

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investigated under uncontrolled pH conditions overlapped within 95% confidence interval with the total metal removal (TQ_t) from B[Cr(0.45)+Pb(0.15)] and B[Cr(0.30)+Pb(0.30)] combinations. The experimental equilibrium metal removal and experimental equilibrium metal uptake obtained from mono-metal ion systems [0.0423 meq/g for Pb(II) removal and 0.0500 meq/g for Cr(III) removal under uncontrolled pH conditions while 0.0348 meq/g for Pb(II) uptake and 0.0300 meq/g for Cr(III) uptake under controlled pH conditions] were comparable with the total metal removal (TQ_t) and total metal uptake (Tq_t) from combinations of binary-metal ion system having total initial metal ions concentration of 0.60 meq/L in aqueous phase [total metal removal of 0.0410-0.0524 meq/g under uncontrolled pH conditions and total metal uptake of 0.0264-0.0283 meq/g under controlled pH conditions].

While investigating metal uptake from mono- and binary-metal ion systems, the initial concentrations of individual metal ions in mono- and binary-metal ions systems have been kept the same (Al-Rub et al., 2006; Li et al., 2011; Mohan et al., 2006; Srivastava et al., 2006) which must have led to change in the experimental conditions in the two systems especially in terms of initial metal ion concentration gradient. In the present study, investigations were also carried out for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions under similar experimental conditions i.e. doubling the total initial metal ion concentration in binary-metal ion system compared to mono-metal ion system comprising of Cr(III) and Pb(II). The variations in individual as well as total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions from M[Cr(0.60)], M[Pb(0.60)] and B[Cr(0.60)+Pb(0.60)] combinations are presented in Fig. 5.33. It revealed that target Pb(II) metal removal [observed Pb(II) removal of 0.0391 meq/g] from B[Cr(0.60)+Pb(0.60)] combination investigated under uncontrolled pH condition had slightly reduced in presence of 0.60 meq/L of non-target Cr(III) metal ion compared to Pb(II) metal removal [observed Pb(II) removal of 0.0423 meq/g] from M[Pb(0.60)] system under uncontrolled pH condition. However, the target Pb(II) metal uptake [observed Pb(II) uptake of 0.0210 meq/g] from B[Cr(0.60)+Pb(0.60)] combination investigated under controlled pH condition had decreased significantly in presence of non-target Cr(III) metal ion compared to Pb(II) metal uptake [observed Pb(II) uptake of 0.0300 meq/g] from M[Pb(0.60)] system under controlled pH condition. In addition, Cr(III) metal removal [observed Cr(III) removal of 0.0461 meq/g] from B[Cr(0.60)+Pb(0.60)] combination investigated under uncontrolled pH condition was

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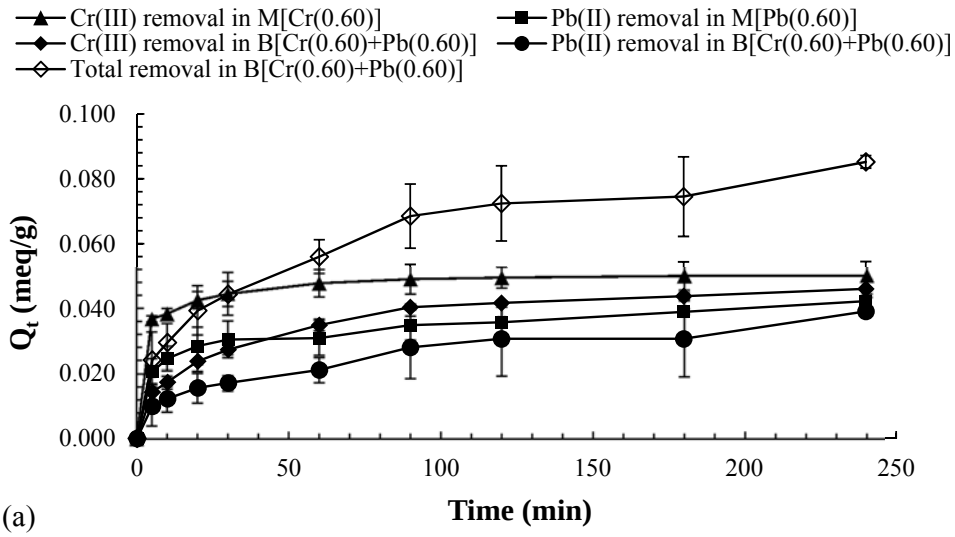
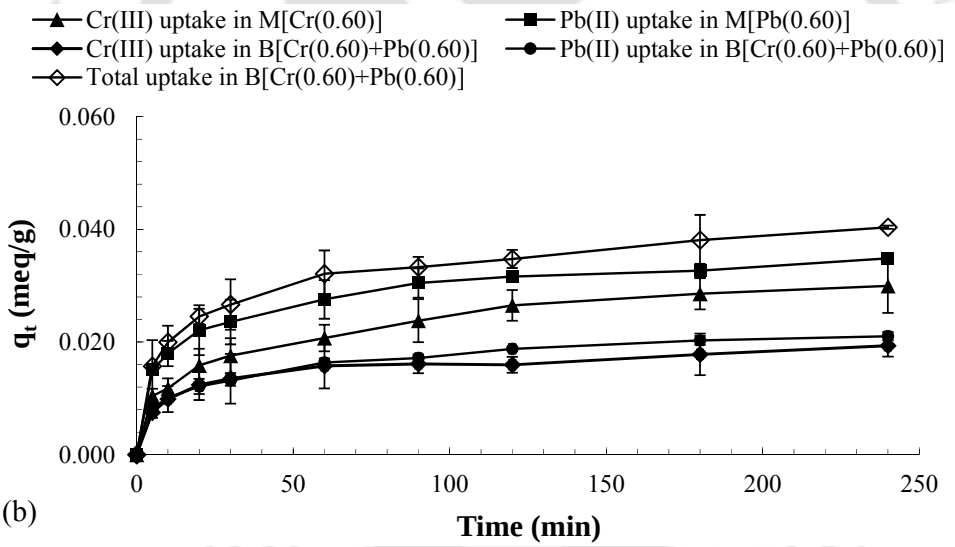


(a)



(b)

Fig. 5.33: Variation in (a) total metal removal under uncontrolled pH conditions and (b) total metal uptake under controlled pH conditions from mono- and binary-metal ion systems comprising of Cr(III) and Pb(II) metal ions investigated at an initial concentration of 0.60 meq/L for individual metal ions.

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slightly lower than Cr(III) metal removal [observed Cr(III) removal of 0.0500 meq/g] from M[Cr(0.60)] system under uncontrolled pH condition. The Cr(III) metal uptake [observed Cr(III) uptake of 0.0193 meq/g] from B[Cr(0.60)+Pb(0.60)] combination investigated under controlled pH condition was considerably lower than Cr(III) metal uptake [observed Cr(III) uptake of 0.0300 meq/g] from M[Cr(0.60)] system under controlled pH condition. Even though Cr(III) and Pb(II) metal removals were slightly reduced in B[Cr(0.60)+Pb(0.60)] combination investigated under uncontrolled pH condition, the metal removal values for Cr(III) and Pb(II) metal ions observed to overlap at 95% confidence interval towards the end of the contact period (Fig. 5.33). These observations appeared to contradict the published findings (Li et al., 2011; Mohan et al., 2006; Srivastava et al., 2006) wherein target metal uptake from binary-metal ion system was reported to decrease due to competition of non-target metal for available adsorption sites. In the present investigation, no effect on the target metal removal under uncontrolled pH conditions from mono- and binary-metal ion systems comprising of Cr(III)+Pb(II) having similar initial concentration of target and non-target metal ions in the solution was observed. It indirectly indicated adequacy of GAA to alter solution pH for target and non-target metal removals under uncontrolled pH conditions. Further, the most striking feature noted in this investigation was the simultaneous metal removals under uncontrolled pH conditions and metal uptakes under controlled pH conditions of both the metal ions (Fig. 5.33) from the binary-metal ion systems comprising of Cr(III)+Pb(II) yielding increased experimental total metal removal and experimental total metal uptake (observed total metal removal of 0.0852 under uncontrolled pH conditions and observed total metal uptake of 0.0404 meq/g under controlled pH conditions) compared to metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from M[Cr(0.60)] and M[Pb(0.60)] systems investigated.

The existence of intra-particle diffusion in combinations of binary-metal ions system was tested using intra-particle diffusion model. The plots of q_t versus $t^{0.5}$ are shown in Fig. 5.34 for all the combinations of binary-metal ions systems investigated under controlled pH conditions only. The plots showed initial curved portions and subsequent linear portions reflecting both external as well as intra-particle diffusion effect (Mahramanlioglu et al., 2002; Yadav et al., 2006). The initial curved and subsequent linear portions were predominantly visible for initial concentrations of 0.30, 0.45 and 0.60 meq/L of target metals while the same was difficult to distinguish for initial concentration of 0.15 meq/L of target metal. Also, the

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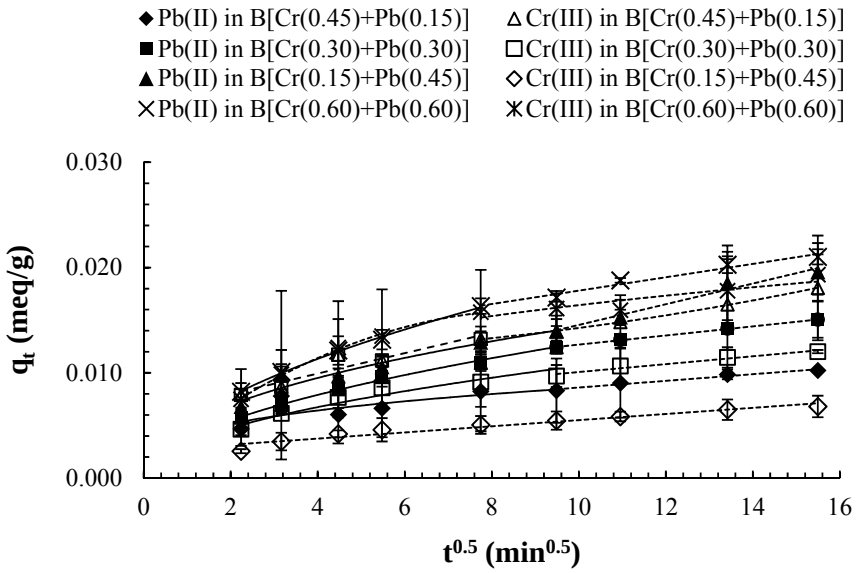

Fig. 5.34: Intra-particle diffusion model for target Cr(III) and target Pb(II) metal ions in presence of respective non-target Pb(II) and non-target Cr(III) metal ions from binary-metal ion systems comprising of Cr(III) and Pb(II) ions investigated under controlled pH conditions.

linear portions didn't pass through origin of the plot suggesting adsorption of target metal ions to be a complex process involving surface adsorption as well as intra-particle diffusion contributing to rate controlling steps (Hawari & Mulligan, 2007).

5.3.4 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from binary-metal ion systems comprising of Cu(II) and Cr(III) ions

The data represented in section 5.2.4 for metal ion concentrations remaining in aqueous phase with contact time from selected combinations of binary-metal ion systems comprising of Cu(II) and Cr(III) have been utilized to investigate metal removal rate under uncontrolled pH conditions and metal uptake kinetics under controlled pH conditions. Since significant precipitation of Cu(II) and Cr(III) metal ions were observed at time t = 0 from B[Cu(0.45)+Cr(0.15)], B[Cu(0.30)+Cr(0.30)] and B[Cu(0.60)+Cr(0.60)] combinations {except for B[Cu(0.15)+Cr(0.45)] combination} under uncontrolled pH conditions, the metal removal rate investigation was restricted to only B[Cu(0.15)+Cr(0.45)] combination. Fig. 5.35 depicts variation in Cu(II) and Cr(III) metal removal from B[Cu(0.15)+Cr(0.45)] combination investigated under uncontrolled pH condition. The Cr(III) metal removal was

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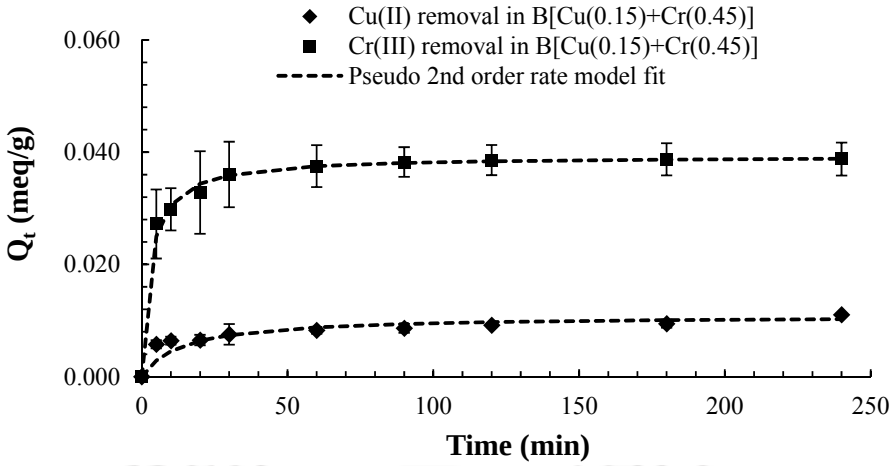

Fig. 5.35: Variation in (a) target Cu(II) and (b) target Cr(III) metal removal from binary-metal ion system comprising of Cu(II)+Cr(III) under uncontrolled pH conditions {Temp. = 30±2 °C, Initial adjusted pH = 5.00±0.05, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combination B[Cu(0.15)+Cr(0.45)] = 0.15±0.00 meq/L of Cu(II) + 0.47±0.03 meq/L of Cr(III)} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

higher compared to Cu(II) metal removal from B[Cu(0.15)+Cr(0.45)] combination under uncontrolled pH condition as Cr(III) metal concentration in the combination was higher. Fig. 5.36 depicts variation in Cu(II) and Cr(III) metal uptake from B[Cu(0.45)+Cr(0.15)], B[Cu(0.30)+Cr(0.30)], B[Cu(0.15)+Cr(0.45)] and B[Cu(0.60)+Cr(0.60)] combinations investigated under controlled pH conditions. The Cu(II) and Cr(III) metal uptake from B[Cu(0.45)+Cr(0.15)], B[Cu(0.30)+Cr(0.30)] and B[Cu(0.15)+Cr(0.45)] combinations investigated under controlled pH conditions didn't overlap at 95% confidence interval while Cu(II) and Cr(III) metal ions uptake from B[Cu(0.60)+Cr(0.60)] combination overlapped at 95% confidence interval with few data points of Cu(II) uptake from B[Cu(0.45)+Cr(0.15)] combination and Cr(III) uptake from B[Cu(0.15)+Cr(0.45)] combination as seen in Fig. 5.36. The estimated kinetic parameters under uncontrolled and controlled pH conditions are presented in Table 5.9 and 5.10 respectively. Higher values of R^2 indicated suitability of pseudo-second-order rate model to describe experimental kinetic data as compared to pseudo-first-order rate model under uncontrolled pH conditions. Similarly higher values of R^2 indicated applicability of pseudo-second-order kinetic model to describe experimental kinetic data obtained under controlled pH conditions. The best fit plots of pseudo-second-order rate and kinetic models are also shown in Fig. 5.35 and 5.36 respectively. From Table 5.10, it was apparent that as the initial concentration of target metal ions had increased, the experimental

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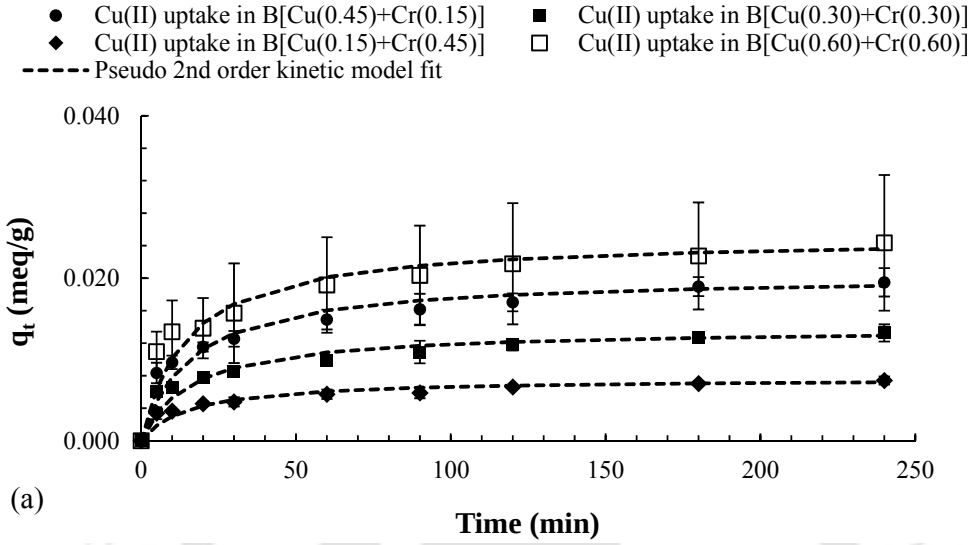

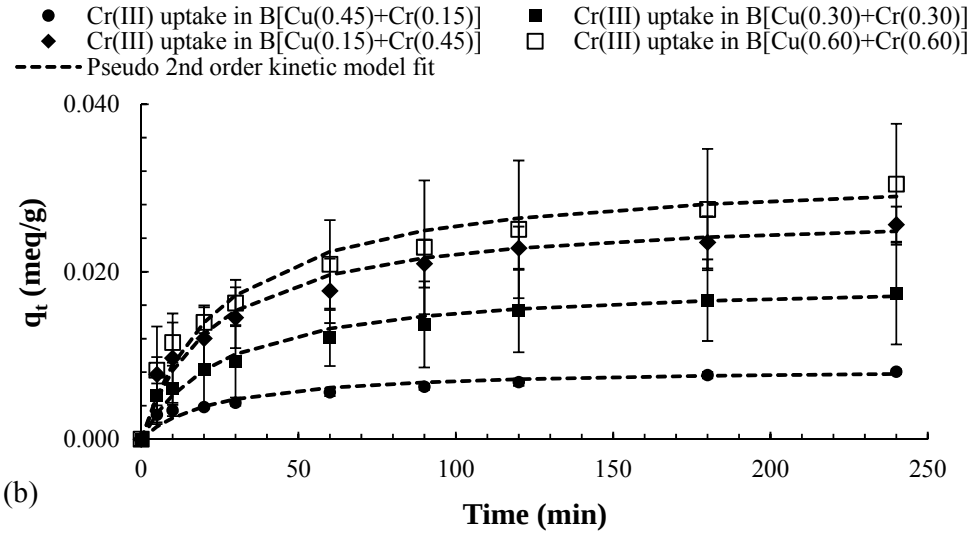

Fig. 5.36: Variation in (a) target Cu(II) and (b) target Cr(III) metal uptake from binary-metal ion systems comprising of Cu(II)+Cr(III) under controlled pH conditions {Temp. = 30±2 °C, Buffered pH = 5.00±0.05, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combinations B[Cu(0.45)+Cr(0.15)] = 0.46±0.01 meq/L of Cu(II) + 0.14±0.01 meq/L of Cr(III), B[Cu(0.30)+Cr(0.30)] = 0.30±0.00 meq/L of Cu(II) + 0.33±0.04 meq/L of Cr(III), B[Cu(0.15)+Cr (0.45)] = 0.15±0.00 meq/L of Cu(II) + 0.49±0.02 meq/L of Cr(III), B[Cu(0.60)+Cr(0.60)] = 0.61±0.08 meq/L of Cu(II) + 0.67±0.05 meq/L of Cr(III)} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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Table 5.9: Summary of estimated kinetic parameters for target metal removal in presence of non-target metal under uncontrolled pH conditions from binary-metal ion systems comprising of Cu(II) and Cr(III) ions.

Target metal	Combination	$Q_{e,exp}$ (meq/g)	Pseudo-first-order rate model			Pseudo-second-order rate model		
			Q_{em} (meq/g)	K_1 (1/min)	R^2	Q_{em} (meq/g)	K_2 (g/meq.min)	R^2
Cu(II) removal in presence of Cr(III)	B[Cu(0.15)+Cr(0.45)]	0.0111±0.0003	0.0087	0.1030	0.856	0.0109	6.6298	0.985
Cr(III) removal in presence of Cu(II)	B[Cu(0.15)+Cr(0.45)]	0.0388±0.0029	0.0377	0.1832	0.968	0.0393	8.9023	1.000

$Q_{e,exp}$ = experimental metal removal at equilibrium, Q_{em} = metal removal at equilibrium calculated using rate models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with three independent data points.

Table 5.10: Summary of estimated kinetic parameters for target metal uptake in presence of non-target metal under controlled pH conditions from binary-metal ion systems comprising of Cu(II) and Cr(III) ions.

Target metal	Combinations	$q_{e,exp}$ (meq/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
			q_{em} (meq/g)	k_1 (1/min)	R^2	q_{em} (meq/g)	k_2 (g/meq.min)	R^2
Cu(II) uptake in presence of Cr(III)	B[Cu(0.15)+Cr(0.45)]	0.0074±0.0005	0.0060	0.0662	0.895	0.0077	8.4013	0.993
	B[Cu(0.30)+Cr(0.30)]	0.0133±0.0011	0.0120	0.0581	0.893	0.0138	4.4940	0.994
	B[Cu(0.45)+Cr(0.15)]	0.0195±0.0017	0.0163	0.0614	0.907	0.0204	3.0632	0.994
	B[Cu(0.60)+Cr(0.60)]	0.0244±0.0083	0.0201	0.0697	0.892	0.0250	2.7367	0.995
Cr(III) uptake in presence of Cu(II)	B[Cu(0.15)+Cr(0.45)]	0.0256±0.0022	0.0224	0.0401	0.944	0.0272	1.5830	0.993
	B[Cu(0.30)+Cr(0.30)]	0.0174±0.0061	0.0142	0.0352	0.947	0.0189	2.0561	0.993
	B[Cu(0.45)+Cr(0.15)]	0.0081±0.0003	0.0075	0.0398	0.903	0.0086	4.9704	0.989
	B[Cu(0.60)+Cr(0.60)]	0.0304±0.0072	0.0254	0.0433	0.927	0.0321	1.1961	0.989

$q_{e,exp}$ = experimental metal uptake capacity at equilibrium, q_{em} = metal uptake capacity at equilibrium calculated using kinetic models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with three independent data points.

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target metal uptake at equilibrium ($q_{e,exp}$) had also increased even though the corresponding initial concentration of non-target metal had decreased. Further, k_2 values for Cu(II) and Cr(III) metal ions from the binary combinations investigated under controlled pH conditions had increased as its concentrations in the combinations had decreased.

An inspection of Fig. 5.35 and 5.36 revealed simultaneous metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from binary-metal ion systems investigated. Hence it was felt appropriate to ascertain how much removal and uptake of both the metals have taken place with variation in contact time. Therefore, data of Fig. 5.35 and 5.36 have been re-plotted in Fig. 5.37 by taking into account the total metal removal (TQ_t) under uncontrolled pH conditions and total metal uptake (Tq_t) under controlled pH conditions. The variation in Tq_t data points under controlled pH conditions was observed to increase with contact time and overlapped at 95% confidence interval for B[Cu(0.45)+Cr(0.15)], B[Cu(0.30)+Cr(0.30)] and B[Cu(0.15)+Cr(0.45)] combinations throughout the contact period as seen in Fig. 5.37(b). Hence, it clearly indicated that the total metal uptake (Tq_t) was similar and fairly independent of proportion of initial metal ions concentrations present in different combinations of binary-metal ion systems comprising of Cu(II) and Cr(III) under controlled pH conditions as long as total initial metal ion concentration was approximately the same, i.e. 0.60 meq/L even though ionic radius, valence as well as atomic weight of the metal ions were different from each other. On the other hand, when total initial metal ion concentration was doubled to 1.20 meq/L in B[Cu(0.60)+Cr(0.60)] combination without increasing GAA dose, total metal uptake (Tq_t) increased and did not overlap at 95% confidence interval with the total metal uptake (Tq_t) from combinations having total initial metal ions concentration near to 0.60 meq/L. The total metal uptake (Tq_t) under controlled pH conditions from B[Cu(0.45)+Cr(0.15)], B[Cu(0.30)+Cr(0.30)] and B[Cu(0.15)+Cr(0.45)] combinations were very close to each other in the range of 0.0275-0.0330 meq/g while the same was 0.0548 meq/g from B[Cu(0.60)+Cr(0.60)] combination. The GAA used has shown to have additional metal uptake capacity due to increase in total initial metal ion concentration. Further, pseudo-first- and pseudo-second-order rate and kinetic models were also used to describe the total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions and estimated kinetic parameters are shown in Table 5.11. Higher R^2 values for pseudo-second-order rate and kinetic models indicated its appropriateness to describe total

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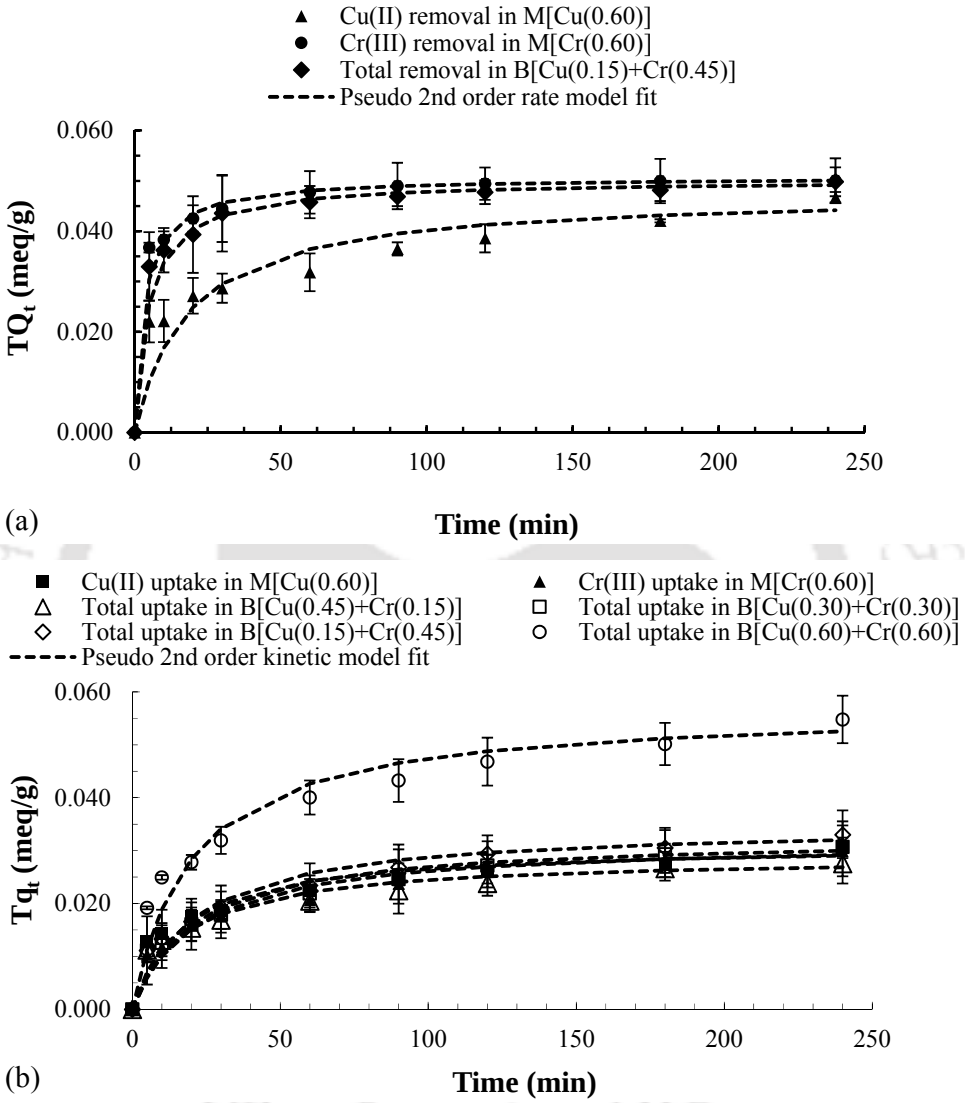

Fig. 5.37: Variation in (a) total metal removal under uncontrolled pH conditions and (b) total metal uptake under controlled pH conditions from mono- and binary-metal ion systems comprising of Cu(II) and Cr(III) ions.

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Table 5.11: Summary of estimated kinetic parameters for total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions from binary-metal ion systems comprising of Cu(II) and Cr(III) ions.

			Pseudo-first-order rate model			Pseudo-second-order rate model		
Uncontrolled pH conditions	Binary-metal ion combination	$TQ_{e,exp}$ (meq/g)	Q_{em} (meq/g)	K_1 (1/min)	R^2	Q_{em} (meq/g)	K_2 (g/meq.min)	R^2
	B[Cu(0.15)+Cr(0.45)]	0.0498±0.0029	0.0463	0.1643	0.951	0.0502	4.1114	0.999
			Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Controlled pH conditions	Binary-metal ion combinations	$Tq_{e,exp}$ (meq/g)	q_{em} (meq/g)	k_1 (1/min)	R^2	q_{em} (meq/g)	k_2 (g/meq.min)	R^2
	B[Cu(0.15)+Cr(0.45)]	0.0330±0.0025	0.0299	0.0636	0.901	0.0345	1.3649	0.994
	B[Cu(0.30)+Cr(0.30)]	0.0307±0.0069	0.0276	0.0435	0.923	0.0326	1.4698	0.993
	B[Cu(0.45)+Cr(0.15)]	0.0275±0.0022	0.0237	0.0548	0.903	0.0289	1.9288	0.993
	B[Cu(0.60)+Cr(0.60)]	0.0548±0.0045	0.0445	0.0539	0.911	0.0570	0.8730	0.992

$TQ_{e,exp}$ = experimental total metal removal at equilibrium, Q_{em} = total metal removal at equilibrium calculated using rate models, $Tq_{e,exp}$ = experimental total metal uptake capacity at equilibrium, q_{em} = total metal uptake capacity at equilibrium calculated using kinetic models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with three independent data points.

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metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions. The best fit plots of pseudo-second-order rate and kinetic models to experimental total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions respectively are also shown in Fig. 5.37.

The variation in total metal removal (TQ_t) under uncontrolled pH conditions and total metal uptake (Tq_t) under controlled pH conditions from binary-metal ion systems having total initial metal ions concentration near to 0.60 meq/L have also been compared with variation in metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from M[Cu(0.60)] and M[Cr(0.60)] systems in Fig. 5.37. The variation in TQ_t from B[Cu(0.15)+Cr(0.45)] combination investigated under uncontrolled pH condition overlapped at 95% confidence interval with Cr(III) metal removal under uncontrolled pH conditions from M[Cr(0.60)] system while Cu(II) metal removal from M[Cu(0.60)] system didn't overlap at 95% confidence interval with TQ_t from B[Cu(0.15)+Cr(0.45)] combination and M[Cr(0.60)] system as seen in Fig. 5.37(a). Further, variation in Cu(II) and Cr(III) metal uptake from mono-metal ion systems investigated under controlled pH conditions overlapped within 95% confidence interval with Tq_t data points from combinations of binary-metal ion system having total initial metal ion concentration near to 0.60 meq/L in solution. The experimental total metal removal (TQ_t) and experimental total metal uptake (Tq_t) from B[Cu(0.45)+Cr(0.15)], B[Cu(0.30)+Cr(0.30)] and B[Cu(0.15)+Cr(0.45)] [observed total metal removal of 0.0498 meq/g under uncontrolled pH condition and total metal uptake of 0.0275-0.033 meq/g under controlled pH conditions] combinations were observed in comparable range with metal removal and metal uptake from M[Cu(0.60)] and M[Cr(0.60)] systems [observed metal removal of 0.0467 meq/g for Cu(II) and 0.0500 meq/g for Cr(III) under uncontrolled pH conditions and observed metal uptake of 0.0305 meq/g for Cu(II) and 0.0300 meq/g for Cr(III) under controlled pH conditions].

In the present study, investigations were also carried out under controlled pH conditions keeping the same initial concentrations of individual metal ions in mono- and binary-metal ion systems. The variations in individual as well as total metal uptake under controlled pH conditions from M[Cu(0.60)], M[Cr(0.60)] and B[Cu(0.60)+Cr(0.60)] combinations are presented in Fig. 5.38. The variation in Cu(II) and Cr(III) metal uptake values were observed to overlap at 95% confidence interval from M[Cu(0.60)], M[Cr(0.60)]

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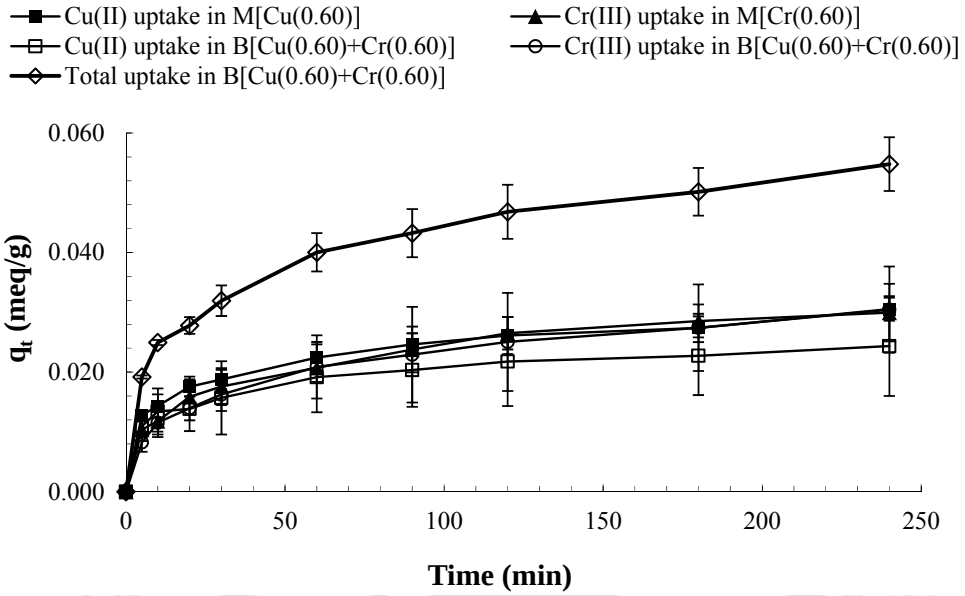

Fig. 5.38: Variation in total metal uptake from mono- and binary-metal ion systems comprising of Cu(II) and Cr(III) ions investigated at an initial concentration of 0.60 meq/L for individual metals under controlled pH conditions.

and B[Cu(0.60)+Cr(0.60)] combinations investigated. This observation appeared to contradict the published findings (Al-Rub et al., 2006; Li et al., 2011; Mohan et al., 2006; Srivastava et al., 2006) wherein target metal ion uptake from binary-metal ion system was reported to decrease due to competition of non-target metal ions for available adsorption sites. In the present investigation, no effect on the uptake of target metal ions from mono- and binary-metal ion systems comprising of Cu(II)+Cr(III) having similar initial concentration of target and non-target metal ions in the solution was observed. It indicated adequacy of available adsorption sites for target and non-target metal uptakes under controlled pH conditions. Further, the most striking feature noted in this investigation was the simultaneous metal uptake under controlled pH conditions of both the metal ions (Fig. 5.38) from the binary-metal ion systems comprising of Cu(II)+Cr(III) yielding increased experimental total metal uptake of 0.0548 meq/g compared to metal uptake from M[Cu(0.60)] and M[Cr(0.60)] systems investigated.

The existence of intra-particle diffusion in combinations of binary-metal ions system was tested using intra-particle diffusion model. The plots of q_t versus $t^{0.5}$ are shown in Fig. 5.39 for combinations of binary-metal systems investigated under controlled pH conditions only. The plots showed initial curved portions and subsequent linear portions reflecting both

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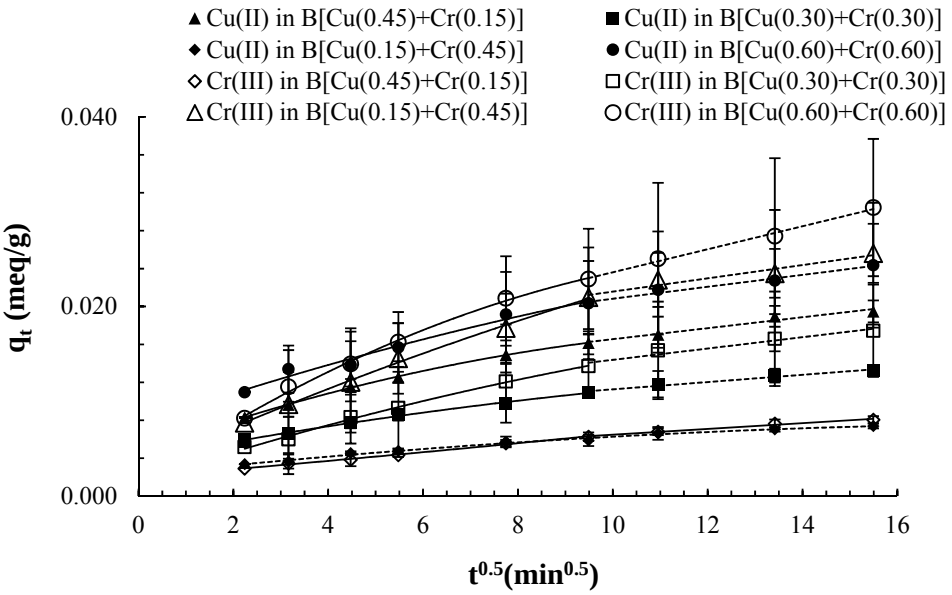

Fig. 5.39: Intra-particle diffusion model for target Cu(II) and target Cr(III) metal ions in presence of respective non-target Cr(III) and non-target Cu(II) metal ions from binary-metal ion systems comprising of Cu(II) and Cr(III) ions investigated under controlled pH conditions.

external as well as intra-particle diffusion effect (Mahramanlioglu et al., 2002; Yadav et al., 2006). The initial curved and subsequent linear portions were predominantly visible for initial concentrations of 0.30, 0.45 and 0.60 meq/L of target metals while the same was difficult to distinguish for initial concentration of 0.15 meq/L of target metal. Also, the linear portions didn't pass through origin of the plot suggesting adsorption of target metal ions be a complex process involving surface adsorption as well as intra-particle diffusion contributing to rate controlling steps (Hawari & Mulligan, 2007).

5.3.5 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions

The data represented in section 5.2.5 for metal ion concentrations remaining in aqueous phase with contact time obtained from selected combinations of ternary-metal ion system comprising of Cu(II), Pb(II) and Cr(III) have been utilized to investigate metal removal rate under uncontrolled pH conditions and metal uptake kinetics under controlled pH conditions. Since significant precipitation of Cu(II) and Cr(III) metal ions were observed at time t = 0 in T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combination under uncontrolled pH condition, metal removal rate investigation was restricted to only T[Cu(0.20)+Pb(0.20)+Cr(0.20)]

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combination. Fig. 5.40 depicts variation in Cu(II), Pb(II) and Cr(III) metal removal from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination investigated under uncontrolled pH condition. The metal removal data points appeared to overlap to each other at 95% confidence interval. Fig. 5.41 depicts variation in Cu(II), Pb(II) and Cr(III) metal ions uptake from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] and T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combinations investigated under controlled pH conditions. The metal uptake data were distinct and didn't overlap at 95% confidence interval (except for the first 20-30 min).

The kinetic data of metal removal obtained under uncontrolled pH conditions were fitted into pseudo-first- and pseudo-second-order rate models and metal uptake under controlled pH conditions were fitted to pseudo-first- and pseudo-second-order kinetic models and estimated kinetic parameters are respectively presented in Table 5.12 and 5.13. Higher values of R^2 indicated suitability of pseudo-second-order rate model to describe experimental metal removal data obtained under uncontrolled pH conditions. Similarly higher values of R^2 indicated applicability of pseudo-second-order kinetic model to describe experimental metal

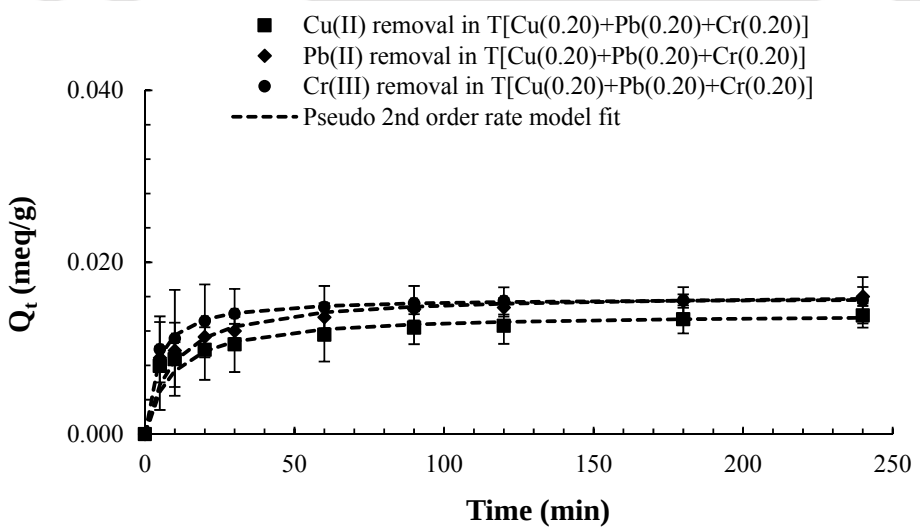

Fig. 5.40: Variation in target Cu(II), target Pb(II) and target Cr(III) metal removal from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination investigated under uncontrolled pH conditions {Temp. = 30±2 °C, Initial adjusted pH = 5.00±0.02, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combination T[Cu(0.20)+Pb(0.20)+Cr(0.20)] = 0.19±0.01 meq/L of Cu(II) + 0.21±0.01 meq/L of Pb(II) + 0.19±0.06 meq/L of Cr(III)} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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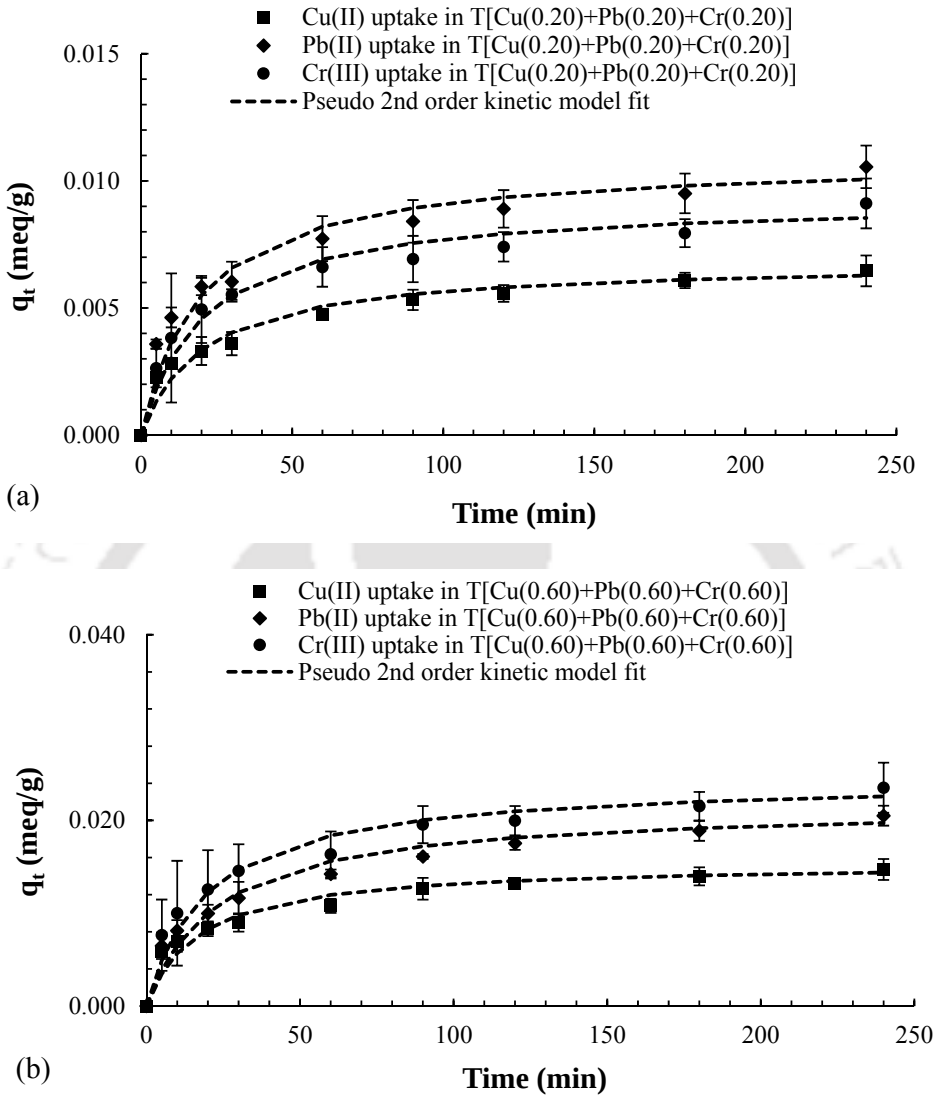

Fig. 5.41: Variation in target Cu(II), target Pb(II) and target Cr(III) metal uptake from (a) T[Cu(0.20)+Pb(0.20)+Cr(0.20)] and (b) T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combinations investigated under controlled pH conditions {Temp. = 30±2 °C, Buffered pH = 5.00±0.02, GAA dose =12 g/L, Mixing speed = 66 rpm, Initial metal conc. in combinations T[Cu(0.20)+Pb(0.20)+Cr(0.20)] = 0.20±0.01 meq/L of Cu(II) + 0.20±0.01 meq/L of Pb(II) + 0.22±0.05 meq/L of Cr(III), T[Cu(0.60)+Pb(0.60)+Cr(0.60)] = 0.60±0.00 meq/L of Cu(II) + 0.59±0.02 meq/L of Pb(II) + 0.64±0.00 meq/L of Cr(III)} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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Table 5.12: Summary of estimated kinetic parameters for target metal removal in presence of non-target metal under uncontrolled pH conditions from ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions.

Target metal	Combination	$Q_{e,exp}$ (meq/g)	Pseudo-first-order rate model			Pseudo-second-order rate model		
			Q_{em} (meq/g)	K_1 (1/min)	R^2	Q_{em} (meq/g)	K_2 (g/meq.min)	R^2
Cu(II) removal in presence of Pb(II) and Cr(III)	T[Cu(0.20)+Pb(0.20)+Cr(0.20)]	0.0138±0.0014	0.0124	0.1047	0.909	0.0141	7.7878	0.998
Pb(II) removal in presence of Cu(II) and Cr(III)	T[Cu(0.20)+Pb(0.20)+Cr(0.20)]	0.0160±0.0011	0.0146	0.0958	0.917	0.0164	6.6903	0.998
Cr(III) removal in presence of Cu(II) and Pb(II)	T[Cu(0.20)+Pb(0.20)+Cr(0.20)]	0.0156±0.0051	0.0148	0.1488	0.969	0.0159	16.7929	1.000

$Q_{e,exp}$ = experimental metal removal at equilibrium, Q_{em} = metal removal at equilibrium calculated using rate models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with three independent data points.

Table 5.13: Summary of estimated kinetic parameters for target metal uptake in presence of non-target metal under controlled pH conditions from ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions.

Target metal	Combinations	$q_{e,exp}$ (meq/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
			q_{em} (meq/g)	k_1 (1/min)	R^2	q_{em} (meq/g)	k_2 (g/meq.min)	R^2
Cu(II) uptake in presence of Pb(II) and Cr(III)	T[Cu(0.20)+Pb(0.20)+Cr(0.20)]	0.0065±0.0006	0.0065	0.0459	0.924	0.0068	7.1045	0.993
	T[Cu(0.60)+Pb(0.60)+Cr(0.60)]	0.0147±0.0011	0.0132	0.0532	0.913	0.0154	3.7964	0.995
Pb(II) uptake in presence of Cu(II) and Cr(III)	T[Cu(0.20)+Pb(0.20)+Cr(0.20)]	0.0106±0.0008	0.0089	0.0559	0.913	0.0109	4.7020	0.991
	T[Cu(0.60)+Pb(0.60)+Cr(0.60)]	0.0205±0.0011	0.0180	0.0444	0.912	0.0216	2.0118	0.992
Cr(III) uptake in presence of Cu(II) and Pb(II)	T[Cu(0.20)+Pb(0.20)+Cr(0.20)]	0.0091±0.0010	0.0065	0.0613	0.929	0.0093	5.2721	0.987
	T[Cu(0.60)+Pb(0.60)+Cr(0.60)]	0.0235±0.0027	0.0187	0.0536	0.929	0.0245	2.0653	0.992

$q_{e,exp}$ = experimental metal uptake capacity at equilibrium, q_{em} = metal uptake capacity at equilibrium calculated using kinetic models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with three independent data points.

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uptake data obtained under controlled pH conditions. The best fit plots of pseudo-second-order rate and kinetic models are also shown in Fig. 5.40 and 5.41. The target metal $Q_{e,exp}$ values were relatively higher for T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination under uncontrolled pH conditions compared to $q_{e,exp}$ values for T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination under controlled pH conditions. Further, the estimated K_2 value for Cr(III) metal ion was higher compared to Cu(II) and Pb(II) metal ions from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination investigated under uncontrolled pH condition even though each metal had similar initial metal ion concentration in aqueous phase. Furthermore, k_2 value for Cu(II) metal ion was higher compared to Cr(III) and Pb(II) metal ions from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] and T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combinations investigated under controlled pH conditions even though each metal had similar initial metal ion concentration in aqueous phase in each of these combinations.

A careful inspection of Fig. 5.40 and 5.41 revealed simultaneous metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from ternary-metal ion systems investigated. Hence it was felt appropriate to ascertain how much removal and uptake of all the three metals have taken place with variation in contact time. Therefore, data of Fig. 5.40 and 5.41 have been re-plotted in Fig. 5.42 by taking into account the total metal removal (TQ_t) under uncontrolled pH conditions and total metal uptake (Tq_t) under controlled pH conditions. The variation in total metal removal (TQ_t) under uncontrolled pH conditions and total metal uptake (Tq_t) under controlled pH conditions from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] and T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combinations have also been compared respectively with variation in metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] systems in Fig. 5.42. The total metal uptake (Tq_t) from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination and metal uptake from M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] systems [Fig. 5.42(b)] investigated under controlled pH conditions overlapped at 95% confidence interval. Hence, it clearly indicated that the total metal uptake (Tq_t) was similar and fairly independent of proportion of initial metal ions concentrations present in ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) under controlled pH conditions as long as total initial metal ion concentration was approximately the same, i.e. 0.60 meq/L even though ionic radius, valence as well as atomic weight of the three metal ions were different from each other. As the total initial metal ions

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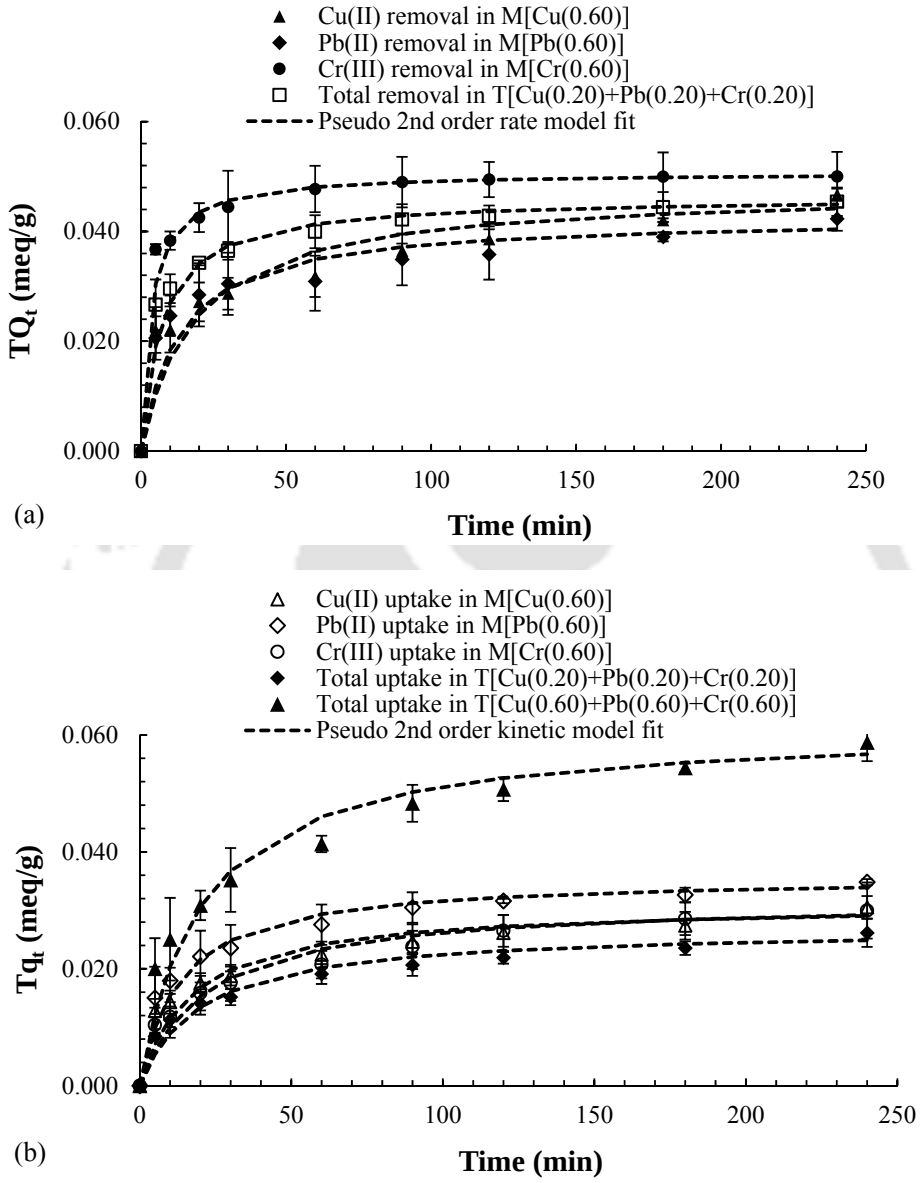

Fig. 5.42: Variation in (a) total metal removal under uncontrolled pH conditions and (b) total metal uptake under controlled pH conditions from mono- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions.

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concentration was increased approximately to 1.80 meq/L in T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combination without increasing GAA dose, total metal uptake (Tq_t) increased and did not overlap at 95% confidence interval with the total metal uptake (Tq_t) from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination as well as from M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] systems having total initial metal ions concentration near to 0.60 meq/L. The GAA used has shown to have additional metal uptake capacity due to increase in total initial metal ion concentration. Similarly, the total metal removal (TQ_t) from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination investigated under uncontrolled pH condition was observed to increase with contact time and overlapped at 95% confidence interval with most of the metal removal data points obtained under uncontrolled pH conditions from M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] systems [Fig. 5.42(a)]. The overlap of the total metal removal from mono- and ternary-metal ion systems under uncontrolled pH conditions was more prominent towards the end of the contact time. The experimental total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions from the combinations of ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) metal ions are presented in Table 5.14. The total metal removal (TQ_t) and total metal uptake (Tq_t) values from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] [observed total metal removal of 0.0454 meq/g under uncontrolled pH conditions and observed total metal uptake of 0.0261 meq/g under controlled pH conditions] combination was in comparable range with metal removal and metal uptake values obtained from M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] systems [observed metal removal of 0.0467 meq/g for Cu(II), 0.0423 meq/g for Pb(II) and 0.0500 meq/g for Cr(III) under uncontrolled pH conditions while observed metal uptake of 0.0305 meq/g for Cu(II), 0.0348 meq/g for Pb(II) and 0.0300 meq/g for Cr(III) under controlled pH conditions]. Further, pseudo-first- and pseudo-second-order rate and kinetic models were also used respectively to describe the total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions and estimated kinetic parameters are shown in Table 5.14. The higher R^2 values for pseudo-second-order rate and kinetic models indicated its appropriateness to describe total metal removal and total metal uptake data obtained respectively under uncontrolled and controlled pH conditions. The best fit plots of pseudo-second-order rate and kinetic models to experimental total metal removal and total metal uptake data are also shown in Fig. 5.42.

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Table 5.14: Summary of estimated kinetic model parameters for total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions from ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions.

Uncontrolled pH conditions	Ternary-metal ion combination	$TQ_{e,exp}$ (meq/g)	Pseudo-first-order rate model			Pseudo-second-order rate model		
			Q_{em} (meq/g)	K_1 (1/min)	R^2	Q_{em} (meq/g)	K_2 (g/meq.min)	R^2
	T[Cu(0.20)+Pb(0.20)+Cr(0.20)]	0.0454±0.0026	0.0419	0.117	0.935	0.0462	3.0411	0.999
Controlled pH conditions	Ternary-metal ion combination	$Tq_{e,exp}$ (meq/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
			q_{em} (meq/g)	k_1 (1/min)	R^2	q_{em} (meq/g)	k_2 (g/meq.min)	R^2
	T[Cu(0.20)+Pb(0.20)+Cr(0.20)]	0.0261±0.0024	0.0220	0.0545	0.925	0.0270	1.8468	0.991
	T[Cu(0.60)+Pb(0.60)+Cr(0.60)]	0.0587±0.0032	0.0496	0.0504	0.925	0.0615	0.8101	0.993

$TQ_{e,exp}$ = experimental total metal removal at equilibrium, Q_{em} = total metal removal at equilibrium calculated using rate models, $Tq_{e,exp}$ = experimental total metal uptake capacity at equilibrium, q_{em} = total metal uptake capacity at equilibrium calculated using kinetic models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with three independent data points.

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In the present study, investigations were also carried out under controlled pH conditions keeping the same initial concentration of individual metal ions in mono- and ternary-metal ion systems. The variations in individual metal uptake as well as total metal uptake from M[Cu(0.60)], M[Pb(0.60)], M[Cr(0.60)] and T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combinations are presented in Fig. 5.43. The variation in Cu(II), Pb(II) and Cr(III) metal uptake values from T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combination did not overlap at 95% confidence interval with each other and were lower compared to their respective uptake values from M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] systems. These observations appeared in accordance with the published findings (Al-Rub et al., 2006; Li et al., 2011; Mohan et al., 2006; Srivastava et al., 2006) wherein target metal ion uptake was reported to decrease due to competition of non-target metal ions for available adsorption sites. However the most striking feature noted in this investigation was the simultaneous uptake of all the three metal ions (Fig. 5.43) from the ternary-metal ion system yielding increased experimental total metal uptake of 0.0587 meq/g under controlled pH conditions compared to metal uptake from M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] systems investigated. It indicated additional metal uptake capacity of the GAA used.

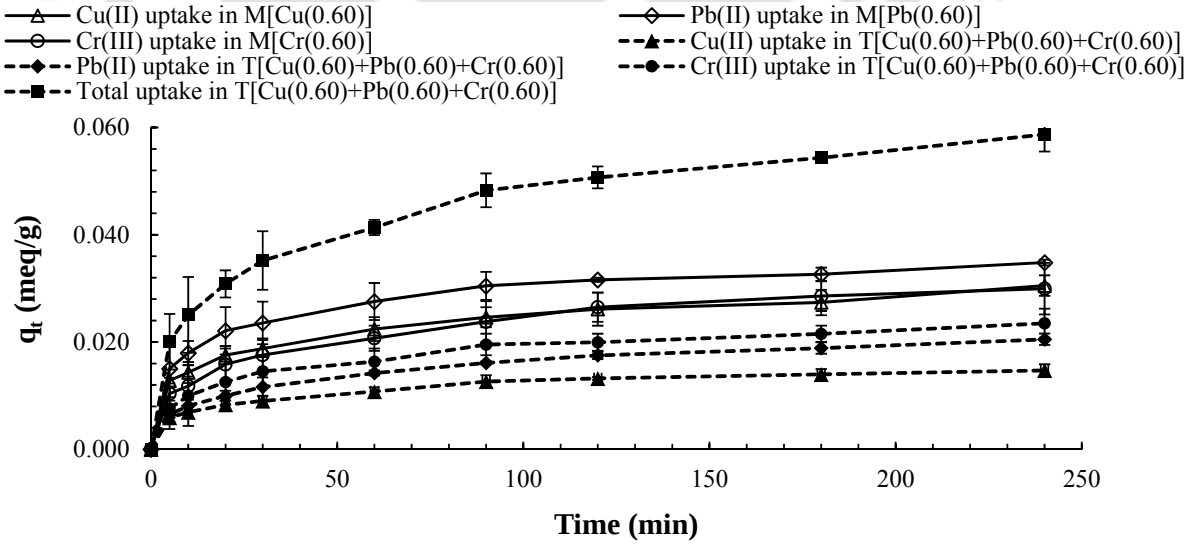

Fig. 5.43: Variation in total metal uptake from mono- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions investigated at an initial concentration of 0.60 meq/L for individual metals under controlled pH conditions.

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The existence of intra-particle diffusion in combinations of ternary-metal ions system was tested using intra-particle diffusion model. The plots of q_t versus $t^{0.5}$ are shown in Fig. 5.44 for T[Cu(0.20)+Pb(0.20)+Cr(0.20)] and T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combinations investigated under controlled pH conditions only. The plots showed initial curved portions and subsequent linear portions reflecting both external as well as intra-particle diffusion effect (Mahramanlioglu et al., 2002; Yadav et al., 2006). Also, the linear portions didn't pass through origin of the plot suggesting the adsorption of target metal ions be a complex process involving surface adsorption as well as intra-particle diffusion contributing to rate controlling steps (Hawari & Mulligan, 2007).

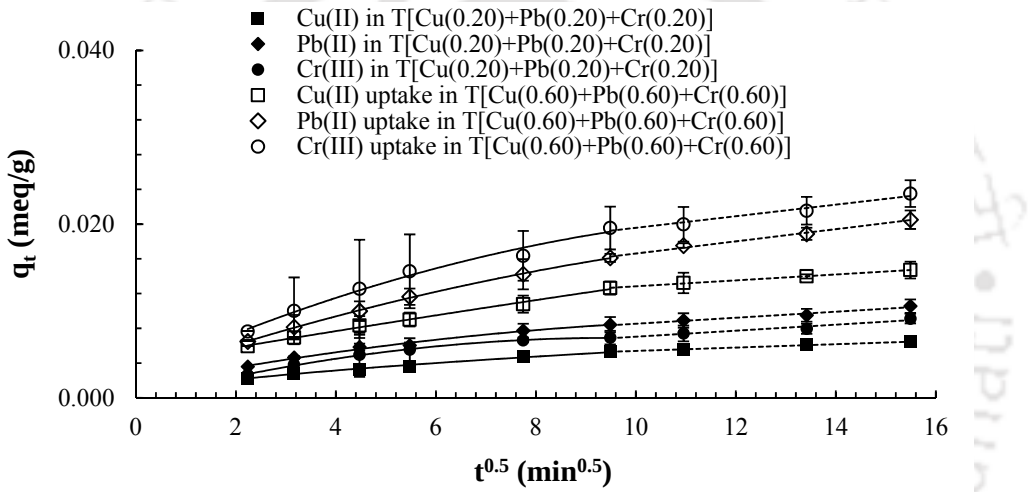

Fig. 5.44: Intra-particle diffusion model for target Cu(II), target Pb(II) and target Cr(III) ions in presence of respective non-target metals from ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions investigated under controlled pH conditions.

5.3.6 Summary

The kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions were investigated from selected combinations of mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) using fixed dose of GAA. The total initial metal ion concentrations in the present work were kept fixed approximately at 0.60 meq/L for all mono-metal ion systems and most of the combinations of binary- and ternary-metal ion systems while three combinations of binary-metal ion systems

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and one combination of ternary-metal ion system were investigated at total initial metal ion concentration approximately of 1.20 meq/L and 1.80 meq/L respectively. Simultaneous metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions were observed from selected combinations of binary- and ternary-metal ion systems. The total metal uptakes under controlled pH conditions were observed to be similar and fairly independent of proportion of initial metal ion concentrations present in selected combinations of binary-metal ion systems investigated as long as total initial metal ion concentration in the combinations was approximately the same (i.e. near to 0.60 meq/L) even though ionic radius, valence and atomic weight of the metal ions were different from each other. Similar trends were observed for total metal removals under uncontrolled pH conditions from combinations of binary-metal ion systems investigated. Further, the total metal removal and total metal uptake from combinations of binary-metal ion systems having total initial metal ion concentration of 0.60 meq/L in solution were observed in comparable range with metal removal and metal uptake from mono-metal ion systems. Similarly, the total metal removal and total metal uptake from ternary-metal ion system having total initial metal ion concentration of 0.60 meq/L in solution was in comparable range with metal removal and metal uptake from mono-metal ion systems. When total initial metal ion concentrations were doubled approximately to 1.20 meq/L for the three combinations of binary-metal ion systems and tripled approximately to 1.80 meq/L for a combination of ternary-metal ion system, enhanced total metal uptakes under controlled pH conditions were observed compared to combinations of mono-, binary- and ternary-metal ion systems having total initial metal ion concentration of approximately 0.60 meq/L. It indicated additional metal uptake capacity of GAA with increase in total initial metal ion concentration. Similar trends were observed for total metal removals under uncontrolled pH conditions from combinations of binary-metal ion systems with doubled total initial metal ion concentrations compared to combinations of mono- and binary-metal ion systems having total initial metal ion concentration approximately 0.60 meq/L indicating additional metal removal capability of GAA used. No effect on the removal and uptake of target metal ions {except for individual metal uptake from B[Cr(0.60)+Pb(0.60)] combination under controlled pH conditions} from selected combinations of mono- and binary-metal ion systems having similar initial metal ion concentration (approximately 0.60 meq/L) of target and non-target metal ions in the solution was observed. It indicated adequacy of GAA to alter solution pH for target and non-target metal removals under uncontrolled pH conditions and availability of adsorption sites for

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target and non-target metal uptakes under controlled pH conditions. This was in contradiction to reported observation of decreased uptake of target metal ion from multi-metal ion system due to competition of non-target metal ions for available adsorption sites. However the uptake of individual metal ions from ternary-metal ion system having similar initial metal ion concentration (approximately 0.60 meq/L for each metal) of target and non-target metal ions in the solution was reduced compared to individual metal ions uptake from mono-metal ion systems. This was in accordance with reported observation of decreased uptake of target metal ion from multi-metal ion system due to competition of non-target metal ions for available adsorption sites. The kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions followed pseudo-second-order rate and kinetic models respectively for the combinations of mono-, binary- and ternary-metal ion systems investigated. The adsorption of target metal ions by GAA from selected combinations of mono-, binary- and ternary-metal ion systems investigated under controlled pH conditions was observed to be a complex process involving surface adsorption as well as intra-particle diffusion contributing to rate controlling steps.

5.4 Batch tests to investigate additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions by GAA when exposed to metal ion systems repeatedly

The increased total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions (refer section 5.3) were observed during batch kinetic studies with three selected combinations of binary-metal ion systems and one combination of ternary-metal ion system having total initial metal ion concentrations of 1.20 meq/L and 1.80 meq/L respectively compared to combinations having total initial metal ion concentration of 0.60 meq/L in aqueous phase. One of the possible reasons for increased total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions from binary- and ternary-metal ion systems might be presence of increased total initial metal ion concentration in the solution. The higher total metal removal under uncontrolled pH conditions from the selected combinations of binary- and ternary-metal ion systems investigated might have been due to additional pH enhancing capacity of the GAA used. The higher total metal uptake under controlled pH conditions from the selected combinations of binary- and ternary-metal ion systems investigated might have been due to additional driving force provided in terms of total initial metal ion concentration gradient. Whether additional

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metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions leading to enhanced total metal removal/uptake possible if the adsorbent exposed to (i) a metal ion once followed by exposure to another metal ion only once and (ii) a metal ion repeatedly for 6-10 cycles followed by exposure to another metal ion only once while keeping the initial metal ion concentration fixed approximately to 0.60 meq/L? In order to investigate the first possibility, 0.6 g of virgin GAA per 50 mL of solution was exposed only once to a target mono-metal ion system {either M[Cu(0.60)] or M[Pb(0.60)] or M[Cr(0.60)]} up to equilibrium time and thereafter, the target metal ion loaded GAA was washed thrice with de-mineralized water to remove the precipitated or un-adsorbed target metal ion without loss of GAA particles and then exposed only once to the other (or non-target) mono-metal ion system {for example, if M[Cu(0.60)] taken as target metal then M[Pb(0.60)] or M[Cr(0.60)] considered as non-target metal} up to equilibrium time. In order to investigate second possibility as mentioned, it was planned to saturate (or utilize all the free sites available on) the virgin adsorbent (0.6 g of GAA) by repeated loadings for 6-10 cycles with the target mono-metal ion system {either M[Cu(0.60)] or M[Pb(0.60)] or M[Cr(0.60)]} before exposing it to the other (or non-target) mono-metal ion system {for example, if M[Cu(0.60)] taken as target metal then M[Pb(0.60)] or M[Cr(0.60)] considered as non-target metal} only once. The investigation was expected to shed light on metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions of the non-target metal ions by the target metal ion saturated GAA and displacement of the target metal ion from the surface of the target metal ion saturated GAA, if any. The results of these investigations are discussed in following sections.

5.4.1 Metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions when exposed to a mono-metal ion system once followed by exposure with another mono-metal ion system

In this investigation, the virgin GAA (0.6 g) was exposed to a target mono-metal ion system {either M[Cu(0.60)] or M[Pb(0.60)] or M[Cr(0.60)]} till equilibrium time and then target metal loaded GAA was washed thrice with de-mineralized water and again exposed only once to the other (or non-target) mono-metal ion system {for example, if M[Cu(0.60)] taken as target metal then M[Pb(0.60)] or M[Cr(0.60)] considered as non-target metal} till equilibrium time. The results of the investigation are represented in Table 5.15, 5.16 and 5.17 for combinations of M[Cu(0.60)]–M[Pb(0.60)], M[Cr(0.60)]–M[Pb(0.60)] and M[Cu(0.60)]–

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Table 5.15: Metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions by virgin GAA loaded once with a target mono-metal ion system and further exposed once to a non-target mono-metal ion system considering M[Cu(0.60)]–M[Pb(0.60)] as combination of target and non-target mono-metal ion system.

Metal	Uncontrolled pH conditions			Controlled pH conditions		
Virgin GAA loaded once with target metal	Target mono-metal ion	M[Cu(0.60)]	M[Pb(0.60)]	Target mono-metal ion	M[Cu(0.60)]	M[Pb(0.60)]
	Initial conc. (meq/L)	0.60±0.01	0.57±0.02	Initial conc. (meq/L)	0.60±0.01	0.57±0.02
	Residual conc. (meq/L)	0.06±0.02	0.06±0.01	Residual conc. (meq/L)	0.28±0.01	0.23±0.01
	Metal removal (meq/g)	0.0447	0.0428	Metal uptake (meq/g)	0.0261	0.0286
Target metal loaded GAA exposed once to non-target metal	Non-target mono-metal ion	M[Pb(0.60)]	M[Cu(0.60)]	Non-target mono-metal ion	M[Pb(0.60)]	M[Cu(0.60)]
	Initial conc. (meq/L)	0.55±0.01	0.60±0.01	Initial conc. (meq/L)	0.57±0.02	0.60±0.01
	Residual conc. (meq/L)	0.18±0.01	0.16±0.04	Residual conc. (meq/L)	0.26±0.01	0.31±0.02
	Metal removal (meq/g)	0.0315	0.0361	Metal uptake (meq/g)	0.0256	0.0241
	Target metal displaced: Conc. (meq/L)	0.09±0.01	0.01±0.01	Target metal displaced: Conc. (meq/L)	0.08±0.01	0.05±0.01
	Target metal displaced: Removal reduction (meq/g)	0.0074	0.0008	Target metal displaced: Uptake reduction (meq/g)	0.0065	0.0044
Total removal (meq/g)		0.0688	0.0781	Total uptake (meq/g)	0.0452	0.0483

Data presented in xx±yy format represents average value as xx and standard deviation as yy estimated with a minimum of three independent data points.

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Table 5.16: Metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions by virgin GAA loaded once with a target mono-metal ion system and further exposed once to a non-target mono-metal ion system considering M[Cr(0.60)]–M[Pb(0.60)] as combination of target and non-target mono-metal ion system.

Metal			Uncontrolled pH conditions		Controlled pH conditions		
Virgin GAA loaded once with target metal	Target mono-metal ion		M[Cr(0.60)]	M[Pb(0.60)]	Target mono-metal ion	M[Cr(0.60)]	M[Pb(0.60)]
	Initial conc. (meq/L)		0.62±0.01	0.58±0.02	Initial conc. (meq/L)	0.62±0.01	0.58±0.01
	Residual conc. (meq/L)		0.011±0.01	0.052±0.01	Residual conc. (meq/L)	0.278±0.01	0.271±0.01
	Metal removal (meq/g)		0.0510	0.0440	Metal uptake (meq/g)	0.0290	0.0260
Target metal loaded GAA exposed once to non-target metal	Non-target mono-metal ion		M[Pb(0.60)]	M[Cr(0.60)]	Non-target mono-metal ion	M[Pb(0.60)]	M[Cr(0.60)]
	Initial conc. (meq/L)		0.58±0.01	0.62±0.01	Initial conc. (meq/L)	0.58±0.02	0.62±0.01
	Residual conc. (meq/L)		0.152±0.03	0.07±0.01	Residual conc. (meq/L)	0.272±0.00	0.284±0.01
	Metal removal (meq/g)		0.0360	0.0460	Metal uptake (meq/g)	0.0260	0.0290
	Target metal displaced	Conc. (meq/L)	-	-	Target metal displaced Conc. (meq/L)	0.05±0.00	0.01±0.00
		Removal reduction (meq/g)	-	-	Uptake reduction (meq/g)	0.0040	0.0010
Total removal (meq/g)			0.0870	0.0900	Total uptake (meq/g)	0.0510	0.0530

Data presented in xx±yy format represents average value as xx and standard deviation as yy estimated with a minimum of three independent data points.

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Table 5.17: Metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions by virgin GAA loaded once with a target mono-metal ion system and further exposed once to a non-target mono-metal ion system considering M[Cu(0.60)]–M[Cr(0.60)] as combination of target and non-target mono-metal ion system.

Metal			Uncontrolled pH conditions		Controlled pH conditions		
Virgin GAA loaded once with target metal	Target mono-metal iom		M[Cu(0.60)]	M[Cr(0.60)]	Target mono-metal ion	M[Cu(0.60)]	M[Cr(0.60)]
	Initial conc. (meq/L)		0.60±0.02	0.61±0.01	Initial conc. (meq/L)	0.58±0.02	0.63±0.02
	Residual conc. (meq/L)		0.016±0.003	0.009±0.001	Residual conc. (meq/L)	0.254±0.006	0.350±0.010
	Metal removal (meq/g)		0.0483	0.0503	Metal uptake (meq/g)	0.0270	0.0232
Target metal loaded GAA exposed once to non-target metal	Non-target mono-metal ion		M[Cr(0.60)]	M[Cu(0.60)]	Non-target mono-metal ion	M[Cr(0.60)]	M[Cu(0.60)]
	Initial conc. (meq/L)		0.61±0.01	0.60±0.02	Initial conc. (meq/L)	0.63±0.02	0.60±0.01
	Residual conc. (meq/L)		0.042±0.011	0.072±0.035	Residual conc. (meq/L)	0.347±0.001	0.328±0.033
	Metal removal (meq/g)		0.0475	0.0437	Metal uptake (meq/g)	0.0234	0.0224
	Target metal displaced	Conc. (meq/L)	0.022±0.010	0.002±0.001	Target metal displaced Conc. (meq/L)	0.041±0.001	0.002±0.001
		Removal reduction (meq/g)	0.0018	0.0001	Uptake reduction (meq/g)	0.0034	0.0001
Total removal (meq/g)			0.0940	0.0938	Total uptake (meq/g)	0.0470	0.0454

Data presented in xx±yy format represents average value as xx and standard deviation as yy estimated with a minimum of three independent data points.

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M[Cr(0.60)] systems of target and non-target mono-metal ion systems respectively. Further, when the target metal ion loaded GAA was washed three times with de-mineralized water, the washings contained approximately 0.01–0.02 meq/L of Cu(II), 0–0.01 meq/L of Pb(II) and 0–0.01 meq/L of Cr(III) metal ions, which were not considered significant and hence ignored in analysis of the results.

The target metal removal [0.0447 meq/g for Cu(II) and 0.0428 meq/g for Pb(II)] under uncontrolled pH conditions and target metal uptake [0.0261 meq/g for Cu(II) and 0.0286 meq/g for Pb(II)] under controlled pH conditions for M[Cu(0.60)]–M[Pb(0.60)] combination of target and non-target mono-metal ion system were observed to be much closer to the metal removal [0.0467 meq/g for Cu(II) and 0.0423 meq/g for Pb(II)] under uncontrolled pH conditions and metal uptake [0.0305 meq/g for Cu(II) and 0.0348 meq/g for Pb(II)] under controlled pH conditions from the mono-metal ion systems of M[Cu(0.60)] and M[Pb(0.60)] (refer Table 5.2). However, when the target mono-metal ion loaded GAA was exposed to the non-target mono-metal ion system subsequently, it not only showed removal and uptake of non-target metal but also led to displacement of the target metal ion from the adsorbent to the solution. The non-target metal removal of 0.0315 meq/g for Pb(II) and 0.0361 meq/g for Cu(II) under uncontrolled pH conditions and non-target metal uptake of 0.0256 meq/g for Pb(II) and 0.0241 meq/g for Cu(II) under controlled pH conditions were observed. The target metal ion appeared in the solution due to displacement up to a concentration of 0.09 meq/L for Cu(II) and 0.01 meq/L for Pb(II) under uncontrolled pH conditions while 0.08 meq/L for Cu(II) and 0.05 meq/L for Pb(II) under controlled pH conditions. The total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions were estimated to be 0.0688 meq/g and 0.0452 meq/g respectively when M[Cu(0.60)] and M[Pb(0.60)] were respectively taken as the target and non-target mono-metal ion system; and 0.0781 meq/g and 0.0483 meq/g respectively when M[Pb(0.60)] and M[Cu(0.60)] were respectively taken as the target and non-target mono-metal ion system (Table 5.15). The estimated total metal removal and total metal uptake when GAA was exposed to two mono-metal ion systems {M[Cu(0.60)]–M[Pb(0.60)]} one after the other were comparatively lower (0.0688-0.0781 meq/g under uncontrolled pH conditions and 0.0452-0.0483 meq/g under controlled pH conditions) than the total metal removal and total metal uptake obtained from B[Cu(0.60)+Pb(0.60)] combination (0.0835 meq/g under uncontrolled pH conditions and 0.0623 meq/g under controlled pH conditions, refer Table 5.5).

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Similarly, for M[Cr(0.60)]–M[Pb(0.60)] combination of target and non-target mono-metal ion system, the target metal removal [0.0510 meq/g for Cr(III) and 0.0440 meq/g for Pb(II)] under uncontrolled pH conditions and target metal uptake [0.0290 meq/g for Cr(III) and 0.0260 meq/g for Pb(II)] under controlled pH conditions were observed to be much closer to the metal removal [0.0500 meq/g for Cr(III) and 0.0428 meq/g for Pb(II)] under uncontrolled pH conditions and metal uptake [0.0300 meq/g for Cr(III) and 0.0348 meq/g for Pb(II)] under controlled pH conditions from the mono-metal ion systems of M[Cr(0.60)] and M[Pb(0.60)] (refer Table 5.2). However, when the target mono-metal ion system loaded GAA was exposed to the non-target mono-metal ion system subsequently, it led to removal and uptake of non-target metal under uncontrolled and controlled pH conditions. The displacement of the target metal ion from the GAA to the solution was observed only under controlled pH conditions. The non-target metal removal of 0.0360 meq/g for Pb(II) and 0.0460 meq/g for Cr(III) under uncontrolled pH conditions and non-target metal uptake of 0.0260 meq/g for Pb(II) and 0.0290 meq/g for Cr(III) under controlled pH conditions were observed. The target metal ion appeared in the solution due to displacement up to a concentration of 0.05 meq/L for Cr(III) and 0.01 meq/L for Pb(II) under controlled pH conditions with no displacement of target metal observed under uncontrolled pH conditions. The total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions were estimated to be 0.0870 meq/g and 0.0510 meq/g respectively when M[Cr(0.60)] and M[Pb(0.60)] were respectively taken as the target and non-target mono-metal ion system; and 0.0900 meq/g and 0.0530 meq/g respectively when M[Pb(0.60)] and M[Cr(0.60)] were respectively taken as the target and non-target mono-metal ion system (Table 5.16). The estimated total metal removal and total metal uptake when GAA was exposed to two mono-metal ion systems of M[Cr(0.60)] and M[Pb(0.60)] one after the other were comparatively higher (0.0870-0.0900 meq/g under uncontrolled pH conditions and 0.0510-0.0530 meq/g under controlled pH conditions) than the total metal removal and total metal uptake obtained from B[Cr(0.60)+Pb(0.60)] combination (0.0852 meq/g under uncontrolled pH conditions and 0.0404 meq/g under controlled pH conditions, refer Table 5.8).

In the case of M[Cu(0.60)]–M[Cr(0.60)] combination of target and non-target mono-metal ion system, the target metal removal [0.0483 meq/g for Cu(II) and 0.0503 meq/g for Cr(III)] under uncontrolled pH conditions and target metal uptake [0.0270 meq/g for Cu(II)

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and 0.0232 meq/g for Cr(III)] under controlled pH conditions were observed to be much closer to the metal removal [0.0467 meq/g for Cu(II) and 0.0500 meq/g for Cr(III)] under uncontrolled pH conditions and metal uptake [0.0305 meq/g for Cu(II) and 0.0300 meq/g for Cr(III)] under controlled pH conditions from the mono-metal ion systems of M[Cu(0.60)] and M[Cr(0.60)] (refer Table 5.2). However, when the target mono-metal ion system loaded GAA was exposed to the non-target mono-metal ion system subsequently, it led to removal and uptake of non-target metal as well as displacement of the target metal ion from the GAA to the solution. The non-target metal removal of 0.0437 meq/g for Cu(II) and 0.0475 meq/g for Cr(III) under uncontrolled pH conditions and non-target metal uptake of 0.0224 meq/g for Cu(II) and 0.0234 meq/g for Cr(III) under controlled pH conditions were observed. The target metal ion appeared in the solution due to displacement up to a concentration of 0.022 meq/L for Cu(II) and 0.002 meq/L for Cr(III) under uncontrolled pH conditions while 0.041 meq/L for Cu(II) and 0.002 meq/L for Cr(III) under controlled pH conditions. The total metal removal and total metal uptake under uncontrolled and controlled pH conditions were estimated to be 0.0940 meq/g and 0.0470 meq/g respectively when M[Cu(0.60)] and M[Cr(0.60)] were respectively taken as the target and non-target mono-metal ion system; and 0.0938 meq/g and 0.0454 meq/g respectively when M[Cr(0.60)] and M[Cu(0.60)] were respectively taken as the target and non-target mono-metal ion system (Table 5.17). The estimated total metal uptake (0.0470-0.0454 meq/g) under controlled pH conditions when GAA was exposed to two mono-metal ion systems of M[Cu(0.60)] and M[Cr(0.60)] one after the other were comparatively lower than the total metal uptake (0.0548 meq/g under controlled pH conditions) obtained from B[Cu(0.60)+Cr(0.60)] combination (refer Table 5.11).

The adsorbent GAA had shown increased total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions when exposed to mono-metal ion systems one after the other. This clearly indicated that the two fold increase in total initial metal ion concentration might not be the sole reason for higher metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from the binary-metal ion systems but the adsorbent must be having enough potential to enhance pH for metal removal and enough free sites for adsorption of non-target metal ions even after loading it with the target metal ions. Since more pH enhancing potential and free sites were available on the adsorbent under the selected experimental conditions and the adsorbent had shown

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affinity for both the metal ions, hence simultaneous metal removal and metal uptake of both the metal ions were observed from the binary-metal ion systems investigated.

5.4.2 Metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions when exposed to a mono-metal ion system repeatedly followed by exposure only once with another mono-metal ion system

In this investigation, attempts were made to saturate (or utilize all the free sites available on) the virgin adsorbent (0.6 g of GAA) by repeated loadings for 6-10 cycles with a target mono-metal ion system {either M[Cu(0.60)] or M[Pb(0.60)] or M[Cr(0.60)]} before exposing it only once with another (non-target) mono-metal ion system {if M[Cu(0.60)] taken as target mono-metal ion system then M[Pb(0.60)] or M[Cr(0.60)] considered as non-target mono-metal ion system}. The results are discussed in subsequent paragraphs.

The results of M[Cu(0.60)]–M[Pb(0.60)] combination of target and non-target mono-metal ion systems investigated under uncontrolled and controlled pH conditions are presented in Table 5.18 and 5.19 respectively. It was observed that the metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions of the target metal ion by GAA reduced after 2nd loading cycle. However, reduced metal removal and reduced metal uptake of the target metal ion continued up to 6th loading cycle indicating that the saturation levels of GAA for metal removal and metal uptake had not yet reached. The cumulative target metal removal under uncontrolled pH conditions and cumulative target metal uptake under controlled pH conditions by GAA after 6th loading cycle was termed as pseudo-saturated GAA in this investigation. The washings contained approximately 0.01-0.02 meq/L of Cu(II) and 0-0.01 meq/L of Pb(II) metal ions, which was not considered significant enough to influence analysis of the results. However, when the target metal ion pseudo-saturated GAA was exposed to the non-target metal ion subsequently only once, the non-target metal removal under uncontrolled pH conditions and non-target metal uptake under controlled pH conditions were estimated to be 0.0337 meq/g and 0.0216 meq/g respectively when M[Cu(0.60)] and M[Pb(0.60)] were respectively taken as the target and non-target mono-metal ion systems while 0.0342 meq/g and 0.0202 meq/g respectively when M[Pb(0.60)] and M[Cu(0.60)] were respectively taken as the target and non-target mono-metal ion systems. At the same time, it led to displacement of the target metal ion from pseudo-saturated GAA in the solution up to a concentration of 0.20 meq/L for Cu(II) and

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Table 5.18: Metal removal by GAA repeatedly exposed to a target mono-metal ion system followed by exposure only once to a non-target mono-metal ion system under uncontrolled pH conditions from M[Cu(0.60)]–M[Pb(0.60)] combination of target and non-target mono-metal ion system.

Target metal removal				Non-target metal removal by target metal loaded GAA				Total removal (meq/g)
						Displaced target metal		
Mono-metal ion (Initial conc. in me/L)	Loading cycle	Removal (meq/g)	Cumulative removal (meq/g)	Mono-metal ion (Initial conc. in meq/L)	Removal (meq/g)	Metal conc. (meq/L)	Removal reduction (meq/g)	
M[Cu(0.60)] (0.58±0.01)	1st	0.0429	0.0429	M[Pb(0.60)] (0.57±0.02)	0.0337	0.20±0.01	0.0166	0.1929
	2nd	0.0289	0.0718					
	3rd	0.0270	0.0988					
	4th	0.0263	0.1251					
	5th	0.0273	0.1524					
	6th	0.0234	0.1758					
M[Pb(0.60)] (0.55±0.02)	1st	0.0403	0.0403	M[Cu(0.60)] (0.58±0.01)	0.0342	0.03±0.01	0.0020	0.1845
	2nd	0.0285	0.0688					
	3rd	0.0246	0.0934					
	4th	0.0192	0.1126					
	5th	0.0219	0.1345					
	6th	0.0187	0.1532					

Data presented in xx±yy format represents average value as xx and standard deviation as yy estimated with a minimum of three independent data points.

0.03 meq/L for Pb(II) under uncontrolled pH conditions while 0.12 meq/L for Cu(II) and 0.09 meq/L for Pb(II) under controlled pH conditions. These results clearly indicated significant non-target metal removal and non-target metal uptake even when GAA was repeatedly loaded with the target metal ion up to 6th loading cycles along with displacement of target metal ions from the pseudo-saturated GAA. The estimated total metal removal and total metal uptake were comparatively higher (0.1854-0.1929 meq/g and 0.0968-0.1287 meq/g under uncontrolled and controlled pH conditions respectively) than the total metal removal and total metal uptake obtained from B[Cu(0.60)+Pb(0.60)] combination (0.0835 meq/g and 0.0623 meq/g under uncontrolled and controlled pH conditions respectively, refer Table 5.5). This study considering combination of M[Cu(0.60)] and M[Pb(0.60)] as target and non-target mono-metal ion system indicated availability of pH enhancing capacity and free sites on the GAA by yielding higher total metal removal and total metal uptake.

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Table 5.19: Metal uptake by GAA repeatedly exposed to a target mono-metal ion system followed by exposure only once to a non-target mono-metal ion system under controlled pH conditions from M[Cu(0.60)]–M[Pb(0.60)] combination of target and non-target mono-metal ion system.

Target metal uptake				Non-target metal uptake by target metal loaded GAA				Total uptake (meq/g)
						Displaced target metal		
Mono-metal ion (Initial conc. in me/L)	Loading cycle	Uptake (meq/g)	Cumulative uptake (meq/g)	Mono-metal ion (Initial conc. in meq/L)	Uptake (meq/g)	Metal conc. (meq/L)	Uptake reduction (meq/g)	
M[Cu(0.60)] (0.58±0.01)	1st	0.0274	0.0274	M[Pb(0.60)] (0.55±0.02)	0.0216	0.12±0.01	0.0079	0.1287
	2nd	0.0174	0.0448					
	3rd	0.0144	0.0592					
	4th	0.0124	0.0716					
	5th	0.0105	0.0821					
	6th	0.0098	0.0919					
	7th	0.0080	0.0999					
	8th	0.0085	0.1084					
	9th	0.0066	0.1150					
M[Pb(0.60)] (0.55±0.02)	1st	0.0285	0.0285	M[Cu(0.60)] (0.58±0.01)	0.0202	0.09±0.05	0.0074	0.0968
	2nd	0.0145	0.0430					
	3rd	0.0088	0.0518					
	4th	0.0087	0.0605					
	5th	0.0079	0.0684					
	6th	0.0077	0.0761					
	7th	0.0079	0.0840					

Data presented in xx±yy format represents average value as xx and standard deviation as yy estimated with a minimum of three independent data points.

Similarly, the results for M[Cr(0.60)]–M[Pb(0.60)] combination of target and non-target mono-metal ion system investigated under uncontrolled and controlled pH conditions are presented in Table 5.20 and 5.21 respectively. Fairly good amounts of target metal removal under uncontrolled pH conditions up to 10th loading cycle and target metal uptake under controlled pH conditions up to 6th loading cycle were observed although it occurred with reduced values with increase in number of loading cycles. The reduced metal removal and reduced metal uptake of the target metal ion continued after each loading cycle indicating that the saturation levels of GAA for metal removal and metal uptake had not yet reached and hence the adsorbent after loading with target metal for 8-10 cycles was termed as pseudo-saturated GAA for this investigation. The washings contained approximately 0-0.01 meq/L of Cr(III) and 0-0.01 meq/L of Pb(II) metal ions, which was not considered significant enough

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Table 5.20: Metal uptake by GAA repeatedly exposed to a target mono-metal ion system followed by exposure only once to a non-target mono-metal ion system under uncontrolled pH conditions from M[Cr(0.60)]–M[Pb(0.60)] combination of target and non-target mono-metal ion system.

Target metal removal				Non-target metal removal by target metal loaded GAA				Total removal (meq/g)
						Displaced target metal		
Mono-metal ion (Initial conc. in meq/L)	Loading cycle	Removal (meq/g)	Cumulative removal (meq/g)	Mono-metal ion (Initial conc. in meq/L)	Removal (meq/g)	Metal conc. (meq/L)	Removal reduction (meq/g)	
M[Cr(0.60)] (0.60±0.01)	1st	0.0491	0.0491	M[Pb(0.60)] (0.54)	0.0280	0.01±0.00	0.0004	0.4241
	2nd	0.0442	0.0933					
	3rd	0.0419	0.1352					
	4th	0.0390	0.1742					
	5th	0.0405	0.2147					
	6th	0.0367	0.2514					
	7th	0.0365	0.2879					
	8th	0.0367	0.3246					
	9th	0.0345	0.3591					
	10th	0.0374	0.3965					
M[Pb(0.60)] (0.54±0.04)	1st	0.0448	0.0448	M[Cr(0.60)] (0.62)	0.0421	0.05±0.00	0.0041	0.3603
	2nd	0.0316	0.0764					
	3rd	0.0334	0.1098					
	4th	0.0319	0.1417					
	5th	0.0323	0.1740					
	6th	0.0301	0.2041					
	7th	0.0284	0.2325					
	8th	0.0310	0.2635					
	9th	0.0287	0.2922					
	10th	0.0301	0.3223					

Data presented in xx±yy format represents average value as xx and standard deviation as yy estimated with a minimum of three independent data points.

to influence analysis of the results. However, when the target metal ion pseudo-saturated GAA was again exposed only once to non-target metal, further non-target metal removal under uncontrolled pH conditions and non-target metal uptake under controlled pH conditions were observed along with displacement of target metal in the solution. The non-target metal removal under uncontrolled pH conditions and non-target metal uptake under controlled pH conditions were estimated to be 0.0280 meq/g and 0.0198 meq/g respectively when M[Cr(0.60)] and M[Pb(0.60)] were respectively taken as the target and non-target mono-metal ion system while 0.0421 meq/g and 0.0180 meq/g respectively when M[Pb(0.60)] and M[Cr(0.60)] were respectively taken as the target and non-target mono-metal ion system. The displacement of the target metal ion from pseudo-saturated GAA in the solution up to a concentration of 0.01 meq/L for Cr(III) and 0.05 meq/L for Pb(II) under

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Table 5.21: Metal uptake by GAA repeatedly exposed to a target mono-metal ion system followed by exposure only once to a non-target mono-metal ion system under controlled pH conditions from M[Cr(0.60)]–M[Pb(0.60)] combination of target and non-target mono-metal ion system.

Target metal uptake				Non-target metal uptake by target metal loaded GAA				Total uptake (meq/g)
						Displaced target metal		
Mono-metal ion (Initial conc. in meq/L)	Loading cycle	Uptake (meq/g)	Cumulative uptake (meq/g)	Mono-metal ion (Initial conc. in meq/L)	Uptake (meq/g)	Metal conc. (meq/L)	Uptake reduction (meq/g)	
M[Cr(0.60)] (0.64±0.03)	1st	0.0272	0.0272	M[Pb(0.60)] (0.58)	0.0198	0.07±0.00	0.0055	0.1356
	2nd	0.0212	0.0484					
	3rd	0.0185	0.0669					
	4th	0.0142	0.0811					
	5th	0.0122	0.0933					
	6th	0.0110	0.1043					
	7th	0.0090	0.1133					
	8th	0.0080	0.1213					
M[Pb(0.60)] (0.55±0.04)	1st	0.0260	0.0260	M[Cr(0.60)] (0.58)	0.0180	0.06±0.00	0.0050	0.1274
	2nd	0.0254	0.0514					
	3rd	0.0100	0.0614					
	4th	0.0126	0.0740					
	5th	0.0134	0.0874					
	6th	0.0103	0.0977					
	7th	0.0073	0.1050					
	8th	0.0094	0.1144					

Data presented in xx±yy format represents average value as xx and standard deviation as yy estimated with a minimum of three independent data points.

uncontrolled pH conditions while 0.07 meq/L for Cr(III) and 0.06 meq/L for Pb(II) under controlled pH conditions were observed. These results clearly indicated significant non-target metal removal under uncontrolled pH conditions and non-target metal uptake under controlled pH conditions even when GAA was repeatedly exposed to the target metal ion up to 8-10th loading cycles along with displacement of the target metal ion from the pseudo-saturated GAA. The estimated total metal removal and total metal uptake were comparatively higher (0.3603-0.4241 meq/g and 0.1274-0.1356 meq/g under uncontrolled and controlled pH conditions respectively) than the total metal removal and total metal uptake obtained from B[Cr(0.60)+Pb(0.60)] combination (0.0852 meq/g and 0.0404 meq/g under uncontrolled and controlled pH conditions respectively, refer Table 5.8). This study considering combination of M[Cr(0.60)] and M[Pb(0.60)] as target and non-target mono-metal ion systems indicated availability of enough pH enhancing capacity and free sites on the GAA by yielding higher total metal removal and total metal uptake.

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The results for M[Cu(0.60)]–M[Cr(0.60)] combination of target and non-target mono-metal ion systems investigated under uncontrolled and controlled pH conditions are presented in Table 5.22 and 5.23 respectively. Fairly good amount of target metal removal under uncontrolled pH conditions up to 9th loading cycle and target metal uptake under controlled pH conditions up to 6th loading cycle were observed although it occurred with reduced values with each new loading cycle. The reduced metal removal and reduced metal uptake of the target metal ion continued after each loading cycle indicating that the saturation levels of GAA for metal removal and metal uptake had not yet reached and hence the adsorbent was termed as pseudo-saturated GAA in this investigation. The washings contained

Table 5.22: Metal uptake by GAA repeatedly exposed to a target mono-metal ion system followed by exposure only once to a non-target mono-metal ion system under uncontrolled pH conditions from M[Cu(0.60)]–M[Cr(0.60)] combination of target and non-target mono-metal ion system.

Target metal removal				Non-target metal removal by target metal loaded GAA				Total removal (meq/g)
						Displaced target metal		
Mono-metal ion (Initial conc. in meq/L)	Loading Cycle	Removal (meq/g)	Cumulative removal (meq/g)	Mono-metal ion (Initial conc. in meq/L)	Removal (meq/g)	Metal conc. (meq/L)	Removal reduction (meq/g)	
M[Cu(0.60)] (0.58±0.01)	1st	0.0470	0.0470	M[Cr(0.60)] (0.62±0.02)	0.0466	0.12±0.00	0.0088	0.3379
	2nd	0.0365	0.0835					
	3rd	0.0354	0.1189					
	4th	0.0348	0.1537					
	5th	0.0340	0.1877					
	6th	0.0304	0.2181					
	7th	0.0280	0.2461					
	8th	0.0273	0.2734					
	9th	0.0267	0.3001					
M[Cr(0.60)] (0.62±0.02)	1st	0.0518	0.0518	M[Cu(0.60)] (0.58±0.01)	0.0297	0.00±0.00	0.0003	0.3897
	2nd	0.0466	0.0984					
	3rd	0.0422	0.1406					
	4th	0.0431	0.1837					
	5th	0.0397	0.2234					
	6th	0.0357	0.2591					
	7th	0.0340	0.2931					
	8th	0.0325	0.3256					
	9th	0.0347	0.3603					

Data presented in xx±yy format represents average value as xx and standard deviation as yy estimated with a minimum of three independent data points.

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Table 5.23: Metal uptake by GAA repeatedly exposed to a target mono-metal ion system followed by exposure only once to a non-target mono-metal ion system under controlled pH conditions from M[Cu(0.60)]–M[Cr(0.60)] combination of target and non-target mono-metal ion system.

Target metal uptake				Non-target metal uptake by target metal loaded GAA				Total uptake (meq/g)
						Displaced target metal		
Mono-metal ion (Initial conc. in meq/L)	Loading Cycle	Uptake (meq/g)	Cumulative uptake (meq/g)	Mono-metal ion (Initial conc. in meq/L)	Uptake (meq/g)	Metal conc. (meq/L)	Uptake reduction (meq/g)	
M[Cu(0.60)] (0.58±0.01)	1st	0.0269	0.0269	M[Cr(0.60)] (0.63±0.02)	0.0161	0.04±0.01	0.0026	0.1425
	2nd	0.0237	0.0506					
	3rd	0.0214	0.0720					
	4th	0.0189	0.0909					
	5th	0.0137	0.1046					
	6th	0.0132	0.1178					
	7th	0.0112	0.1290					
M[Cr(0.60)] (0.62±0.02)	1st	0.0246	0.0246	M[Cu(0.60)] (0.58±0.01)	0.0214	0.06±0.00	0.0052	0.1227
	2nd	0.0207	0.0453					
	3rd	0.0154	0.0607					
	4th	0.0140	0.0747					
	5th	0.0121	0.0868					
	6th	0.0115	0.0983					
	7th	0.0082	0.1065					

Data presented in xx±yy format represents average value as xx and standard deviation as yy estimated with a minimum of three independent data points.

approximately 0.01-0.02 meq/L of Cu(II) and 0-0.01 meq/L of Cr(III) metal ions which was not considered significant enough to influence analysis of the results. However, when the target mono-metal ion pseudo-saturated GAA was again exposed only once to non-target mono-metal ion system, further non-target metal removal under uncontrolled pH conditions and non-target metal uptake under controlled pH conditions were observed along with displacement of target metal in the solution. The non-target metal removal under uncontrolled pH conditions and non-target metal uptake under controlled pH conditions were estimated to be 0.0466 meq/g and 0.0161 meq/g respectively when M[Cu(0.60)] and M[Cr(0.60)] were respectively taken as the target and non-target mono-metal ion system while 0.0297 meq/g and 0.0214 meq/g respectively when M[Cr(0.60)] and M[Cu(0.60)] were respectively taken as the target and non-target mono-metal ion system. The displacement of the target metal ion from pseudo-saturated GAA up to a concentration of 0.12 meq/L for Cu(II) and 0.00 meq/L

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for Cr(III) under uncontrolled pH conditions while 0.04 meq/L for Cu(II) and 0.06 meq/L for Cr(III) under controlled pH conditions were observed. These results clearly indicated significant non-target metal removal under uncontrolled pH conditions and non-target metal uptake under controlled pH conditions even when GAA was repeatedly exposed to the target mono-metal ion system up to 7-9th loading cycles along with displacement of the target metal ions from the pseudo-saturated GAA. The estimated total metal uptake under controlled pH conditions were comparatively higher (0.1227-0.1425 meq/g under controlled pH conditions) than the total metal uptake obtained from B[Cu(0.60)+Cr(0.60)] combination (0.0548 meq/g under controlled pH conditions, refer Table 5.11). This study considering combination of M[Cu(0.60)] and M[Cr(0.60)] as target and non-target mono-metal ion systems indicated availability of enough free sites on the GAA by yielding higher total metal uptake.

Several authors have attempted to investigate preferential adsorption of metal ions considering characteristics of metal ions such as atomic weight, ionic size, electronegativity, hydrated radii, covalent index and standard reduction potential (Christophi & Axe, 2000; Hawari & Mulligan, 2007; Prasher et al., 2004). Depending on the predominant mechanism of adsorption such as electrostatic surface interactions, ion exchange or chelate formation; a corresponding set of properties could explain the relative order of metal adsorption with indication of metal ion likely to be displaced in the presence of competing metal ions. Higher uptake for Cu(II) metal ion compared to Cd(II) and Pb(II) metal ion onto goethite has been reported (Christophi & Axe, 2000). Since more electronegative metal ions are more strongly attracted to the negative surface of the adsorbent, higher uptake for Cu(II) metal ion was observed due to higher electronegativity. In the case of Cu(II)-Pb(II) competition studies, 60% of Pb(II) was displaced by Cu(II) when Pb(II) was introduced first to the system due to higher affinity of Cu(II) metal ions for adsorption sites compared to Pb(II) metal ions. However, entirely different observations were reported for the competitive adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) onto anaerobic biomass (Hawari & Mulligan, 2007). A higher affinity for Pb(II) metal ion was observed for adsorption sites compared to Cu(II), Ni(II) and Cd(II) metal ions. Higher affinity for Pb(II) metal ion was due to less hydrated ion radius, lower pK value (lower pK value would lower the degree of salvation of metal ions) and higher strength of covalent bonding. The higher affinity of Pb(II) metal ions for adsorption sites eventually resulted in displacement of lower affinity metal ions in the effluent of flow through column test of multi-metal ion adsorption. The displacement of

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Ni(II) and Cd(II) in the effluent of column was caused due to an ion exchange effect, whereby the high affinity Cu(II) and Pb(II) displaced the low affinity Ni(II) and Cd(II) which were previously adsorbed on to the biomass in the bed. The high affinity Pb(II) also displaced the lower affinity Cu(II) which was previously adsorbed on to the biomass. Unfortunately, no consistent rule of metal ion selectivity for adsorbent is available, as selectivity depends on a number of factors beyond the properties of the metals it including: (a) the functional group involved in binding, (b) pH at which adsorption is measured and (c) the ionic strength of the solution in which adsorption is measured as it determines the intensity of competition by other cations for the adsorption sites (McBride, 1994). In the present work, both sets of investigations indicated displacement of target metal ion from the surface of the target metal ion loaded GAA to the solution when exposed to the non-target metal ion. The active sites of GAA have following surface groups: $\equiv Al–OH_2^+$, $\equiv Al–OH$ and $\equiv Al–O^-$, where $\equiv$ represents the surface of the activated alumina. The first and the last group are formed when $\equiv Al–OH$ group is protonated and deprotonated according to the following reactions (Hao & Huang, 1986; Ramos et al., 2008):

$$\equiv Al\text{-}OH + H^+ \rightarrow \equiv Al\text{-}OH_2^+$$
$$\equiv Al\text{-}OH \rightarrow \equiv Al\text{-}O^- + H^+$$

When the solution pH is below pH_{zpc} value of the activated alumina, protonated ($\equiv Al–OH_2^+$) and neutral ($\equiv Al–OH$) aluminol sites are formed whereas if the solution pH is above pH_{zpc} value of the activated alumina, deprotonated negatively charged ($\equiv Al–O^-$) surface group is formed (Hao & Huang, 1986; Kasprzyk-Hordern, 2004; Ramos et al., 2008). In the present investigation, the pH_{zpc} value of GAA was estimated following a published procedure (Srivastava et al., 2011). Fig. 5.45 depicts the plot between "pH_{final} vs $pH_{initial}$". The point of intersection of the "pH_{final} vs $pH_{initial}$" curves represented the pH_{zpc} of the GAA and was observed in the range of 6.90-7.00. Since the initial pH of the solution was maintained at 5.00 (below pH_{zpc} value), the active sites on GAA were expected to be dominant with surface groups of $\equiv Al–OH_2^+$ and $\equiv Al–OH$. The metal ions could be adsorbed at an oxide-water interface in an inner-sphere or an outer-sphere complex, depending on whether a chemical bond is formed (i.e., a largely covalent bond between the metal and the electron-donating oxygen ions, as in an inner-sphere complex) or whether a cation of opposite charge

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approaches the surface groups within a critical distance. The two mechanisms for Cu(II) and Pb(II) metal ions adsorption onto GAA may be represented by following reactions:

Inner-sphere complex: $\equiv Al–OH + M^{2+} \leftrightarrow \equiv Al–OM^{+} + H^{+}$

$2\equiv Al–OH + M^{2+} \leftrightarrow (\equiv Al–O)_2M + 2H^{+}$

Outer-sphere complex: $(\equiv Al–O)_2 + M^{2+} \leftrightarrow (\equiv Al–O)_2\ldots\ldots M^{2+}$

where 'M' stands for metal ions. The outer-sphere complexes involve electrostatic interactions and are weaker than inner-sphere complexes (Hohl & Stumm, 1976; Kasprzyk-Hordern, 2004; Sparks, 1995). On the other hand, inner-sphere complexes are usually much more stable than outer-sphere complexes because it involves either ionic or covalent bonding, or a combination of both. Inner-sphere complexes are often irreversible and adsorption by this mechanism is weakly affected by the ionic strength of the aqueous phase. Metals that form outer-sphere complexes, on the other hand, are readily exchangeable (Sposito, 1989) and are expected to be more easily displaced from the adsorbent surface. The adsorption of Cu(II) and Pb(II) metal ions was found via both inner-sphere as well as outer-sphere complexes onto alumina surface (Hohl & Stumm, 1976; Kasprzyk-Hordern, 2004). Hence, when the GAA loaded with the target metal ion was exposed to the non-target metal ion subsequently, a fraction of the target metal ions bound to the surface of GAA through outer-sphere complexation might have been displaced by the non-target metal ion in the solution.

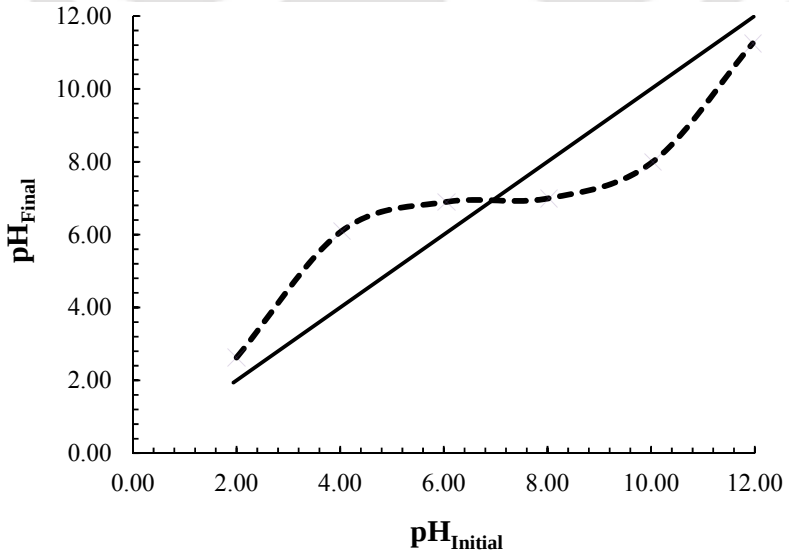

Fig. 5.45: Plot for determination of pH_{zpc} for GAA.

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5.4.3 Summary

Target mono-metal ion loaded adsorbent GAA when exposed only once to a non-target mono-metal ion system indicated additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions. The displacement of target mono-metal ion into solution was also observed possibly due to displacement of target mono-metal ions loosely bound to the surface of GAA possibly via outer-sphere complexation mechanism. Investigations carried out with repeated exposures of GAA to 6-10 loading cycles to target mono-metal ions concentration of 0.60 meq/L indicated additional metal removal capacity under uncontrolled pH conditions and additional metal uptake capacity under controlled pH conditions in each cycles. The target metal removal and target metal uptake continued even up to 10^{th} loading cycle but with decreasing amounts. When the GAA exposed to 6-10 loading cycles of target mono-metal ion system was again exposed to a non-target mono-metal ion system once, additional removal of non-target mono-metal ion under uncontrolled pH conditions and additional uptake of non-target mono-metal ion under controlled pH conditions were observed along with displacement of target mono-metal ion into the solution. These results tempted to undertake further kinetic studies with repeated loadings of GAA with a metal ion and then followed by loading only once with the other metal ion.

5.5 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for four loading cycles with mono- and binary-metal ions systems comprising of Cu(II), Pb(II) and Cr(III) ions

Batch test results presented in section 5.4 had revealed additional target metal removal under uncontrolled pH conditions and additional target metal uptake under controlled pH conditions by GAA with increase in number of loading cycles. Further when the target mono-metal ion loaded GAA was exposed to non-target mono-metal ion system, additional non-target mono-metal removal under uncontrolled pH conditions and additional non-target mono-metal uptake under controlled pH conditions were observed along with displacement of target mono-metal ions from GAA surface to the solution. Hence, it was tempting to investigate the kinetics of metal removal under uncontrolled pH conditions and kinetics of metal uptake under controlled pH conditions by GAA (a) with three loading cycles of a target mono-metal ion system followed with fourth loading cycle with another (non-target) mono-

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metal ion system and (b) with three loading cycles of a combinations of binary-metal ion system followed with fourth loading cycle with the same combination of binary-metal ion system but with interchanged concentrations of the two metal ions. In the present investigation, kinetic studies were only carried out with mono- and binary-metal systems comprising of Cu(II)–Pb(II) and Cr(III)–Pb(II) ions.

5.5.1 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for four loading cycles with mono-metal ion systems comprising of Cu(II) and Pb(II) ions

The kinetic studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions by GAA from mono-metal ion systems of M[Cu(0.60)] and M[Pb(0.60)] were investigated. The studies were carried out in the first set by exposing the virgin GAA to consecutive three loading cycles with M[Cu(0.60)] system followed by fourth loading cycle with M[Pb(0.60)] system and in the second set, with three loading cycles with M[Pb(0.60)] system followed by fourth loading cycle with M[Cu(0.60)] system. The results are discussed in following sub-sections.

5.5.1.1 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for three loading cycles with M[Cu(0.60)] system followed by fourth loading cycle with M[Pb(0.60)] system

The variation in metal removal and solution pH under uncontrolled pH conditions and metal uptake under controlled pH conditions obtained for three loading cycles with M[Cu(0.60)] system followed by fourth loading cycle with M[Pb(0.60)] system are shown in Fig. 5.46 and 5.47 respectively.

Under uncontrolled pH conditions, the solution pH increased to 5.40 in the beginning of the first loading cycle from the initially adjusted pH of 5.00 which further increased to 5.80-5.90 and remained stable till the end of the cycle [Fig. 5.46(a)]. Similarly, in the second loading cycle, the solution pH increased quickly to around 5.60 during the first 30 min. and then the solution pH gradually increased to 5.90 towards the end of the cycle. In the initial phase of the third loading cycle, the solution pH increased to 5.80 and then reached to a value of 5.90 towards the end of the cycle. In the fourth loading cycle, the solution pH fluctuated between 5.45-5.60 during initial 20 min. and then showed slow decreasing trend and solution

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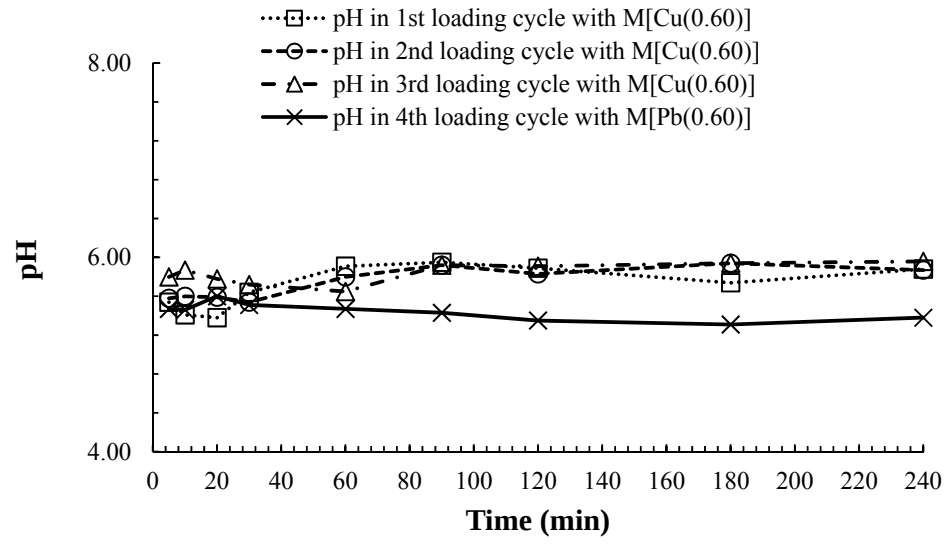
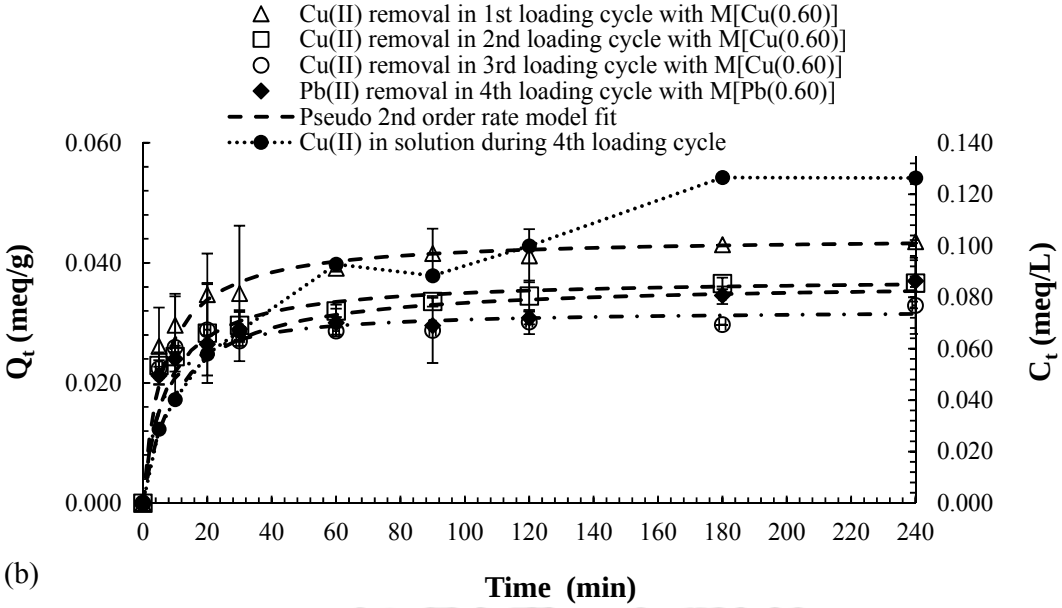


(a)



(b)

Fig. 5.46: Variation in (a) solution pH and (b) Cu(II) and Pb(II) metal removal in three loading cycles with M[Cu(0.60)] systems followed by fourth loading cycle with M[Pb(0.60)] system under uncontrolled pH conditions {Initial metal conc. in M[Cu(0.60)] = 0.59±0.01 meq/L, M[Pb(0.60)] = 0.59±0.02 meq/L, Initial adjusted pH = 5.00±0.05, Temp. = 30±1 °C, GAA dose = 12 g/L, Mixing speed = 66 rpm} (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

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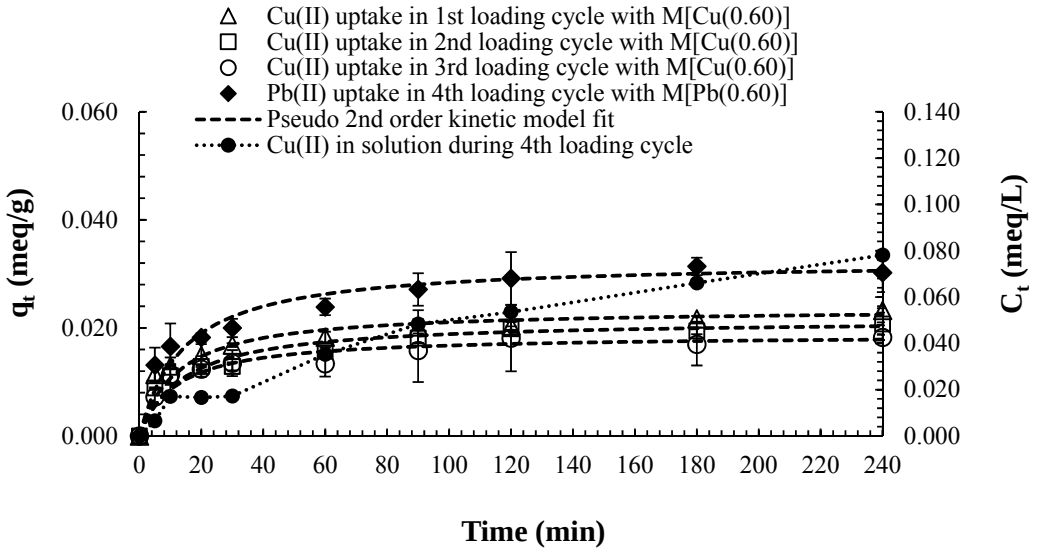

Fig. 5.47: Variation in Cu(II) and Pb(II) metal uptake in three loading cycles with M[Cu(0.60)] systems followed by fourth loading cycle with M[Pb(0.60)] system under controlled pH conditions {Initial metal conc. in M[Cu(0.60)] = 0.60±0.01 meq/L, M[Pb(0.60)] = 0.62±0.00 meq/L, Buffered pH = 5.00±0.01, Temp. = 30±1 °C, GAA dose = 12 g/L, Mixing speed = 66 rpm} (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

pH stabilized around 5.38 towards the end of the fourth loading cycle. It indicated influence of GAA to raise the solution pH up to third loading cycles while the rising trend of solution pH appeared to get reduced in the fourth loading cycle. Since the solution pH increased beyond 5.50 in the first three loading cycles with M[Cu(0.60)] system and in the fourth loading cycle with M[Pb(0.60)] system, the removal of Cu(II) and Pb(II) metal ions from aqueous phase might be attributed to combined effects of precipitation and adsorption. However, under controlled pH conditions, pH of the solution during each loading cycle remained fixed to the initially buffered pH of 5.00 during course of the experimentation. Hence, the removal of Cu(II) and Pb(II) metal ions from the solution might be attributed to adsorption only.

Under uncontrolled pH conditions of loading cycles [Fig. 5.46(b)], rapid Cu(II) metal removal was observed up to first 20 min. of the first loading cycle with M[Cu(0.60)] system. The Cu(II) metal removal was observed to be approximately 0.0347 meq/g at 20 min. of the first loading cycle and approximately 0.0435 meq/g of Cu(II) metal removal towards the end of the cycle. The GAA of the first loading cycle was again loaded with M[Cu(0.60)] system

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in the second loading cycle. The variation in Cu(II) metal removal during the second loading cycle was observed to be lower than the variation in metal removal observed during the first loading cycle. At the end of the second loading cycle, approximately 0.0366 meq/g of Cu(II) metal removal was observed. Similarly, when the GAA of second loading cycle was again loaded with M[Cu(0.60)] system in the third loading cycle, the variation in Cu(II) metal removal was observed to increase slowly in the initial phase compared to the first and second loading cycles. This might be due to reduced capacity of the GAA in raising the solution pH compared to the first and second loading cycles. The Cu(II) metal removal was observed to be approximately 0.0329 meq/g towards the end of the third loading cycle. In the fourth loading cycle, the GAA of the third loading cycle was exposed to M[Pb(0.60)] system. In this cycle, attention was paid to the two metal ions present in the experimental mixture – the part of non-precipitated Cu(II) metal accumulated on to GAA surfaces from three previous loading cycles and Pb(II) metal ions present in the bulk solution. Since the bulk solution was devoid of Cu(II) metal ions, there existed a possibility of migration of Cu(II) metal ions from surface of the GAA to the bulk solution due to formation of Cu(II) metal concentration gradient towards the bulk solution. Also the GAA with previous three loading cycle has had potential to raise the solution pH thereby causing a part of Pb(II) removal by precipitation while non-precipitated part of Pb(II) might get adsorbed onto GAA. As the GAA surface was devoid of Pb(II) metal ions, the migration of non-precipitated part of Pb(II) metal ions on to GAA surface was likely to be caused due to formation of Pb(II) metal concentration gradient towards the GAA. Therefore, while studying the fourth loading cycle, efforts were made to estimate residual concentration of Cu(II) metal ions in the bulk solution along with Pb(II) metal removal [Fig. 5.46(b)]. It presented the following interesting observations: (a) the concentration of migrated Cu(II) metal ions in the bulk solution increased with cycle time and was approximately 0.13 meq/L towards the end of the loading cycle which indicated migration of a part of accumulated Cu(II) metal from the surface of GAA under the experimental conditions of the fourth loading cycle, and (b) the observed variation in Pb(II) metal removal was lower than Cu(II) metal removal observed during the third loading cycles with most of the data points of Pb(II) metal removals overlapped at 95% confidence interval to Cu(II) metal removals. The Pb(II) metal removal was observed approximately 0.0370 meq/g towards the end of the fourth loading cycle.

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Under controlled pH conditions of first loading cycle with M[Cu(0.60)] system (Fig. 5.47), the surface of virgin GAA had zero concentration of Cu(II) metal ions while the bulk solution had Cu(II) concentration of approximately 0.60 meq/L. The difference in concentration of Cu(II) metal ions in the bulk solution and on the surface of virgin GAA might had formed a concentration gradient of metal ions – from the bulk solution to the surface of GAA. This concentration gradient of Cu(II) metal ions might had caused migration of metal ions from the bulk solution to the surface of GAA which had resulted in decrease in Cu(II) metal ions concentration in the bulk solution and corresponding increase in Cu(II) metal uptake on the surface of virgin GAA. The Cu(II) metal uptake of approximately 0.0129 meq/g was observed up to the first 10 min. of the first loading cycle and approximately 0.0232 meq/g of Cu(II) metal uptake towards the end of the cycle. The GAA of the first loading cycle was again loaded with M[Cu(0.60)] system in the second loading cycle. Here, it was important to note that the GAA surface had already accumulated some amount of Cu(II) metal ions on its surface from the first loading cycle thereby developing lower concentration gradient of metal ion in the second loading cycle compared to the first loading cycle. The variation in Cu(II) metal uptake during the second loading cycle was slightly lower compared to the variation in metal uptake observed during the first loading cycle. At the end of the second loading cycle, approximately 0.0207 meq/g of Cu(II) metal uptake was observed. Similarly, when the GAA of the second loading cycle was again loaded with M[Cu(0.60)] sysetm in the third loading cycle, the developed concentration gradient of metal ion might be lower than the second loading cycle due to additional accumulation of Cu(II) metal ions on the GAA surfaces. The observed variation in Cu(II) metal uptake was slightly lower compared to the variation in metal uptake observed in the second loading cycle. The equilibrium Cu(II) metal uptake was approximately 0.0182 meq/g in the third loading cycle. The observed variations in Cu(II) metal ion uptakes in the three loading cycles appeared to overlap indicating migration of similar amount of Cu(II) metal ions onto GAA surfaces in each loading cycles. In the fourth loading cycle, the GAA of the third loading cycle was exposed to M[Pb(0.60)] system. In this cycle, attention was paid to the two metal ions present in the experimental mixture – Cu(II) metal accumulated on to GAA surfaces from three previous loading cycles and Pb(II) metal ions present in the bulk solution. Since the bulk solution was devoid of Cu(II) metal ions, there existed a possibility of migration of Cu(II) metal ion from the surface of GAA to the bulk solution due to formation of Cu(II) metal concentration gradient towards the bulk solution. Similarly, the GAA surface was devoid of

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Pb(II) metal ions, the migration of Pb(II) metal ions on to GAA surface was likely to be caused due to formation of Pb(II) metal concentration gradient towards the GAA. Therefore, while studying the fourth loading cycle, efforts were made to estimate residual concentration of Cu(II) metal ions in the bulk solution along with Pb(II) metal uptake. It presented the following interesting observations: (a) the concentration of migrated Cu(II) metal ions in the bulk solution increased with cycle time and concentration was observed to be approximately 0.08 meq/L towards the end of the loading cycle which indicated migration of a part of accumulated Cu(II) metal from the surface of GAA to the solution under the experimental conditions of the fourth loading cycle, and (b) the observed variation in Pb(II) metal uptake was higher than Cu(II) metal uptakes observed during the previous three loading cycles as most of the data points of Pb(II) metal uptakes did not overlap at 95% confidence interval. The significantly higher equilibrium Pb(II) metal uptake of approximately 0.0302 meq/g was observed in the fourth loading cycle compared to equilibrium Cu(II) uptakes in the previous three loading cycles in the range of 0.0182-0.0232 meq/g.

Furthermore, variations in metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions carried out for four loading cycles were fitted to pseudo-first- and pseudo-second-order rate and kinetic models. The estimated rate and kinetic model parameters are presented in Table 5.24. The higher R^2 values for pseudo-second-order rate model indicated its suitability to describe metal removal under uncontrolled pH conditions and pseudo-second-order kinetic model for metal uptake under controlled pH conditions. The best fit plots of pseudo-second-order rate and kinetic models to experimental metal removal and metal uptake data are also presented in Fig. 5.46(b) and 5.47 respectively. An inspection of Table 5.24 revealed decreasing trend in values of $Q_{e,exp}$ and $q_{e,exp}$ as well as Q_{em} and q_{em} with increase in number of loading cycles with M[Cu(0.60)] systems. However, the values of $Q_{e,exp}$ and Q_{em} for the fourth loading cycle with M[Pb(0.60)] system under uncontrolled pH conditions were higher compared to similar values obtained with the second and third loading cycles with M[Cu(0.60)] system, while the values of $q_{e,exp}$ and q_{em} for the fourth loading cycle with M[Pb(0.60)] system under controlled pH conditions were higher compared to similar values obtained with the previous three loading cycles with M[Cu(0.60)] system. It indicated preferential removal and uptake of Pb(II) in the fourth loading cycle by the previously three cycles loaded GAA with M[Cu(0.60)] system.

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Table 5.24: Summary of estimated pseudo-first- and pseudo-second-order rate and kinetic models parameters for three loading cycles with M[Cu(0.60)] system followed by fourth loading cycle with M[Pb(0.60)] system under uncontrolled and controlled pH conditions.

				Pseudo-first-order rate model			Pseudo-second-order rate model		
Uncontrolled pH conditions	Metal ion system (initial conc., meq/L)	Loading cycle	$Q_{e,exp}$ (meq/g)	K_1 (1/min)	Q_{em} (meq/g)	R^2	K_2 (g/meq.min)	Q_{em} (meq/g)	R^2
	M[Cu(0.60)] (0.59±0.01)	1st	0.0435	0.1312	0.0404	0.944	3.6439	0.0444	0.999
		2nd	0.0366	0.1223	0.0335	0.923	3.7515	0.0375	0.998
		3rd	0.0329	0.3151	0.0289	0.968	5.7044	0.0322	0.994
	M[Pb(0.60)] (0.59±0.02)	4th	0.0370	0.1480	0.0311	0.914	2.5817	0.0369	0.990
				Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Controlled pH conditions	Metal ion system (initial conc., meq/L)	Loading cycle	$q_{e,exp}$ (meq/g)	k_1 (1/min)	q_{em} (meq/g)	R^2	k_2 (g/meq.min)	q_{em} (meq/g)	R^2
	M[Cu(0.60)] (0.60±0.01)	1st	0.0232	0.0860	0.0198	0.913	3.5441	0.0236	0.995
		2nd	0.0207	0.0657	0.0183	0.897	3.2755	0.0215	0.995
		3rd	0.0182	0.0940	0.0160	0.914	4.5759	0.0187	0.993
	M[Pb(0.60)] (0.62±0.00)	4th	0.0302	0.0596	0.0285	0.907	2.2114	0.0324	0.995

$Q_{e,exp}$ = experimental metal removal at equilibrium, Q_{em} = metal removal at equilibrium calculated using rate models, $q_{e,exp}$ = experimental metal uptake capacity at equilibrium, q_{em} = metal uptake capacity at equilibrium calculated using kinetic models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with two independent data points.

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In addition, variations in cumulative metal mass removed under uncontrolled pH conditions and cumulative metal mass adsorbed under controlled pH conditions by GAA with three loading cycles with M[Cu(0.60)] systems followed by fourth loading cycle with M[Pb(0.60)] system have been presented in Fig. 5.48. It appeared that the GAA had ability to remove additional amount of Cu(II) metal ions under uncontrolled pH conditions and to uptake additional amount of Cu(II) metal ions under controlled pH conditions during the first three loading cycles. However, the cumulative Cu(II) metal removal under uncontrolled pH conditions and cumulative Cu(II) metal uptake under controlled pH conditions decreased in the fourth loading cycle due to migration of adsorbed Cu(II) metal. The cumulative metal removal under uncontrolled pH conditions and cumulative metal uptake under controlled pH conditions up to fourth loading cycle were observed to be 0.0874 and 0.0551 meq respectively.

5.5.1.2 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for three loading cycles with M[Pb(0.60)] system followed by fourth loading cycle with M[Cu(0.60)] system

The variation in metal removal and solution pH under uncontrolled pH conditions and metal uptake under controlled pH conditions obtained for three loading cycles with M[Pb(0.60)] system followed by fourth loading cycle with M[Cu(0.60)] system are shown in Fig. 5.49 and 5.50 respectively.

Under uncontrolled pH conditions, the solution pH increased to 5.90 within 30 min. of the first loading cycle from initially adjusted pH of 5.00 which decreased to 5.55 around 120 min. and thereafter increased to 5.87 towards the end of the cycle [Fig. 5.49(a)]. Similarly, in the second loading cycle, the solution pH increased to 5.60-5.80 in the beginning and remained at the same level in the middle of the cycle and then decreased to around 5.63 in the last phase of the cycle. In the initial phase of the third loading cycle, the solution pH increased to 5.60 and then reached a value of 5.68 towards the end of the cycle. In the fourth loading cycle, pH of the solution was near to 5.15 in the begining and thereafter it increased gradually to around 5.61 at the end of the cycle. It indicated influence of GAA to raise the solution pH up to third loading cycles while the rising trend of solution pH appeared to get reduced in the fourth loading cycle. Since the solution pH increased beyond 5.50 in the first three loading cycles with M[Pb(0.60)] system and in the fourth loading cycle with

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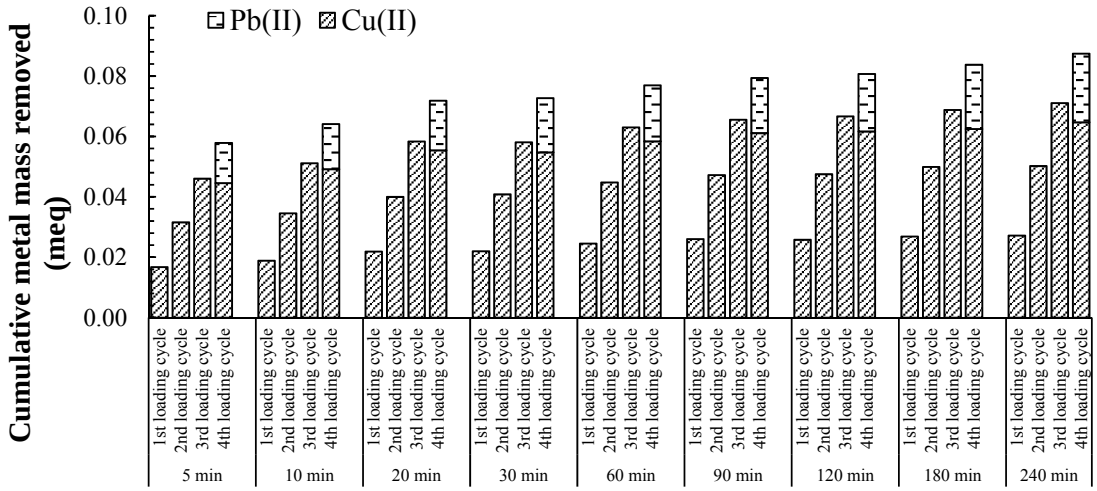
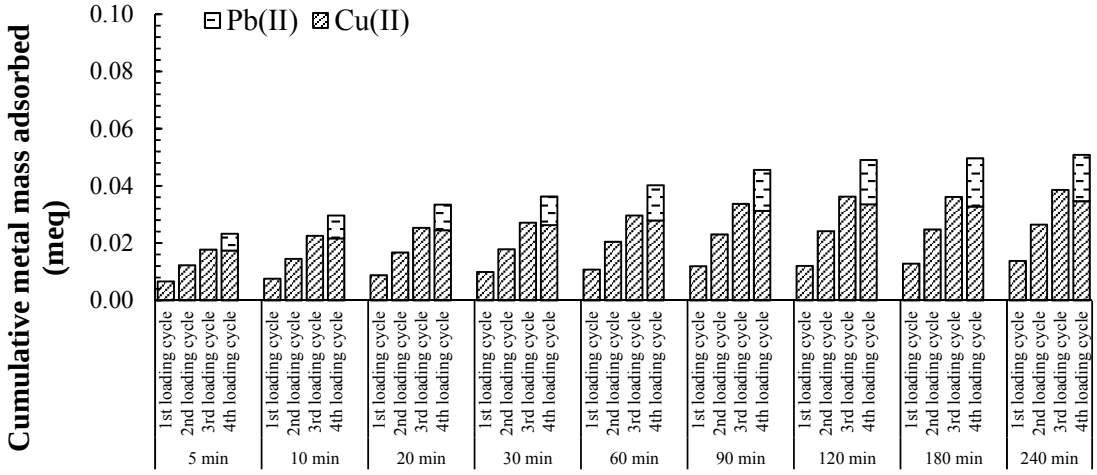


(a)



(b)

Fig. 5.48: Variation in (a) cumulative metal mass removed under uncontrolled pH conditions and (b) cumulative metal mass adsorbed under controlled pH conditions by GAA with three loading cycles with M[Cu(0.60)] system followed by fourth loading cycle with M[Pb(0.60)] system (Each data represents an average of two independent experimental values).

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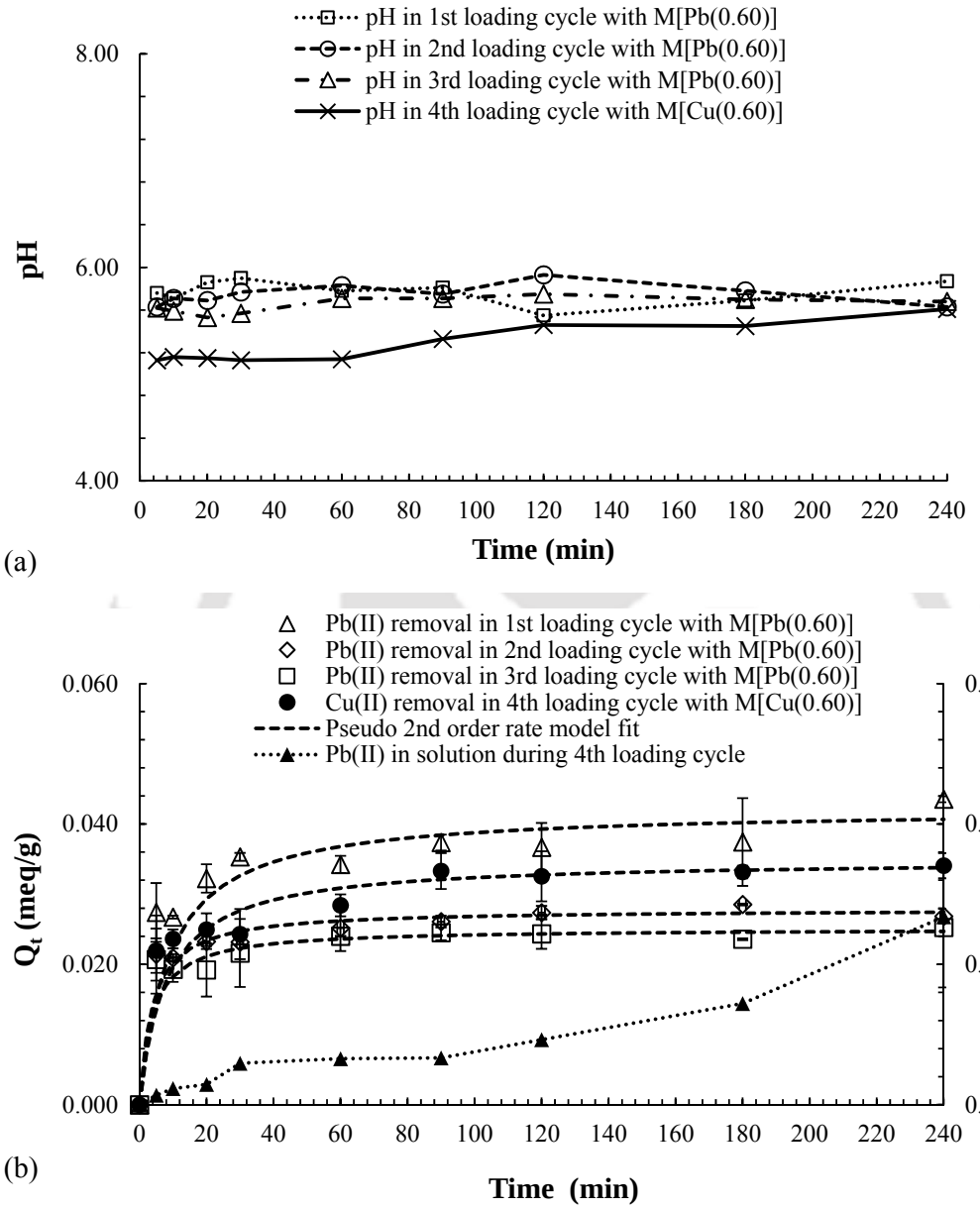

Fig. 5.49: Variation in (a) solution pH and (b) Pb(II) and Cu(II) metal removal in three loading cycles with M[Pb(0.60)] systems followed by fourth loading cycle with M[Cu(0.60)] system under uncontrolled pH conditions {Initial metal conc. in M[Pb(0.60)] = 0.60±0.01 meq/L, M[Cu(0.60)] = 0.59±0.01 meq/L, Initial adjusted pH = 5.00±0.05, Temp. = 30±1 °C, GAA dose = 12 g/L, Mixing speed = 66 rpm} (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

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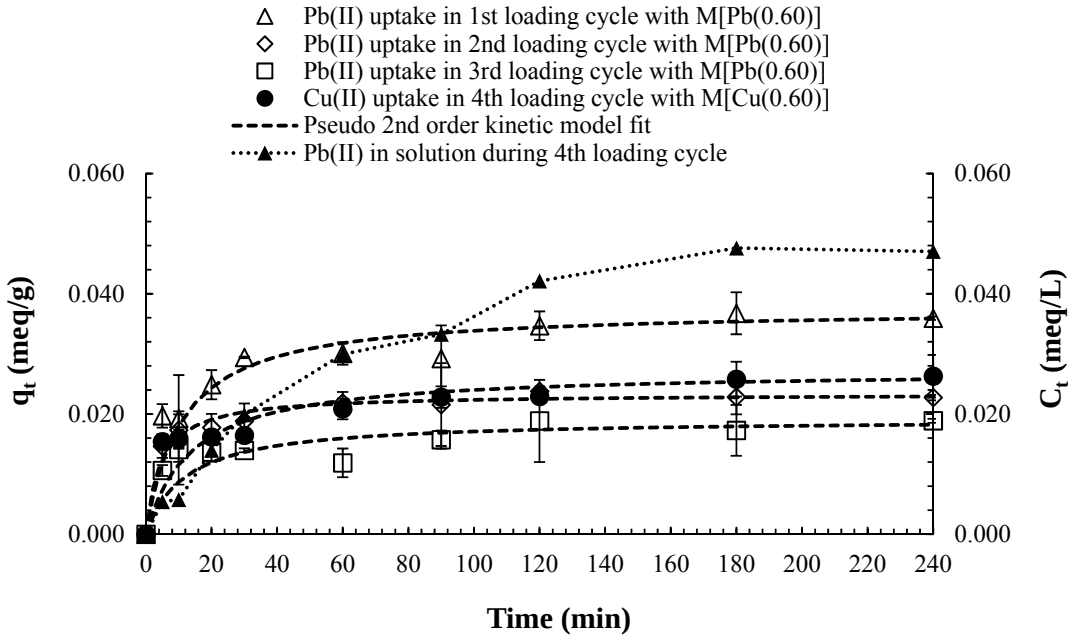

Fig. 5.50: Variation in Pb(II) and Cu(II) metal uptake in three loading cycles with M[Pb(0.60)] systems followed by fourth loading cycle with M[Cu(0.60)] system under controlled pH conditions {Initial metal conc. in M[Pb(0.60)] = 0.61±0.03 meq/L, M[Cu(0.60)] = 0.62±0.00 meq/L, Buffered pH = 5.00±0.01, Temp. = 30±1 °C, GAA dose = 12 g/L, Mixing speed = 66 rpm } (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

M[Cu(0.60)] system, the removal of Pb(II) and Cu(II) metal ions from aqueous phase might be attributed to combined effects of precipitation and adsorption. However, under controlled pH conditions, pH of the solution during each loading cycle remained fixed to the initially buffered pH of 5.00 during course of the experimentation. Hence, the removal of Pb(II) and Cu(II) metal ions from solution might be attributed to adsorption only.

Under uncontrolled pH conditions of loading cycles [Fig. 5.49(b)], rapid Pb(II) metal removal was observed up to first 20 min. of the first loading cycle with M[Pb(0.60)] system. The Pb(II) metal removal was observed to be approximately 0.0322 meq/g at 20 min. of the first loading cycle and approximately 0.0435 meq/g of Pb(II) metal removal was observed towards the end of the cycle. The GAA of the first loading cycle was again loaded with M[Pb(0.60)] system in the second loading cycle. The variation in Pb(II) metal removal during the second loading cycle was observed to be lower than the variation in metal removal observed during the first loading cycle as most of the data points did not overlap at 95%

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confidence interval excluding few data points at the beginning of the cycle. At the end of the second loading cycle, approximately 0.0269 meq/g of Pb(II) metal removal was observed. Similarly, when the GAA of second loading cycle was again loaded with M[Pb(0.60)] system in the third loading cycle, the variation in Pb(II) metal removal increased slowly in the initial phase compared to the first loading cycle. This might be due to reduced capacity of the GAA in raising the solution pH compared to the first loading cycle. The variation in Pb(II) metal removal closely followed the trend of variation obtained in the second loading cycle as most of the data points overlapped at 95% confidence interval. The Pb(II) metal removal was approximately 0.0253 meq/g towards the end of the third loading cycle. In the fourth loading cycle, the GAA of the third loading cycle was exposed to M[Cu(0.60)] system. While studying the fourth loading cycle, efforts were made to estimate residual concentration of Pb(II) metal ions in the bulk solution along with Cu(II) metal removal [Fig. 5.49(b)]. It indicated rise in concentration of migrated Pb(II) metal ions in the bulk solution with cycle time and Pb(II) concentration was observed to be approximately 0.03 meq/L towards the end of the loading cycle. It indicated migration of a part of accumulated Pb(II) metal from the surface of GAA under the experimental conditions of the fourth loading cycle. The observed variation in Cu(II) metal removal was higher than Pb(II) metal removal observed during the second and third loading cycles. The Cu(II) metal removal was observed approximately 0.0341 meq/g towards the end of the fourth loading cycle.

Under controlled pH conditions of first loading cycle with M[Pb(0.60)] system (Fig. 5.50), Pb(II) metal uptake of approximately 0.0193 meq/g was observed up to the first 10 min. of the loading cycle and approximately 0.0359 meq/g of Pb(II) metal uptake was observed towards the end of the cycle. The GAA of the first loading cycle was again loaded with M[Pb(0.60)] system in the second loading cycle. Here, it was important to note that the GAA surface had already accumulated some amount of Pb(II) metal ions on its surface from the first loading cycle thereby developing lower concentration gradient in the second loading cycle compared to the first loading cycle. The variation in Pb(II) metal uptake during the second loading cycle was lower compared to the variation in metal uptake observed during the first loading cycle. At the end of the second loading cycle, approximately 0.0227 meq/g of Pb(II) metal uptake was observed. Similarly, when the GAA of the second loading cycle was again loaded with M[Pb(0.60)] system in the third loading cycle, the developed concentration gradient might have been lower than the second loading cycle due to additional

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accumulation of Pb(II) metal ions on the GAA surfaces. The observed variation in Pb(II) metal uptake was lower compared to the variation in metal uptake observed in the second loading cycle. The equilibrium Pb(II) metal uptake was approximately 0.0189 meq/g in the third loading cycle. In the fourth loading cycle, the GAA of the third loading cycle was exposed to M[Cu(0.60)] system. In this cycle, attention was paid to the two metal ions present in the experimental mixture and efforts were made to estimate residual concentration of Pb(II) metal ions in the bulk solution along with Cu(II) metal uptake. The concentration of migrated Pb(II) metal ions in the bulk solution increased with cycle time and concentration was observed to be approximately 0.05 meq/L towards the end of the loading cycle. It indicated migration of a part of accumulated Pb(II) metal from the surface of GAA under the experimental conditions of the fourth loading cycle. The observed variation in Cu(II) metal uptake was higher than Pb(II) metal uptake observed during the third loading cycle while most of the data points of Cu(II) metal uptake overlapped at 95% confidence interval with the Pb(II) metal uptake obtained during second loading cycle. A higher equilibrium Cu(II) metal uptake of approximately 0.0263 meq/g was observed in the fourth loading cycle compared to equilibrium Pb(II) uptakes in the second and third loading cycles.

The variations in metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions carried out for four loading cycles were fitted to pseudo-first- and pseudo-second-order rate and kinetic models. The estimated rate and kinetic model parameters are presented in Table 5.25. The higher R^2 values for pseudo-second-order rate model indicated its suitability to describe metal removal under uncontrolled pH conditions and pseudo-second-order kinetic model for metal uptake under controlled pH conditions. The best fit plots of pseudo-second-order rate and kinetic models to experimental metal removal and metal uptake data are also presented in Fig. 5.49(b) and 5.50 respectively. An inspection of Table 5.25 revealed decreasing trend in values of $Q_{e,exp}$ and $q_{e,exp}$ as well as Q_{em} and q_{em} with increase in number of loading cycles with M[Pb(0.60)] systems. However, the values of $Q_{e,exp}$, Q_{em}, $q_{e,exp}$ and q_{em} for the fourth loading cycle with M[Cu(0.60)] system under uncontrolled and controlled pH conditions were higher compared to similar values obtained with the second and third loading cycles with M[Pb(0.60)] system. It indicated preferential removal and uptake of Cu(II) in the fourth loading cycle by the previously three cycles loaded GAA with M[Pb(0.60)] system.

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Table 5.25: Summary of estimated pseudo-first and pseudo-second-order rate and kinetic models parameters for three loading cycles with M[Pb(0.60)] system followed by fourth loading cycle with M[Cu(0.60)] system under uncontrolled and controlled pH conditions.

				Pseudo-first-order rate model			Pseudo-second-order rate model		
Uncontrolled pH conditions	Metal ion system (initial conc., meq/L)	Loading cycle	$Q_{e,exp}$ (meq/g)	K_1 (1/min)	Q_{em} (meq/g)	R^2	K_2 (g/meq.min)	Q_{em} (meq/g)	R^2
	M[Pb(0.60)] (0.60±0.01)	1st	0.0435	0.1420	0.0366	0.905	2.7256	0.0421	0.988
		2nd	0.0269	0.1293	0.0271	0.872	9.4504	0.0279	0.997
		3rd	0.0253	0.0801	0.0250	0.751	10.6258	0.0251	0.998
	M[Cu(0.60)] (0.59±0.01)	4th	0.0341	0.0938	0.0320	0.847	3.6777	0.0349	0.997
				Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Controlled pH conditions	Metal ion system (initial conc., meq/L)	Loading cycle	$q_{e,exp}$ (meq/g)	k_1 (1/min)	q_{em} (meq/g)	R^2	k_2 (g/meq.min)	q_{em} (meq/g)	R^2
	M[Pb(0.60)] (0.61±0.03)	1st	0.0359	0.0694	0.0331	0.897	2.4818	0.0375	0.993
		2nd	0.0227	0.1376	0.0218	0.927	9.6746	0.0233	0.998
		3rd	0.0189	0.1059	0.0170	0.792	4.3813	0.0191	0.981
	M[Cu(0.60)] (0.62±0.00)	4th	0.0263	0.0582	0.0241	0.809	2.7321	0.0272	0.993

$Q_{e,exp}$ = experimental metal removal at equilibrium, Q_{em} = metal removal at equilibrium calculated using rate models, $q_{e,exp}$ = experimental metal uptake capacity at equilibrium, q_{em} = metal uptake capacity at equilibrium calculated using kinetic models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with two independent data points.

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In addition, variations in cumulative metal mass removed under uncontrolled pH conditions and cumulative metal mass adsorbed under controlled pH conditions by GAA with three loading cycles with M[Pb(0.60)] systems followed by fourth loading cycle with M[Cu(0.60)] system have been presented in Fig. 5.51. It appeared that the GAA had ability to remove additional amount of Pb(II) metal ions under uncontrolled pH conditions and to uptake additional amount of Pb(II) metal ions under controlled pH conditions during the first three loading cycles. However, the cumulative Pb(II) metal removal under uncontrolled pH conditions and cumulative Pb(II) metal uptake under controlled pH conditions decreased in the fourth loading cycle due to migration of adsorbed Pb(II) metal. The cumulative metal removal under uncontrolled pH conditions and cumulative metal uptake under controlled pH conditions up to fourth loading cycle were observed to be 0.0764 and 0.0580 meq respectively.

5.5.2 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for four loading cycles with mono-metal ion systems comprising of Cr(III) and Pb(II) ions

The kinetic studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions by GAA from mono-metal ion systems of M[Cr(0.60) and M[Pb(0.60)] were investigated. The studies were carried out in the first set by exposing the virgin GAA to consecutive three loading cycles with M[Cr(0.60)] system followed by fourth loading cycle with M[Pb(0.60)] system and in the second set, three loading cycles with M[Pb(0.60)] system followed by fourth loading cycle with M[Cr(0.60)] system. The results are discussed in following sub-sections.

5.5.2.1 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for three loading cycles with M[Cr(0.60)] system followed by fourth loading cycle with M[Pb(0.60)] system

The variation in metal removal and solution pH under uncontrolled pH conditions and metal uptake under controlled pH conditions obtained for three loading cycles with M[Cr(0.60)] system followed by fourth loading cycle with M[Pb(0.60)] system are shown in Fig. 5.52 and 5.53 respectively.

Under uncontrolled pH conditions, pH of the solution increased up to 6.90 within 30 min. of the first loading cycle from initially adjusted pH of 5.00 which then decreased to 6.50

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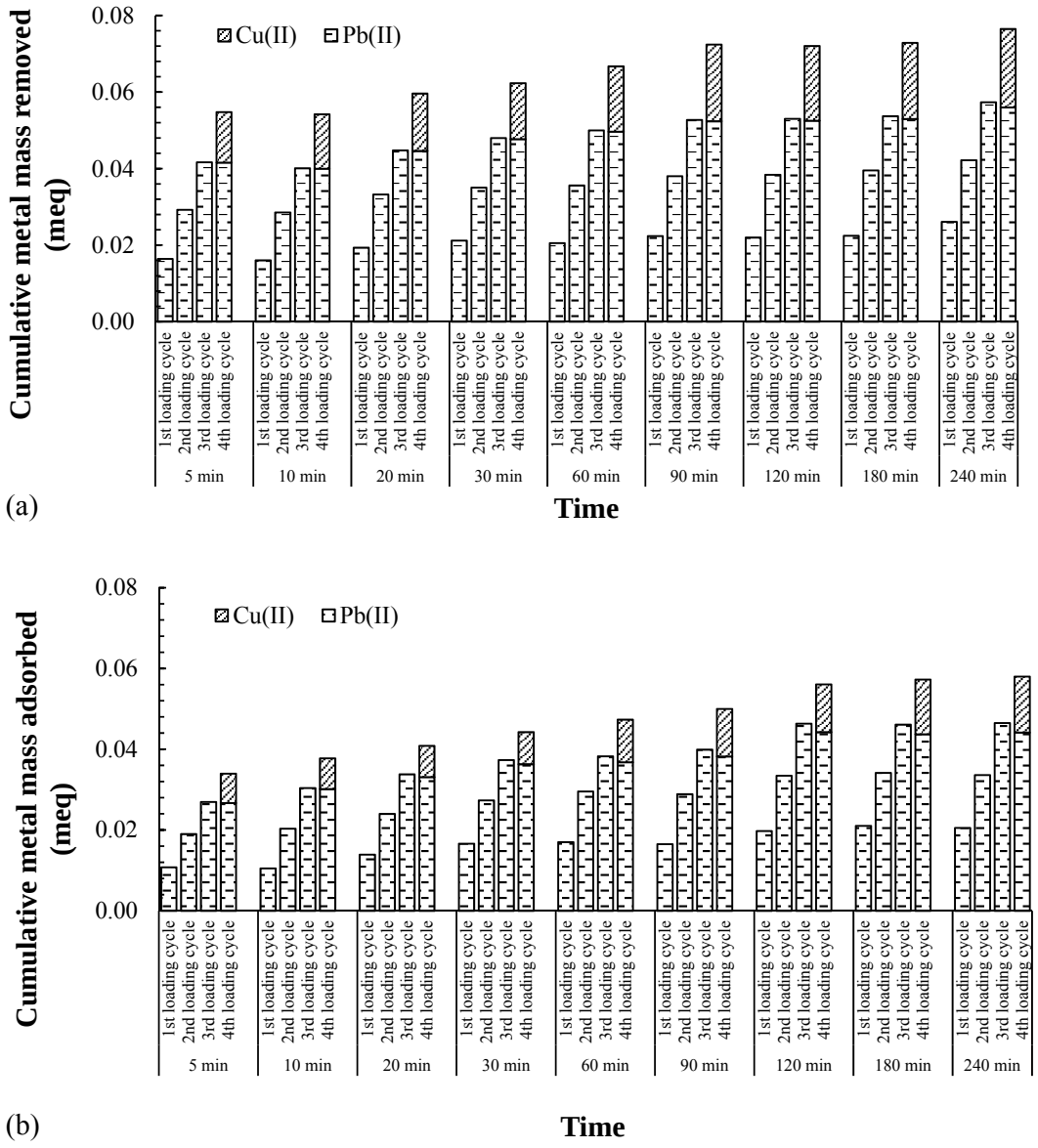

Fig. 5.51: Variation in (a) cumulative metal mass removed under uncontrolled pH conditions and (b) cumulative metal mass adsorbed under controlled pH conditions by GAA with three loading cycles with M[Pb(0.60)] system followed by fourth loading cycle with M[Cu(0.60)] system (Each data represents an average of two independent experimental values).

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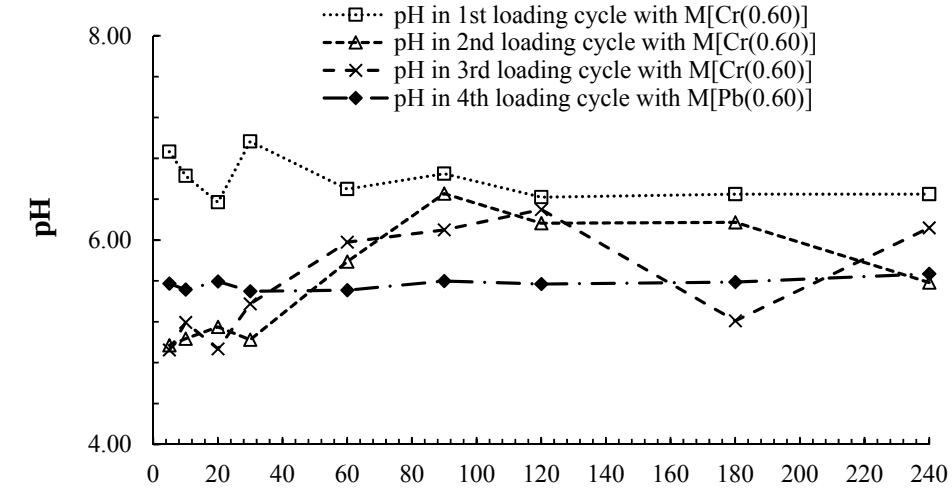
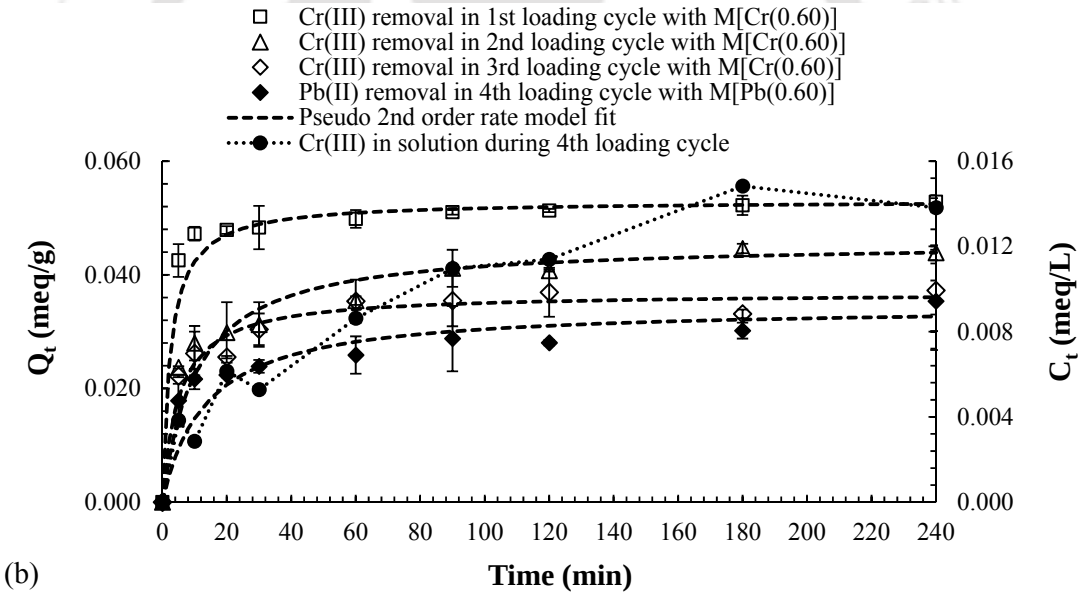


(a)



(b)

Fig. 5.52: Variation in (a) solution pH and (b) Cr(III) and Pb(II) metal removal in three loading cycles with M[Cr(0.60)] systems followed by fourth loading cycle with M[Pb(0.60)] system under uncontrolled pH conditions {Initial metal conc. in M[Cr(0.60)] = 0.62±0.02 meq/L, M[Pb(0.60)] = 0.58±0.01 meq/L, Initial adjusted pH = 5.00±0.10, Temp. = 30±1 °C, GAA dose = 12 g/L, Mixing speed = 66 rpm} (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

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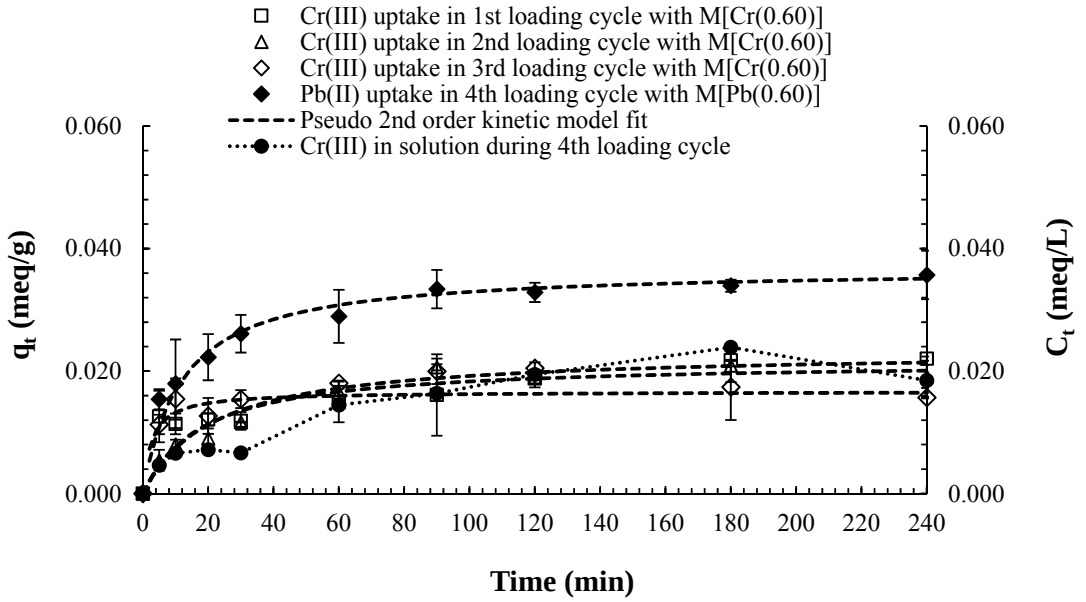

Fig. 5.53: Variation in Cr(III) and Pb(II) metal uptake in three loading cycles with M[Cr(0.60)] systems followed by fourth loading cycle with M[Pb(0.60)] system under controlled pH conditions {Initial metal conc. in M[Cr(0.60)] = 0.61±0.01 meq/L, M[Pb(0.60)] = 0.60±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1 ^{o}C, GAA dose = 12 g/L, Mixing speed = 66 rpm} (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

and remained almost at the same level till the end of the cycle [Fig. 5.52(a)]. Similarly, in the second loading cycle, pH of the solution was near to 5.00 during initial 30 min. of cycle and thereafter fluctuated in the range of 5.59-6.45 in the later phase of the cycle. During the third loading cycle, pH of the solution remained near to 5.00 till initial 20 min. of cycle and gradually increased to 6.10-6.30 during middle of the cycle and then decreased to 6.12 towards the end of the cycle. In the fourth loading cycle, the solution pH increased to a value near to 5.67 in the beginning and remained at the same level towards the end of the cycle. It indicated influence of GAA to raise the solution pH up to third loading cycles while the rising trend of solution pH appeared to get reduced in the fourth loading cycle. Since the solution pH increased beyond 5.50 in the first three loading cycles with M[Cr(0.60)] system and in the fourth loading cycle with M[Pb(0.60)] system, the removal of Cr(III) and Pb(II) metal ions from aqueous phase might be attributed to combined effects of precipitation and adsorption. However, under controlled pH conditions, pH of the solution during each loading cycle remained fixed to the initially buffered pH of 5.00 during course of the experimentation.

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Hence, the removal of Cr(III) and Pb(II) metal ions from solution might be attributed to adsorption only.

Under uncontrolled pH conditions of loading cycles [Fig. 5.52(b)], rapid Cr(III) metal removal was observed up to first 10 min. of the first loading cycle with M[Cr(0.60)] system. The Cr(III) metal removal was observed to be approximately 0.0470 meq/g at 10 min. of the first loading cycle and approximately 0.0528 meq/g of Cr(III) metal removal was observed towards the end of the cycle. The GAA of the first loading cycle was again loaded with M[Cr(0.60)] system in the second loading cycle. The variation in Cr(III) metal removal during the second loading cycle was observed to be lower than the variation in metal removal observed during the first loading cycle. At the end of the second loading cycle, approximately 0.0439 meq/g of Cr(III) metal removal was observed. Similarly, when the GAA of second loading cycle was again loaded with M[Cr(0.60)] system in the third loading cycle, Cr(III) metal removal was 0.0260 meq/g for the first 5 min. of the cycle while the metal removal was approximately 0.0372 meq/g towards the end of the loading cycle. In the fourth loading cycle, the GAA of the third loading cycle was exposed to M[Pb(0.60)] system. In this cycle, attention was paid to the two metal ions present in the experimental mixture and efforts were made to estimate residual concentration of Cr(III) metal ions in the bulk solution along with Pb(II) metal removal [Fig. 5.52(b)]. The concentration of migrated Cr(III) metal ions in the bulk solution was observed to increase with cycle time and its concentration was approximately 0.01 meq/L towards the end of the loading cycle which indicated migration of a part of accumulated Cr(III) metal from the surface of GAA under the experimental conditions of the fourth loading cycle. The observed Pb(II) metal removal was close to observed Cr(III) metal removal during the third loading cycle as data points overlapped at 95% confidence interval. The Pb(II) metal removal was observed approximately 0.0357 meq/g towards the end of the fourth loading cycle.

Under controlled pH conditions of the first loading cycle with M[Cr(0.60)] system (Fig. 5.53), Cr(III) metal uptake of approximately 0.0100 meq/g was observed up to 10 min. of the first loading cycle and approximately 0.0220 meq/g of Cr(III) metal uptake was observed towards the end of the cycle. The GAA of the first loading cycle was again loaded with M[Cr(0.60)] system in the second loading cycle. The variation in Cr(III) metal uptake during the second loading cycle overlapped at 95% confidence interval with the variation in

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metal uptake observed during the first loading cycle. At the end of the second loading cycle, approximately 0.0191 meq/g of Cr(III) metal uptake was observed. Similarly, when the GAA of the second loading cycle was again loaded with M[Cr(0.60)] system in the third loading cycle, the observed variation in Cr(III) metal uptake overlapped at 95% confidence interval with the variation in metal uptake observed in the second loading cycle. The equilibrium Cr(III) metal uptake was approximately 0.0157 meq/g in the third loading cycle. In the fourth loading cycle, the GAA of the third loading cycle was exposed to M[Pb(0.60)] system. In this cycle, attention was paid to the two metal ions present in the experimental mixture and efforts were made to estimate residual concentration of Cr(III) metal ions in the bulk solution along with Pb(II) metal uptake. The concentration of migrated Cr(III) metal ions in the bulk solution was observed to increase with cycle time and its concentration was approximately 0.02 meq/L towards the end of the loading cycle. It indicated migration of a part of accumulated Cr(III) metal from the surface of GAA under the experimental conditions of the fourth loading cycle. The significantly higher Pb(II) metal uptake was observed in the fourth loading cycle as data points did not overlap at 95% confidence interval with the first three loading cycles. The Pb(II) metal uptake of 0.0357 meq/g was observed towards the end of the fourth loading cycle which was much higher compared to Cr(III) metal uptakes during previous three loading cycles.

The variations in metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions carried out for four loading cycles were fitted to pseudo-first- and pseudo-second-order rate and kinetic models. The estimated rate and kinetic model parameters are presented in Table 5.26. The higher R^2 values for pseudo-second-order rate model indicated its suitability to describe metal removal under uncontrolled pH conditions and pseudo-second-order kinetic model for metal uptake under controlled pH conditions. The best fit plots of pseudo-second-order rate and kinetic models to experimental metal removal and metal uptake data are also presented in Fig. 5.52(b) and 5.53 respectively. An inspection of Table 5.26 revealed decreasing trend in values of $Q_{e,exp}$ and $q_{e,exp}$ as well as Q_{em} and q_{em} with increase in number of loading cycles with M[Cr(0.60)] systems. However, the values of $Q_{e,exp}$ and Q_{em} for the fourth loading cycle with M[Pb(0.60)] system under uncontrolled pH conditions were lower compared to values obtained with the third loading cycle while the values of $q_{e,exp}$ and q_{em} for the fourth loading cycle with M[Pb(0.60)] system under controlled pH conditions were significantly higher compared to similar values obtained with the

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Table 5.26: Summary of estimated pseudo-first- and pseudo-second-order rate and kinetic models parameters for three loading cycles with M[Cr(0.60)] system followed by fourth loading cycle with M[Pb(0.60)] system under uncontrolled and controlled pH conditions.

				Pseudo-first-order rate model			Pseudo-second-order rate model		
Uncontrolled pH conditions	Metal ion system (initial conc., meq/L)	Loading cycle	$Q_{e,exp}$ (meq/g)	K_1 (1/min)	Q_{em} (meq/g)	R^2	K_2 (g/meq.min)	Q_{em} (meq/g)	R^2
	M[Cr(0.60)] (0.62±0.02)	1st	0.0528	0.4483	0.0502	0.986	7.4995	0.0530	0.999
		2nd	0.0439	0.0853	0.0399	0.884	2.1030	0.0458	0.997
		3rd	0.0372	0.1143	0.0341	0.910	5.3337	0.0368	0.994
	M[Pb(0.60)] (0.58±0.01)	4th	0.0353	0.1308	0.0275	0.874	2.1668	0.0345	0.983
				Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Controlled pH conditions	Metal ion system (initial conc., meq/L)	Loading cycle	$q_{e,exp}$ (meq/g)	k_1 (1/min)	q_{em} (meq/g)	R^2	k_2 (g/meq.min)	q_{em} (meq/g)	R^2
	M[Cr(0.60)] (0.61±0.01)	1st	0.0220	0.0233	0.0215	0.768	2.0223	0.0233	0.979
		2nd	0.0191	0.0336	0.0208	0.969	2.5879	0.0216	0.985
		3rd	0.0157	0.1060	0.0189	0.837	23.5219	0.0166	0.983
	M[Pb(0.60)] (0.60±0.01)	4th	0.0357	0.0667	0.0315	0.947	2.3145	0.0368	0.996

$Q_{e,exp}$ = experimental metal removal at equilibrium, Q_{em} = metal removal at equilibrium calculated using rate models, $q_{e,exp}$ = experimental metal uptake capacity at equilibrium, q_{em} = metal uptake capacity at equilibrium calculated using kinetic models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with two independent data points.

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previous three loading cycles. It indicated preferential removal and uptake of Pb(II) in the fourth loading cycle with M[Pb(0.60)] system by the previously three cycle loaded GAA with M[Cr(0.60)] system.

In addition, variations in cumulative metal mass removed under uncontrolled pH conditions and cumulative metal mass adsorbed under controlled pH conditions by GAA with three loading cycles with M[Cr(0.60)] systems followed by fourth loading cycle with M[Pb(0.60)] system have been presented in Fig. 5.54. It appeared that the GAA had ability to remove additional amount of Cr(III) metal ions under uncontrolled pH conditions and to uptake additional amount of Cr(III) metal ions under controlled pH conditions during the first three loading cycles. However, the cumulative Cr(III) metal removal under uncontrolled pH conditions and cumulative Cr(III) metal uptake under controlled pH conditions decreased in the fourth loading cycle due to migration of adsorbed Cr(III) metal. The cumulative metal removal under uncontrolled pH conditions and cumulative metal uptake under controlled pH conditions up to fourth loading cycle were observed to be 0.1002 and 0.0517 meq respectively.

5.5.2.2 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for three loading cycles with M[Pb(0.60)] system followed by fourth loading cycle with M[Cr(0.60)] system

The variation in metal removal and solution pH under uncontrolled pH conditions and metal uptake under controlled pH conditions obtained for three loading cycles with M[Pb(0.60)] system followed by fourth loading cycle with M[Cr(0.60)] system are shown in Fig. 5.55 and 5.56 respectively.

Under uncontrolled pH conditions, pH of the solution increased up to 5.70 within 5 min. of the first loading cycle from initially adjusted pH of 5.00 which then decreased to 5.45 and thereafter fluctuated in the range of 5.62-5.88 in the later phase of the cycle [Fig. 5.55(a)]. Similarly, in the second loading cycle, pH of the solution increased beyond 5.90 within first 10 min. of the loading cycle and thereafter fluctuated in the range of 5.80-6.00 till the end of the cycle. During the third loading cycle, the solution pH remained within a range of 5.65-5.75 till 120 min. of the cycle but increased to 5.85 towards the end of the cycle. In the fourth loading cycle, the solution pH fluctuated in the range of 5.63-5.85 during entire

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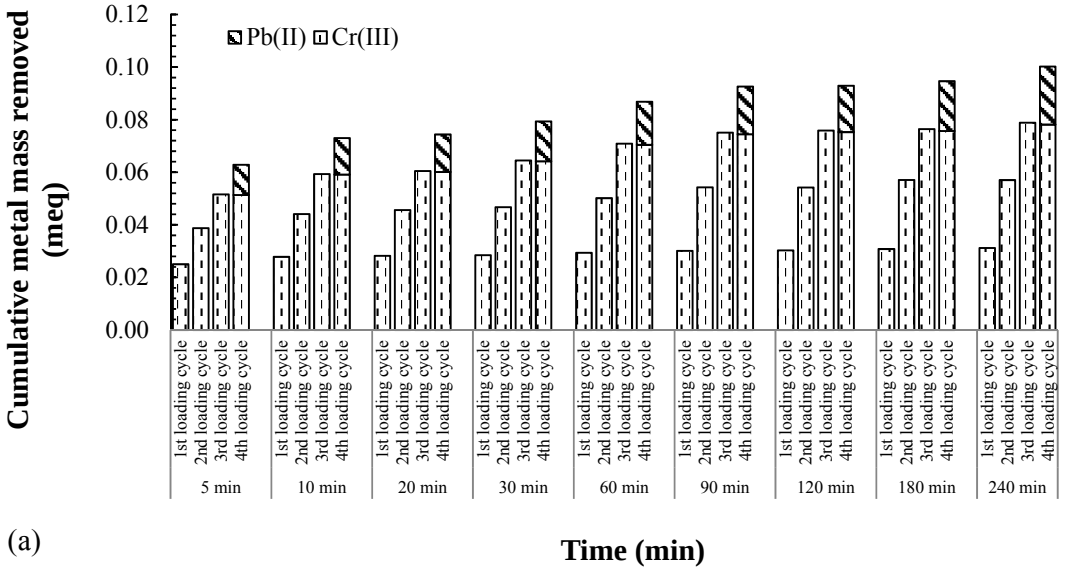
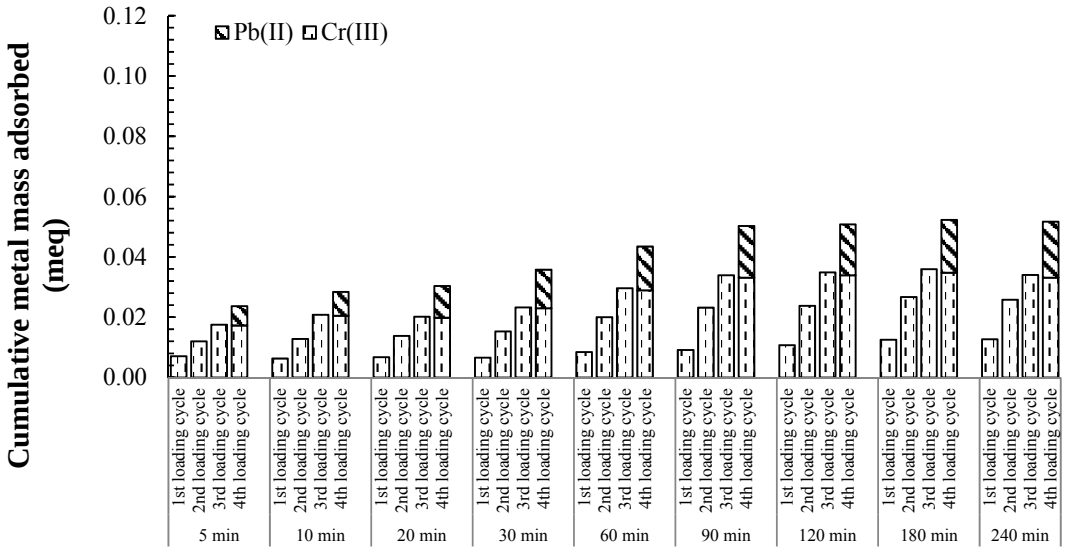


(a)



(b)

Fig. 5.54: Variation in (a) cumulative metal mass removed under uncontrolled pH conditions and (b) cumulative metal mass adsorbed under controlled pH conditions by GAA with three loading cycles with M[Cr(0.60)] system followed by fourth loading cycle with M[Pb(0.60)] system (Each data represents an average of two independent experimental values).

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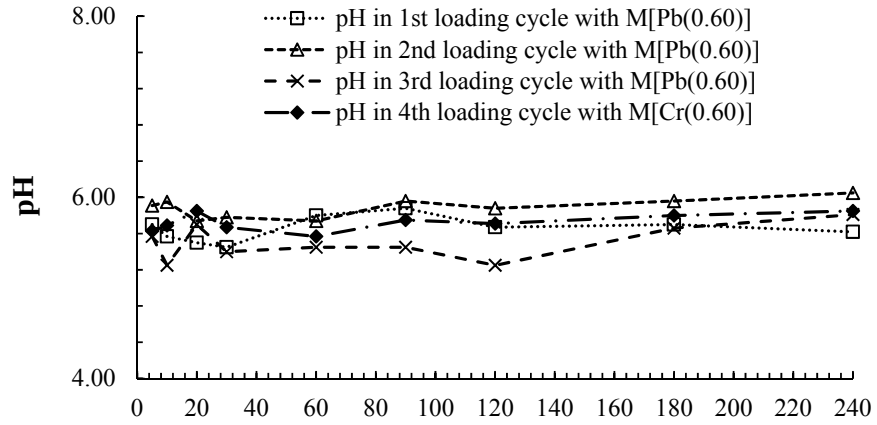
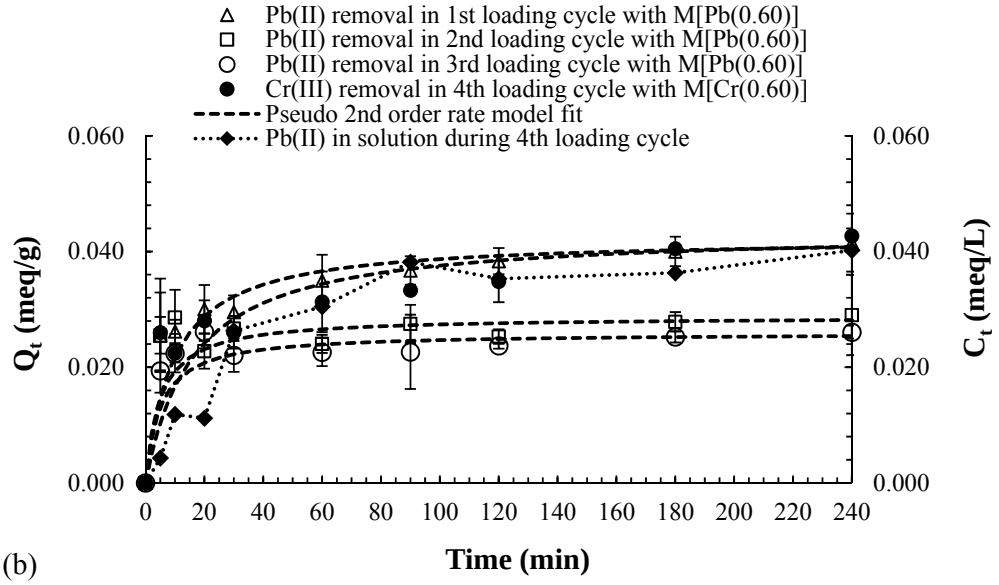


(a)



(b)

Fig. 5.55: Variation in (a) solution pH and (b) Pb(II) and Cr(III) metal removal in three loading cycles with M[Pb(0.60)] systems followed by fourth loading cycle with M[Cr(0.60)] system under uncontrolled pH conditions {Initial metal conc. in M[Pb(0.60)] = 0.58±0.01 meq/L, M[Cr(0.60)] = 0.62±0.02 meq/L, Initial adjusted pH = 5.00±0.03, Temp. = 30±1 °C, GAA dose = 12 g/L, Mixing speed = 66 rpm} (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

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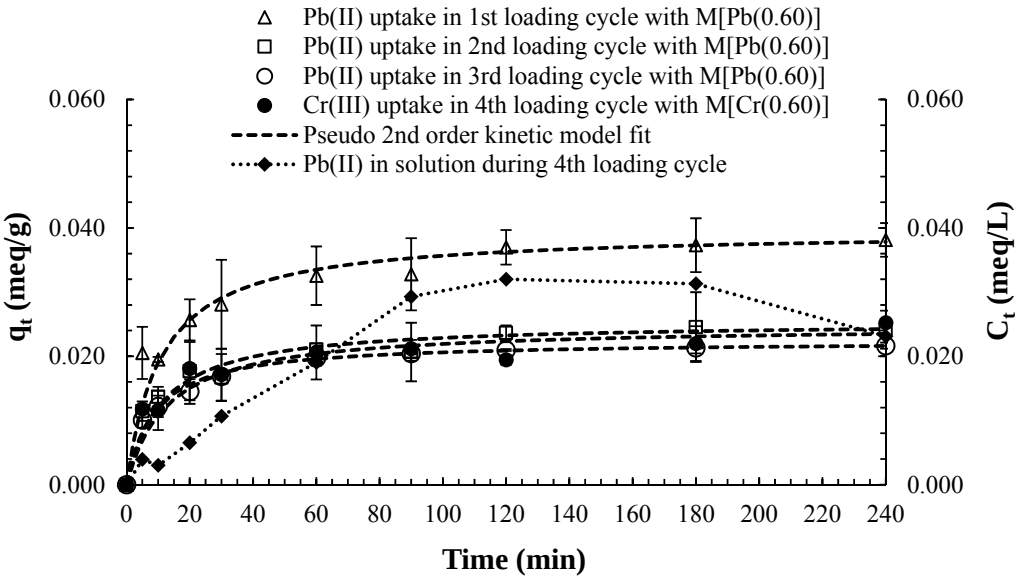

Fig. 5.56: Variation in Pb(II) and Cr(III) metal uptake in three loading cycles with M[Pb(0.60)] systems followed by fourth loading cycle with M[Cr(0.60)] system under controlled pH conditions {Initial metal conc. in M[Pb(0.60)] = 0.62±0.02 meq/L, M[Cr(0.60)] = 0.61±0.02 meq/L, Buffered pH = 5.00±0.04, Temp. = 30±1 ºC, GAA dose = 12 g/L, Mixing speed = 66 rpm} (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

duration of the cycle. It indicated influence of GAA to raise the solution pH up to fourth loading cycles. Since the solution pH increased beyond 5.50 in the first three loading cycles with M[Pb(0.60)] system and in the fourth loading cycle with M[Cr(0.60)] system, the removal of Pb(II) and Cr(III) metal ions from aqueous phase might be attributed to combined effects of precipitation and adsorption. However, under controlled pH conditions, pH of the solution during each loading cycle remained fixed to the initially buffered pH of 5.00 during course of the experimentation. Hence, the removal of Pb(II) and Cr(III) metal ions from solution might be attributed to adsorption only.

Under uncontrolled pH conditions of loading cycles [Fig. 5.55(b)], rapid Pb(II) metal removal was observed up to 20 min. of the first loading cycle with M[Pb(0.60)] system. The Pb(II) metal removal was observed to be approximately 0.0300 meq/g at 20 min. of the first loading cycle and approximately 0.0415 meq/g of Pb(II) metal removal was observed towards the end of the cycle. The GAA of the first loading cycle was again loaded with M[Pb(0.60)] system in the second loading cycle. The variation in Pb(II) metal removal during

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the second loading cycle was observed to be lower than the variation in metal removal observed during the first loading cycle as most of the data points beyond 30 min. of the cycle did not overlap at 95% confidence interval. At the end of the second loading cycle, approximately 0.0290 meq/g of Pb(II) metal removal was observed. Similarly, when the GAA of second loading cycle was again loaded with M[Pb(0.60)] system in the third loading cycle, the variation in Pb(II) metal removal closely followed trend of metal removal from the second loading cycle as the data points overlapped at 95% confidence interval. The Pb(II) metal removal was approximately 0.0261 meq/g towards the end of the third loading cycle. In the fourth loading cycle, the GAA of the third loading cycle was exposed to M[Cr(0.60)] system. In this cycle, attention was paid to the two metal ions present in the experimental mixture and efforts were made to estimate residual concentration of Pb(II) metal ions in the bulk solution along with Cr(III) metal removal [Fig. 5.55(b)]. The concentration of migrated Pb(II) metal ions in the bulk solution was observed to increase with cycle time and its concentration was approximately 0.04 meq/L towards the end of the loading cycle. It indicated migration of a part of accumulated Pb(II) metal from the surface of GAA under the experimental conditions of the fourth loading cycle. The variation in Cr(III) metal removal closely followed Pb(II) metal removal observed during the first loading cycle. The Cr(III) metal removal was observed approximately 0.0427 meq/g towards the end of the fourth loading cycle.

Under controlled pH conditions of the first loading cycle with M[Pb(0.60)] system (Fig. 5.56), Pb(II) metal uptake of approximately 0.0256 meq/g was observed up to the first 20 min. of the loading cycle and approximately 0.0381 meq/g of Pb(II) metal uptake was observed towards the end of the cycle. The GAA of the first loading cycle was again loaded with M[Pb(0.60)] system in the second loading cycle. Here, it was important to note that the GAA surface had already accumulated some amount of Pb(II) metal ions on its surface from the first loading cycle thereby developing lower concentration gradient in the second loading cycle compared to the first loading cycle. The variation in Pb(II) metal uptake during the second loading cycle was lower compared to the variation in metal uptake observed during the first loading cycle as most of the data points did not overlap at 95% confidence interval. At the end of the second loading cycle, approximately 0.0242 meq/g of Pb(II) metal uptake was observed. Similarly, when the GAA of the second loading cycle was again loaded with M[Pb(0.60)] system in the third loading cycle, the developed concentration gradient might be

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lower than the second loading cycle due to additional accumulation of Pb(II) metal ions on the GAA surface. The variation in Pb(II) metal uptake was observed to overlap at 95% confidence interval with the same from the second loading cycle indicating migration of same amount of Pb(II) metal on to GAA surface. The equilibrium Pb(II) metal uptake was approximately 0.0216 meq/g in the third loading cycle. In the fourth loading cycle, the GAA of the third loading cycle was exposed to M[Cr(0.60)] system. In this cycle, attention was paid to the two metal ions present in the experimental mixture and efforts were made to estimate residual concentration of Pb(II) metal ions in the bulk solution along with Cr(III) metal uptake. The concentration of migrated Pb(II) metal ions in the bulk solution was observed to increase with cycle time up to 120 min. and showed decreasing trend after 180 min. The Pb(II) concentration of approximately 0.02 meq/L was observed towards the end of the loading cycle. It indicated migration of a part of accumulated Pb(II) metal from the surface of GAA under the experimental conditions of the fourth loading cycle. The variation in Cr(III) metal uptake in the fourth loading cycle closely followed Pb(II) uptakes during second and third loading cycles.

The variations in metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions carried out for four loading cycles were fitted to pseudo-first- and pseudo-second-order rate and kinetic models. The estimated rate and kinetic model parameters are presented in Table 5.27. The higher R^2 values for pseudo-second-order rate model indicated its suitability to describe metal removal under uncontrolled pH conditions and pseudo-second-order kinetic model for metal uptake under controlled pH conditions. The best fit plots of pseudo-second-order rate and kinetic models to experimental metal removal and metal uptake data are also presented in Fig. 5.55(b) and 5.56 respectively. An inspection of Table 5.27 revealed decreasing trend in values of $Q_{e,exp}$ and $q_{e,exp}$ as well as Q_{em} and q_{em} with increase in number of loading cycles with M[Pb(0.60)] systems. However, the values of $Q_{e,exp}$ and Q_{em} for the fourth loading cycle with M[Cr(0.60)] system under uncontrolled pH conditions were higher compared to similar values obtained with the previous three loading cycles with M[Pb(0.60)] system while the values of $q_{e,exp}$ and q_{em} for the fourth loading cycle with M[Cr(0.60)] system under controlled pH conditions were approximately similar to the values obtained from the second loading cycle with M[Pb(0.60)] system. It indicated preferential removal and uptake of Cr(III) in the fourth loading cycle with M[Cr(0.60)] system by the previously three cycles loaded GAA with M[Pb(0.60)] system.

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Table 5.27: Summary of estimated pseudo-first- and pseudo-second-order rate and kinetic models parameters for three loading cycles with M[Pb(0.60)] system followed by fourth loading cycle with M[Cr(0.60)] system under uncontrolled and controlled pH conditions.

				Pseudo-first-order rate model			Pseudo-second-order rate model		
Uncontrolled pH conditions	Metal ion system (initial conc., meq/L)	Loading cycle	$Q_{e,exp}$ (meq/g)	K_1 (1/min)	Q_{em} (meq/g)	R^2	K_2 (g/meq.min)	Q_{em} (meq/g)	R^2
	M[Pb(0.60)] (0.58±0.01)	1st	0.0415	0.0945	0.0370	0.871	2.5210	0.0423	0.997
		2nd	0.0290	0.0616	0.0308	0.490	7.1702	0.0287	0.995
		3rd	0.0261	0.2803	0.0243	0.963	7.7765	0.0259	0.996
	M[Cr(0.60)] (0.62±0.02)	4th	0.0427	0.0424	0.0401	0.753	1.4327	0.0436	0.985
				Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Controlled pH conditions	Metal ion system (initial conc., meq/L)	Loading cycle	$q_{e,exp}$ (meq/g)	k_1 (1/min)	q_{em} (meq/g)	R^2	k_2 (g/meq.min)	q_{em} (meq/g)	R^2
	M[Pb(0.60)] (0.62±0.02)	1st	0.0381	0.0625	0.0352	0.909	2.3603	0.0395	0.997
		2nd	0.0242	0.0787	0.0216	0.921	3.6385	0.0254	0.995
		3rd	0.0216	0.0778	0.0206	0.958	5.1746	0.0224	0.999
	M[Cr(0.60)] (0.61±0.02)	4th	0.0252	0.0789	0.0215	0.910	3.1482	0.0248	0.984

$Q_{e,exp}$ = experimental metal removal at equilibrium, Q_{em} = metal removal at equilibrium calculated using rate models, $q_{e,exp}$ = experimental metal uptake capacity at equilibrium, q_{em} = metal uptake capacity at equilibrium calculated using kinetic models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with two independent data points.

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In addition, the variations in cumulative metal mass removed under uncontrolled pH conditions and cumulative metal mass adsorbed under controlled pH conditions by GAA with three loading cycles with M[Pb(0.60)] systems followed by fourth loading cycle with M[Cr(0.60)] system have been presented in Fig. 5.57. It appeared that the GAA had ability to remove additional amount of Pb(II) metal ions under uncontrolled pH conditions and to uptake additional amount of Pb(II) metal ions under controlled pH conditions during the first three loading cycles. However, the cumulative Pb(II) metal removal under uncontrolled pH conditions and cumulative Pb(II) metal uptake under controlled pH conditions decreased in the fourth loading cycle due to migration of adsorbed Pb(II) metal. The cumulative metal removal under uncontrolled pH conditions and cumulative metal uptake under controlled pH conditions up to fourth loading cycle were observed to be 0.0817 and 0.0644 meq respectively.

5.5.3 Summary

The experimental kinetics results obtained for three loading cycles with a mono-metal ion system followed with fourth loading cycle with another mono-metal ion system comprising of Cu(II), Pb(II) and Cr(III) metals may be summarized as: (a) During the first three loading cycles with a mono-metal ion system, additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions was observed in each loading cycle. (b) Additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions decreased with increase in number of loading cycles during the first three loading cycles. (c) When three cycle loaded GAA with a mono-metal ion system was exposed to another mono-metal ion system in the fourth loading cycle, additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions was observed for the loaded metal ion. (d) The migration of adsorbed metal ion from three cycle loaded GAA surface was observed into the bulk solution during the fourth loading cycle. (e) The cumulative metal removal under uncontrolled pH conditions and cumulative metal uptake under controlled pH conditions increased with number of loading cycles. (f) Based upon cumulative metal mass removal, a definite preference of metal removal by GAA was observed when loaded with metal ion systems in different cycles. However, based upon cumulative metal mass uptake, no definite preference of metal uptake by GAA was observed when loaded with metal ion systems in different cycles.

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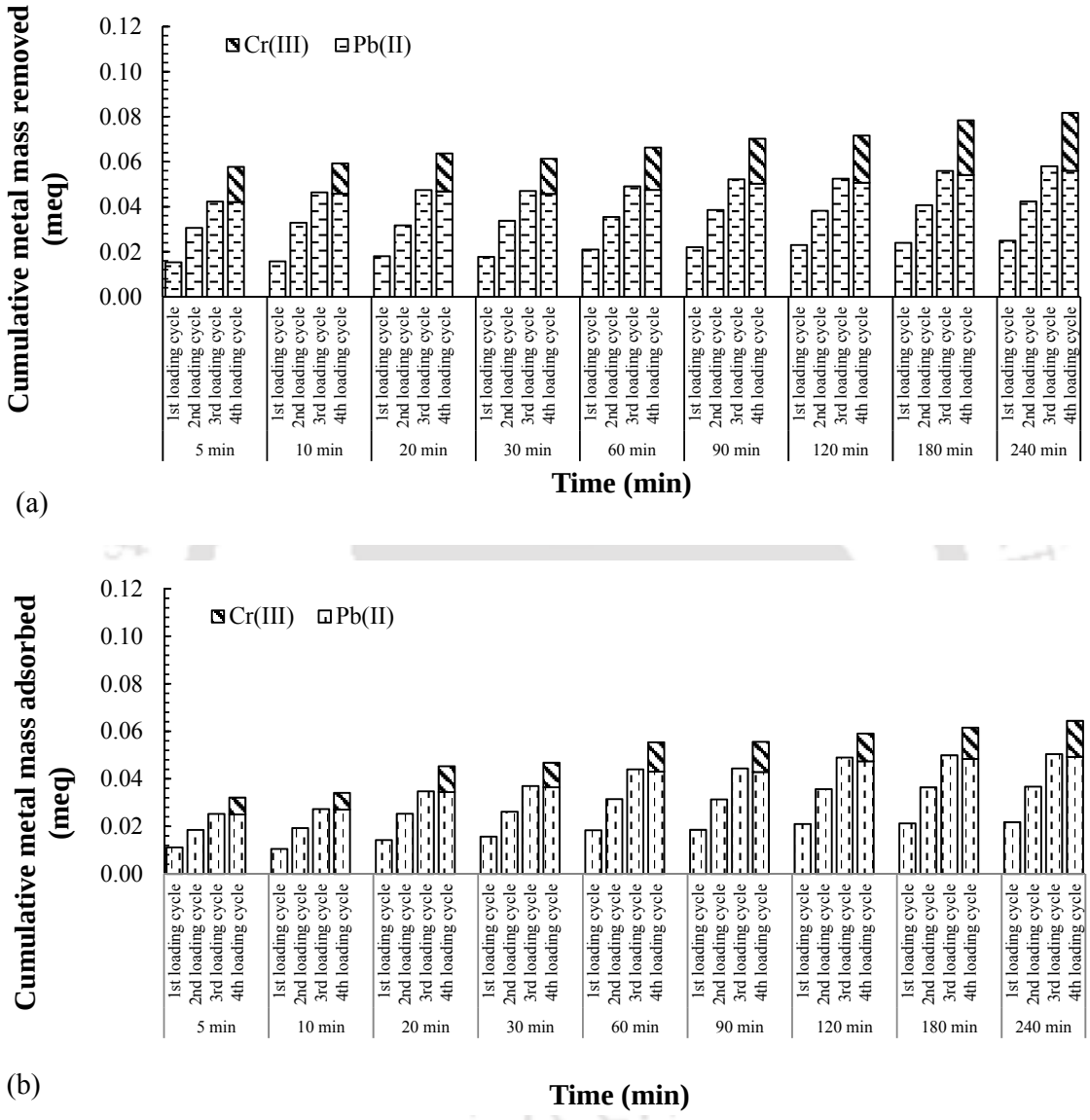

Fig. 5.57: Variation in (a) cumulative metal mass removed under uncontrolled pH conditions and (b) cumulative metal mass adsorbed under controlled pH conditions by GAA with three loading cycles with M[Pb(0.60)] system followed by fourth loading cycle with M[Cr(0.60)] system (Each data represents an average of two independent experimental values).

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5.5.4 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for four loading cycles with binary-metal ion system comprising of Cu(II) and Pb(II) ions

The kinetic studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions by GAA from binary-metal ion systems comprising of Cu(II) and Pb(II) ions were investigated. The studies were carried out in the first set by exposing the virgin GAA to consecutive three loading cycles with B[Cu(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cu(0.15)+Pb(0.45)] combination and in the second set, three loading cycles with B[Cu(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cu(0.45)+Pb(0.15)] combination. The results are discussed in following sub-sections.

5.5.4.1 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for three loading cycles with B[Cu(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cu(0.15)+Pb(0.45)] combination

The variation in solution pH and metal removals during three loading cycles with B[Cu(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cu(0.15)+Pb(0.45)] combination under uncontrolled pH conditions are shown in Fig. 5.58 while metal uptakes under controlled pH conditions with similar loading cycles are shown in Fig. 5.59.

Under uncontrolled pH conditions of loading cycles, the solution pH fluctuated in the range of 5.28-5.79 during the first loading cycle [Fig. 5.58(a)]. At the end of the second loading cycle, the observed solution pH was 5.59. The solution pH in the third loading cycle fluctuated in the range of 5.03-5.56 for the entire duration. In the fourth loading cycle, solution pH increased to 5.35 in the first 20 min. and then fluctuated in the range of 5.19-5.27 during later phase of the cycle. The GAA was able to influence solution pH with rising trend up to third loading cycles while the rising trend of solution pH appeared to get reduced in the fourth loading cycle. Since the solution pH increased beyond 5.50 in the first three loading cycles with B[Cu(0.45)+Pb(0.15)] combination, the removal of Cu(II) and Pb(II) metal ions from aqueous phase might be attributed to combined effects of precipitation and adsorption. However in the fourth loading cycle with B[Cu(0.15)+Pb(0.45)] combination, the variation in

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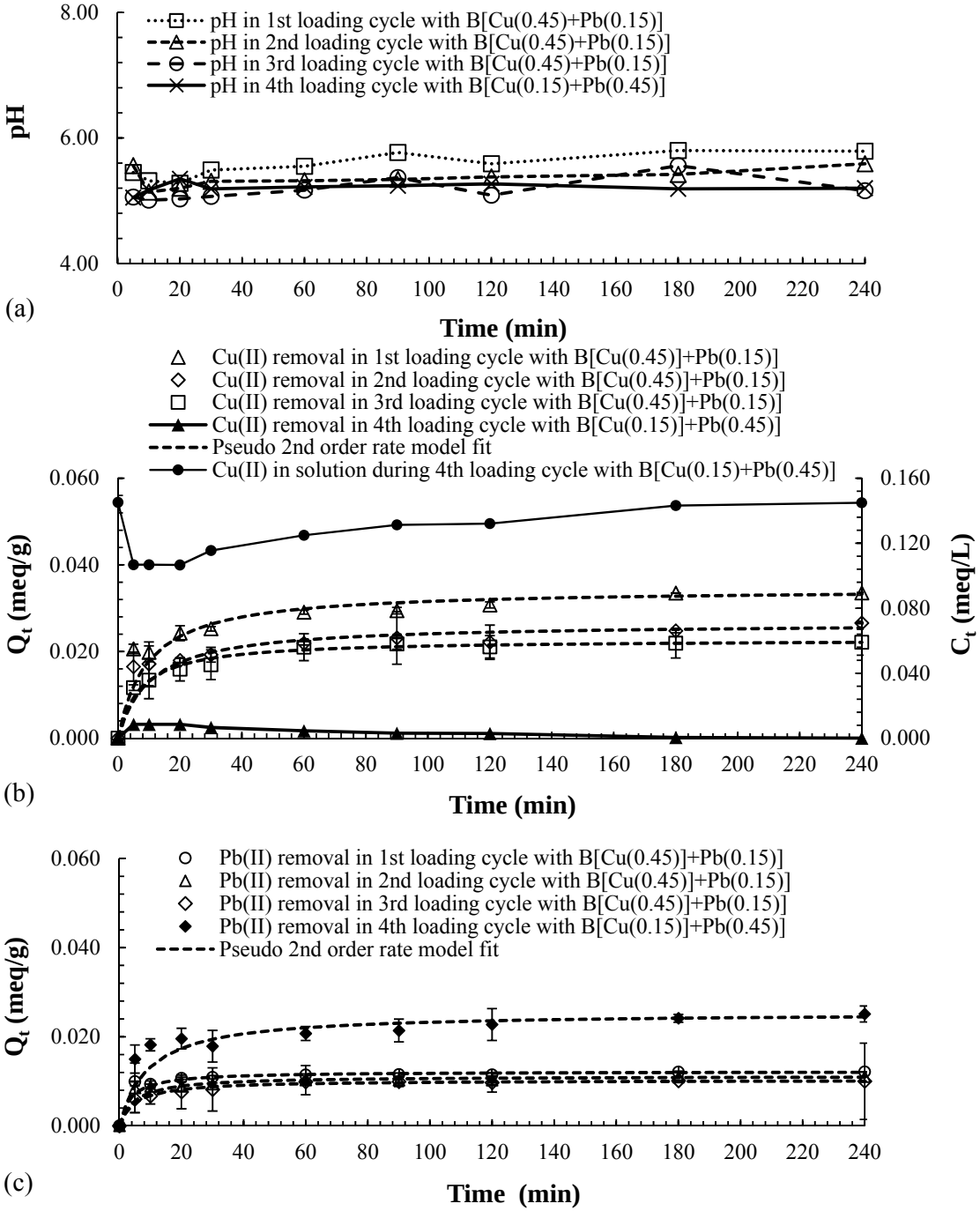

Fig. 5.58: Variation in (a) solution pH (b) Cu(II) and (c) Pb(II) metal removals in three loading cycles with B[Cu(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cu(0.15)+Pb(0.45)] combination under uncontrolled pH conditions {Initial metal conc. in B[Cu(0.45)+Pb(0.15)] combination = 0.45±0.01 meq/L of Cu(II) + 0.15±0.00 meq/L of Pb(II), B[Cu(0.15)+Pb(0.45)] combination = 0.15±0.01 meq/L of Cu(II) + 0.45±0.02 meq/L of Pb(II), Initial adjusted pH = 5.00±0.03, Temp. = 30±1 °C, GAA dose = 12 g/L, Mixing speed = 66 rpm} (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

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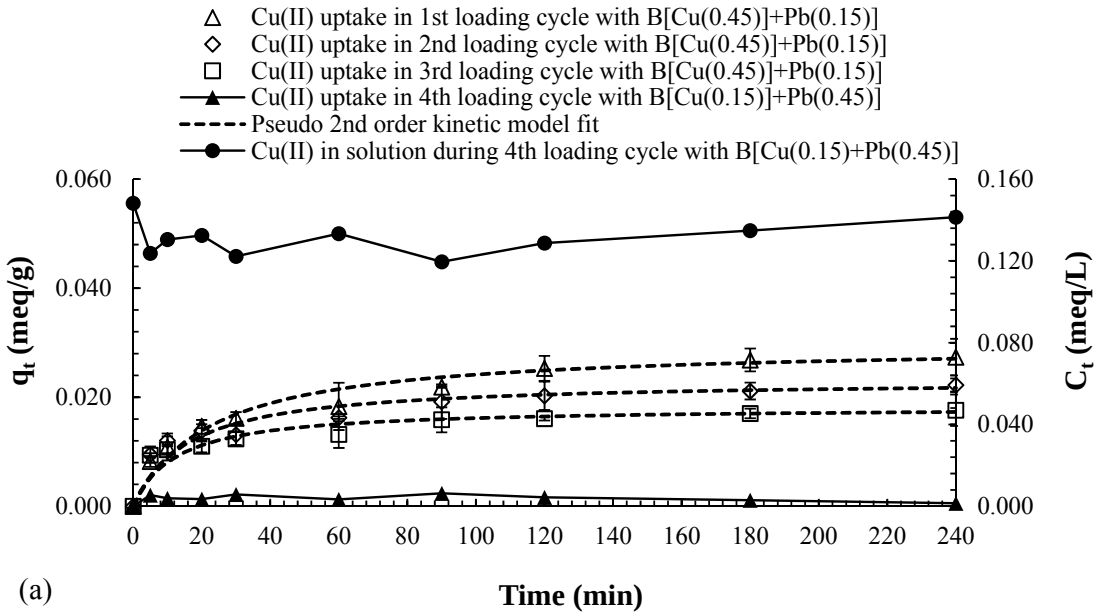
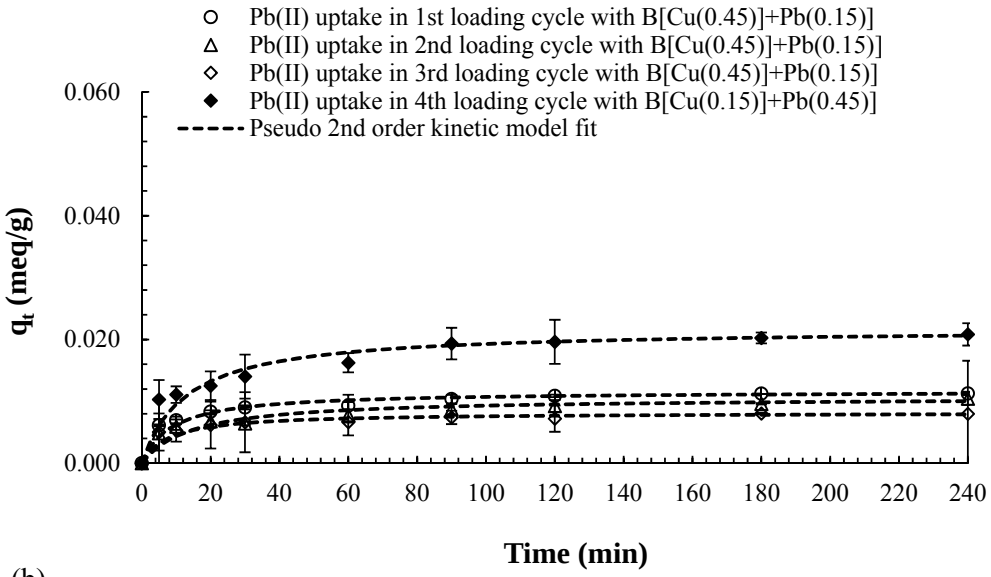


(a)



(b)

Fig. 5.59: Variation in (a) Cu(II) and (b) Pb(II) metal uptakes in three loading cycles with B[Cu(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cu(0.15)+Pb(0.45)] combination under controlled pH conditions {Initial metal ion conc. in B[Cu(0.45)+Pb(0.15)] combination: 0.45±0.02 meq/L of Cu(II) + 0.15±0.01 meq/L of Pb(II), B[Cu(0.15)+Pb(0.45)] combination: 0.15±0.02 meq/L of Cu(II) + 0.44±0.02 meq/L of Pb(II), Buffered pH = 4.90±0.10, Temp. = 30±1 ^{o}C, GAA dose = 12 g/L, Mixing speed = 66 rpm} (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

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solution pH was observed well below 5.50 throughout the cycle, the removal of Cu(II) and Pb(II) metal ions from solution might be attributed to adsorption only. Further, under controlled pH conditions, pH of the solution during each loading cycle remained very close to the initially buffered pH of 5.00 during course of the experimentation. Hence, the removal of Cu(II) and Pb(II) metal ions from solution might be attributed to adsorption only.

Under uncontrolled pH conditions of loading cycles, rapid Cu(II) and Pb(II) metal removal was observed up to 10-20 min. of the first loading cycle with B[Cu(0.45)+Pb(0.15)] combination [Fig. 5.58(b)&(c)]. The Cu(II) and Pb(II) metal removals were observed to be approximately 0.0242 meq/g and 0.0107 meq/g respectively at 20 min. of the first loading cycle. The total metal removal in the first 20 min. of the loading cycle was estimated as 0.0349 meq/g. As the first loading cycle proceeded beyond 20 min., the removal of Cu(II) and Pb(II) metal ions increased slowly and observed removal was 0.0335 meq/g of Cu(II) and 0.0121 meq/g of Pb(II) at the end of the cycle. The GAA of the first loading cycle was again loaded with B[Cu(0.45)+Pb(0.15)] combination in the second loading cycle. The variation in Cu(II) metal removal during the second loading cycle was observed to be lower than the variation in Cu(II) metal removal observed during the first loading cycle as no data overlapped at 95% confidence intervals. The variation in Pb(II) metal removal during the second loading cycle was observed to overlap at 95% confidence interval with the variation in Pb(II) metal removal observed during the first loading cycle. At the end of the second loading cycle, approximately 0.0265 meq/g of Cu(II) and 0.0110 meq/g of Pb(II) metal removal was observed. Similarly, when the GAA of the second loading cycle was again loaded with B[Cu(0.45)+Pb(0.15)] combination in the third loading cycle, the variation in Cu(II) and Pb(II) metal removals were observed to overlap at 95% confidence interval with the variation in Cu(II) and Pb(II) metal removals observed during the second loading cycle. The Cu(II) and Pb(II) metal removals were approximately 0.0221 meq/g and 0.0100 meq/g respectively at the end of the third loading cycle. The GAA was able to remove relatively higher amounts of Cu(II) metal ions in comparison to amounts of Pb(II) metal ions from the solution up to third loading cycle. During the fourth loading cycle with B[Cu(0.15)+Pb(0.45)] combination, the solution pH varied but remained well below the value of 5.50, indicating metal removals from the bulk solution due to adsorption. However, while studying the fourth loading cycle, efforts were made to estimate and present removals of Cu(II) and Pb(II) metal ions from the solution rather than metal uptakes by GAA. When the GAA was exposed to

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B[Cu(0.15)+Pb(0.45)] combination in the fourth loading cycle, Cu(II) metal concentration marginally decreased to 0.10 meq/L within first 20 min. of cycle from the initial Cu(II) metal concentration of 0.15 meq/L in the combination. After 20 min., Cu(II) metal ion concentration in solution gradually increased to 0.14 meq/L [Fig. 5.58(b)] yielding negligible Cu(II) metal removal in the fourth loading cycle. This might be attributed to lack of adequate concentration gradient of Cu(II) metal ions towards the GAA surfaces. The variation in Pb(II) metal removal during the fourth loading cycle was observed to be higher than the variation in Pb(II) metal removal observed during the first three loading cycles. Estimated Pb(II) metal removal at the end of the fourth loading cycle was observed as 0.0251 meq/g – a higher value due to formation of higher concentration gradient of Pb(II) metal ions towards the GAA surfaces.

Under controlled pH conditions of loading cycles with B[Cu(0.45)+Pb(0.15)] combination (Fig. 5.59), higher Cu(II) and Pb(II) metal uptakes were observed up to 20 min. of the first loading cycle and approximately 0.0273 meq/g of Cu(II) and 0.0113 meq/g of Pb(II) metal uptake was observed at the end of the cycle. The GAA of the first loading cycle was again loaded with B[Cu(0.45)+Pb(0.15)] combination in the second loading cycle. Here, it was important to note that the GAA surface had already accumulated some amount of Cu(II) and Pb(II) metal ions on its surface from the first loading cycle thereby developing lower concentration gradient in the second loading cycle compared to the first loading cycle. The variation in Cu(II) and Pb(II) metal uptakes during the second loading cycle were observed to overlap at 95% confidence interval with the variation in Cu(II) and Pb(II) metal uptakes observed during the first loading cycle. At the end of the second loading cycle, approximately 0.0222 meq/g of Cu(II) and 0.0105 meq/g of Pb(II) metal uptake were observed. Similarly, when the GAA of second loading cycle was again loaded with B[Cu(0.45)+Pb(0.15)] combination in the third loading cycle, the variation in Cu(II) and Pb(II) metal uptakes during the third loading cycle were observed to overlap at 95% confidence interval with the variation in Cu(II) and Pb(II) metal uptakes observed during the second loading cycle indicating migration of same amount of Cu(II) and Pb(II) metals on to GAA surface. The Cu(II) and Pb(II) metal uptakes were approximately 0.0176 meq/g and 0.0080 meq/g respectively at the end of the third loading cycle. In the fourth loading cycle, the GAA of the third loading cycle was exposed to B[Cu(0.15)+Pb(0.45)] combination. In this cycle, attention was paid to (i) Cu(II) and Pb(II) metals accumulated on to GAA surfaces

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from three previous loading cycles and (ii) Cu(II) and Pb(II) metal ions present in the bulk solution. As the GAA was previously loaded with three cycles of B[Cu(0.45)+Pb(0.15)] combination, it had accumulated relatively higher amount of Cu(II) metal ions and relatively lower amount of Pb(II) metal ions on its surface. When the GAA was exposed to B[Cu(0.15)+Pb(0.45)] combination in the fourth loading cycle, the concentration of accumulated Cu(II) metal ions on surface of the GAA might be more than (or almost equal to) the concentration of Cu(II) metal ions in the bulk solution. This might not be sufficient to induce concentration gradient for migration of Cu(II) metal ions from the bulk solution to the surface of GAA. The residual Cu(II) concentration varied in the range of 0.12-0.14 meq/L indicating no significant Cu(II) metal uptake in the fourth loading cycle (Fig. 5.59). Further, the concentration of accumulated Pb(II) metal ions on surface of the GAA might be lower than the concentration of Pb(II) metal ions in the bulk solution. This might be sufficient to induce concentration gradient for migration of Pb(II) metal ions from the bulk solution to the surface of GAA. Estimated Pb(II) metal uptake at the end of the fourth loading cycle was 0.0208 meq/g.

The variation in total metal removals (TQ_t) under uncontrolled pH conditions and total metal uptakes (Tq_t) under controlled pH conditions from each of the loading cycles have been presented in Fig. 5.60. The variation in total metal removals (TQ_t) and total metal uptakes (Tq_t) were observed to decrease with increase in number of loading cycles as most of the data points did not overlap at 95% confidence interval.

The variations in metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions carried out for four loading cycles were fitted to pseudo-first- and pseudo-second-order rate and kinetic models. The kinetic parameters for Cu(II) metal removal under uncontrolled pH conditions and Cu(II) metal uptake under controlled pH conditions during fourth loading cycle with B[Cu(0.15)+Pb(0.45)] combination were not estimated as no significant removal/uptake was observed. The estimated model parameters under uncontrolled and controlled pH conditions are presented in Table 5.28 and 5.29 respectively. The higher R^2 values for pseudo-second-order rate model indicated its suitability to describe metal removal under uncontrolled pH conditions and pseudo-second-order kinetic model for metal uptake under controlled pH conditions. The best fit plots of pseudo-second-order rate and kinetic models to experimental metal removal and metal uptake

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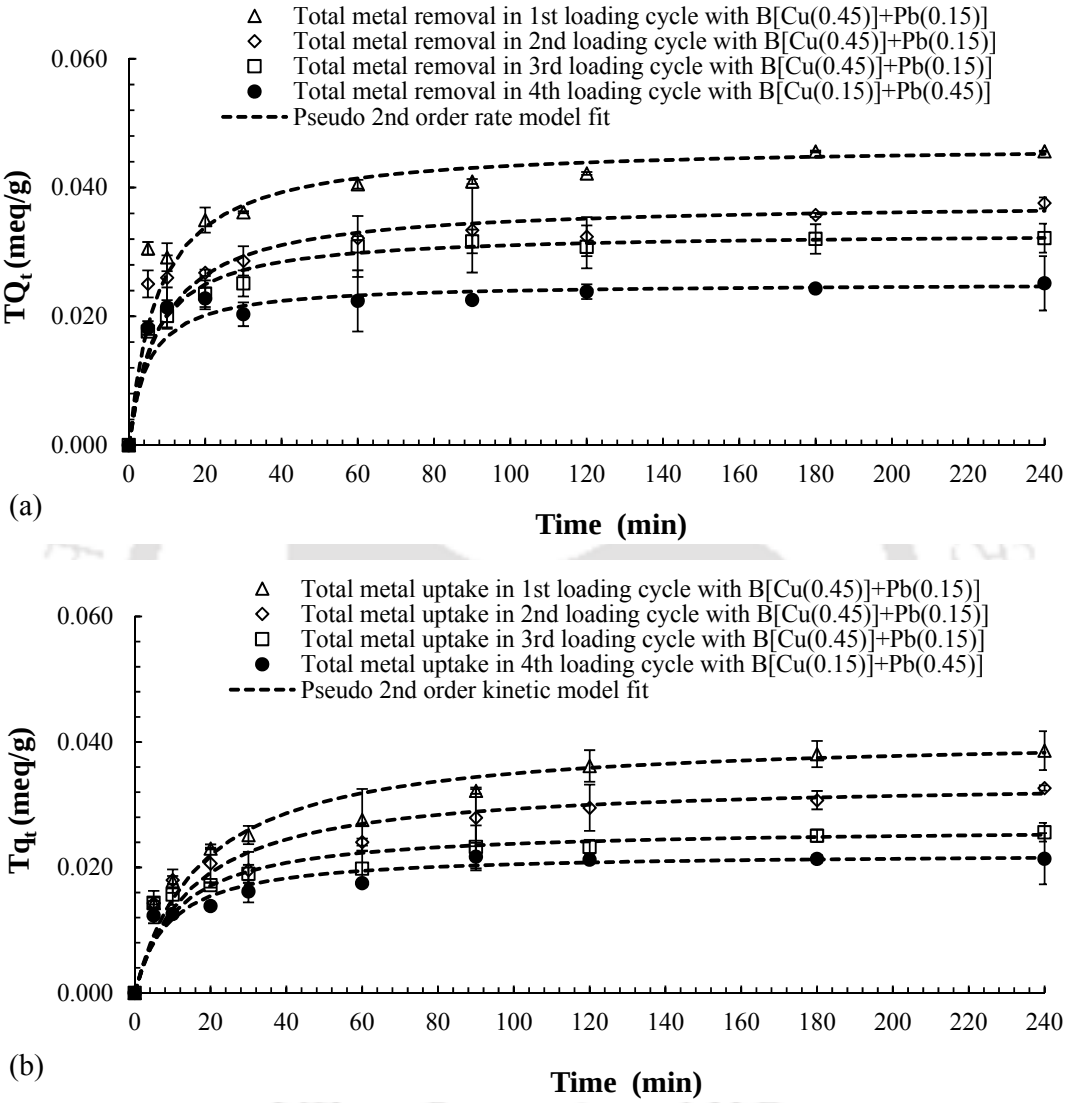

Fig. 5.60: Variation in (a) total metal removal under uncontrolled pH conditions and (b) total metal uptake under controlled pH conditions from three loading cycles with B[Cu(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cu(0.15)+Pb(0.45)] combination.

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Table 5.28: Summary of estimated pseudo-first- and pseudo-second-order rate models parameters for three loading cycles with B[Cu(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cu(0.15)+Pb(0.45)] combination under uncontrolled pH conditions.

Metal ion combinations	Loading cycle	Metal with initial conc. (meq/L)	$Q_{e,exp}$ (meq/g)	Pseudo-first-order rate model			Pseudo-second-order rate model		
				K_1 (1/min)	Q_{em} (meq/g)	R^2	K_2 (g/meq.min)	Q_{em} (meq/g)	R^2
B[Cu(0.45)+Pb(0.15)]	1st	Cu(II) = 0.45±0.01	0.0335	0.0812	0.0308	0.881	3.1150	0.0345	0.997
		Pb(II) = 0.15±0.00	0.0121	0.1715	0.0117	0.911	23.3381	0.0122	0.999
	2nd	Cu(II) = 0.45±0.01	0.0266	0.1066	0.0225	0.857	3.6685	0.0266	0.992
		Pb(II) = 0.15±0.00	0.0110	0.1859	0.0102	0.912	18.3448	0.0111	0.998
	3rd	Cu(II) = 0.45±0.01	0.0221	0.0863	0.0209	0.941	6.2016	0.0228	0.999
		Pb(II) = 0.15±0.00	0.0100	0.1028	0.0097	0.935	18.8435	0.0103	0.999
B[Cu(0.15)+Pb(0.45)]	4th	Cu(II) = 0.15±0.01	-	-	-	-	-	-	-
		Pb(II) = 0.45±0.02	0.0251	0.1559	0.0218	0.908	4.2796	0.0254	0.995

$Q_{e,exp}$ = experimental metal removal at equilibrium, Q_{em} = metal removal at equilibrium calculated using rate models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with two independent data points.

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Table 5.29: Summary of estimated pseudo-first- and pseudo-second-order kinetic models parameters for three loading cycles with B[Cu(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cu(0.15)+Pb(0.45)] combination under controlled pH conditions.

Metal ion combinations	Loading cycle	Metal with initial conc. (meq/L)	$q_{e,exp}$ (meq/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
				k_1 (1/min)	q_{em} (meq/g)	R^2	k_2 (g/meq.min)	q_{em} (meq/g)	R^2
B[Cu(0.45)+Pb(0.15)]	1st	Cu(II) = 0.45±0.02	0.0273	0.0432	0.0231	0.926	1.4920	0.0296	0.991
		Pb(II) = 0.15±0.01	0.0113	0.0987	0.0101	0.930	10.0696	0.0116	0.998
	2nd	Cu(II) = 0.45±0.02	0.0222	0.0664	0.0196	0.879	2.7583	0.0231	0.994
		Pb(II) = 0.15±0.01	0.0105	0.0817	0.0086	0.875	6.5604	0.0106	0.993
	3rd	Cu(II) = 0.45±0.02	0.0176	0.0743	0.0162	0.867	4.4212	0.0182	0.995
		Pb(II) = 0.15±0.01	0.0080	0.1244	0.0072	0.916	15.7702	0.0082	0.997
B[Cu(0.15)+Pb(0.45)]	4th	Cu(II) = 0.15±0.02	-	-	-	-	-	-	-
		Pb(II) = 0.44±0.02	0.0208	0.0581	0.0189	0.898	3.6075	0.2170	0.997

$q_{e,exp}$ = experimental metal uptake capacity at equilibrium, q_{em} = metal uptake capacity at equilibrium calculated using kinetic models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with two independent data points.

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data are also presented in Fig. 5.58 and 5.59. An inspection of Table 5.28 and 5.29 revealed decreasing trend in values of $Q_{e,exp}$ and $q_{e,exp}$ as well as Q_{em} and q_{em} for Cu(II) metal with increase in number of loading cycles with B[Cu(0.45)+Pb(0.15)] combination. However, the values of $Q_{e,exp}$ and $q_{e,exp}$ as well as Q_{em} and q_{em} for Pb(II) metal in the fourth loading cycle with B[Cu(0.15)+Pb(0.45)] combination were higher compared to similar values obtained with the previous three loading cycle with B[Cu(0.45)+Pb(0.15)] combination. Similarly, the variations in total metal removals under uncontrolled pH conditions and total metal uptakes under controlled pH conditions carried out for four loading cycles were also fitted to pseudo-first- and pseudo-second-order rate and kinetic models. The estimated rate and kinetic model parameters are presented in Table 5.30. The higher R^2 values for pseudo-second-order rate model indicated its suitability to describe total metal removal under uncontrolled pH conditions and pseudo-second-order kinetic model for total metal uptake under controlled pH conditions. An inspection of Table 5.30 revealed decreasing trend in values of $TQ_{e,exp}$ and Q_{em} as well as $Tq_{e,exp}$ and q_{em} with increase in number of loading cycles.

In addition, the variations in cumulative metal mass removed under uncontrolled pH conditions and cumulative metal mass adsorbed under controlled pH conditions by GAA with three loading cycles with B[Cu(0.45)+Pb(0.15)] combination followed with fourth loading cycle with B[Cu(0.15)+Pb(0.45)] combination have been presented in Fig. 5.61 and 5.62 respectively. It is very clear that the GAA had the ability to remove additional amount of Cu(II) and Pb(II) metal ions under uncontrolled pH conditions and to uptake additional amount of Cu(II) and Pb(II) metal ions under controlled pH conditions during the first three loading cycles. The cumulative Cu(II) metal removal and cumulative Cu(II) metal uptake in the fourth loading cycle were very near to the cumulative Cu(II) metal removal and cumulative Cu(II) metal uptake in the third loading cycle. However, the cumulative Pb(II) metal removal and cumulative Pb(II) metal uptake in the fourth loading cycle were higher than the cumulative Pb(II) metal removal and cumulative Pb(II) metal uptake in the third loading cycle. It indicated relatively higher Pb(II) metal removal and Pb(II) metal uptake in the fourth loading cycle as compared to the previous three loading cycles. The cumulative Cu(II), Pb(II) and total metal removal under uncontrolled pH conditions were 0.0493 meq, 0.0350 meq and 0.0843 meq respectively while cumulative Cu(II), Pb(II) and total metal uptake under controlled pH conditions were 0.0406 meq, 0.0303 meq and 0.0709 meq respectively up to fourth loading cycle (Fig. 5.61 and 5.62).

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Table 5.30: Summary of estimated kinetic parameters for total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions from three loading cycles with B[Cu(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cu(0.15)+Pb(0.45)] combination.

				Pseudo-first-order rate model			Pseudo-second-order rate model		
Uncontrolled pH conditions	Metal ion combinations	Loading cycle	$TQ_{e,exp}$ (meq/g)	K_1 (1/min)	Q_{em} (meq/g)	R^2	K_2 (g/meq.min)	Q_{em} (meq/g)	R^2
	B[Cu(0.45)+Pb(0.15)]	1st	0.0456	0.0988	0.0425	0.880	2.8436	0.0467	0.998
		2nd	0.0376	0.1249	0.0328	0.871	3.1157	0.0377	0.995
		3rd	0.0321	0.0917	0.0305	0.939	4.6878	0.0331	0.999
	B[Cu(0.15)+Pb(0.45)]	4th	0.0251	0.2953	0.0230	0.969	8.0782	0.0252	0.998
				Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Controlled pH conditions	Metal ion combinations	Loading cycle	$Tq_{e,exp}$ (meq/g)	k_1 (1/min)	q_{em} (meq/g)	R^2	k_2 (g/meq.min)	q_{em} (meq/g)	R^2
	B[Cu(0.45)+Pb(0.15)]	1st	0.0386	0.0551	0.0345	0.920	1.4072	0.0411	0.994
		2nd	0.0327	0.0717	0.0279	0.877	1.9457	0.0338	0.994
		3rd	0.0256	0.0680	0.0265	0.869	3.5178	0.0264	0.996
	B[Cu(0.15)+Pb(0.45)]	4th	0.0214	0.0594	0.0202	0.880	5.0465	0.0223	0.997

$TQ_{e,exp}$ = experimental total metal removal at equilibrium, $Tq_{e,exp}$ = experimental total metal uptake at equilibrium Q_{em} = total metal removal at equilibrium calculated using rate models, q_{em} = total metal uptake at equilibrium calculated using kinetic models.

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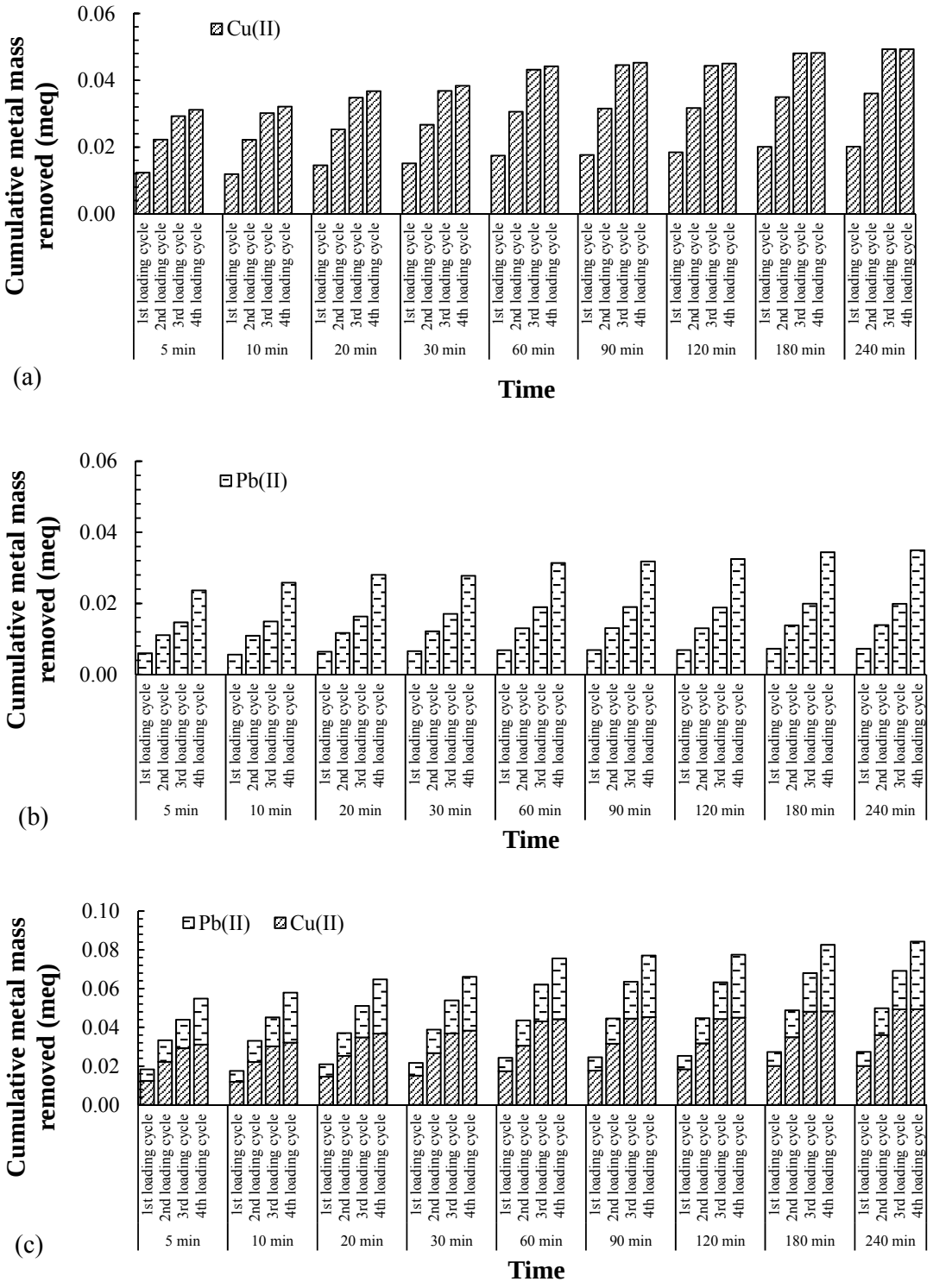

Fig. 5.61: Variation in cumulative (a) Cu(II), (b) Pb(II) and (c) total metal mass removed under uncontrolled pH conditions by GAA with three loading cycles with B[Cu(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cu(0.15)+Pb(0.45)] combination (Each data represents an average of two independent experimental values).

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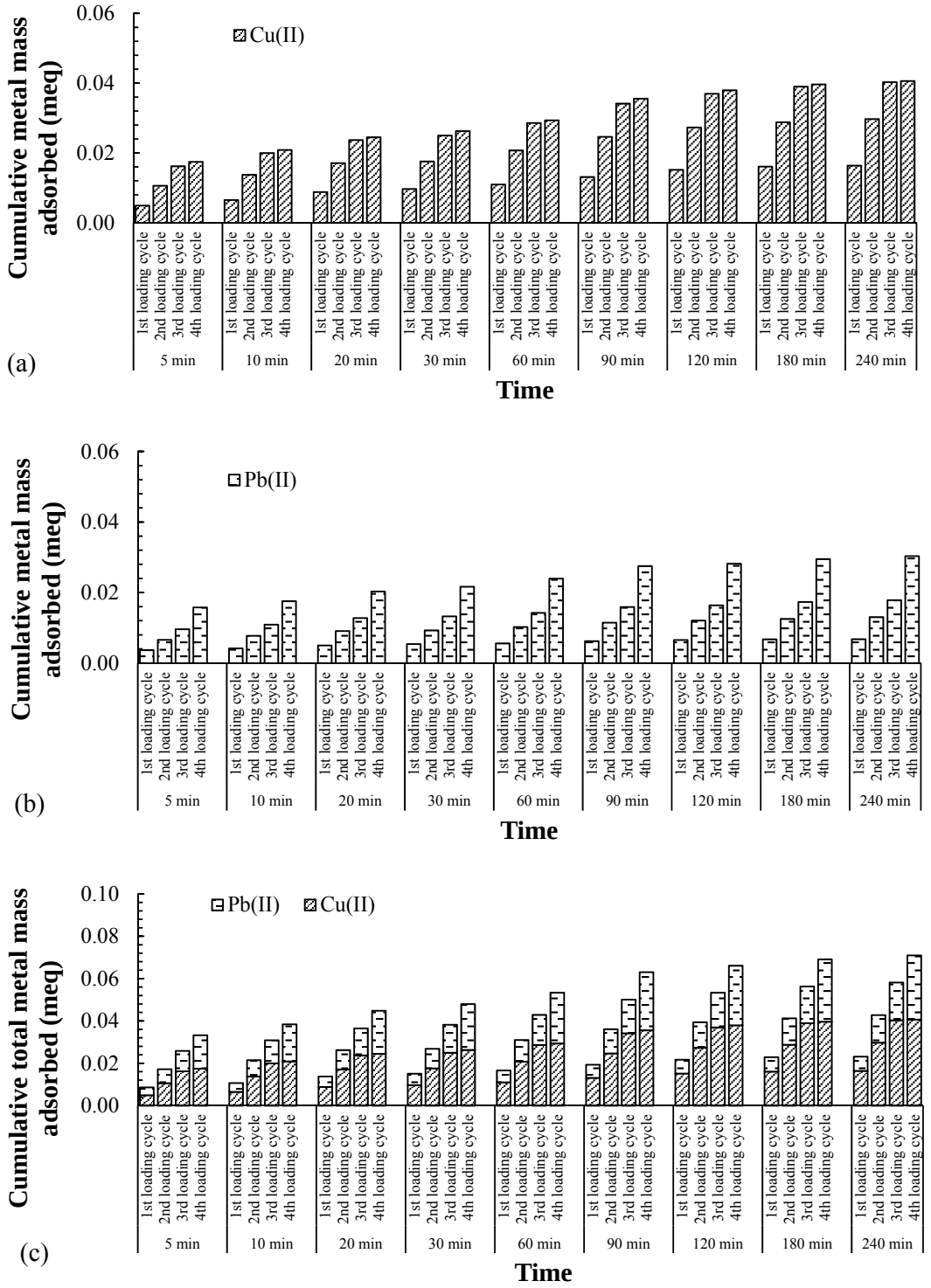

Fig. 5.62: Variation in cumulative (a) Cu(II), (b) Pb(II) and (c) total metal mass adsorbed under controlled pH conditions by GAA with three loading cycles with B[Cu(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cu(0.15)+Pb(0.45)] combination (Each data represents an average of two independent experimental values).

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5.5.4.2 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for three loading cycles with B[Cu(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cu(0.45)+Pb(0.15)] combination

The variation in solution pH and metal removals during three loading cycles with B[Cu(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cu(0.45)+Pb(0.15)] combination under uncontrolled pH conditions are shown in Fig. 5.63 while metal uptakes under controlled pH conditions with similar loading cycles are shown in Fig. 5.64.

Under uncontrolled pH conditions of loading cycles, the solution pH fluctuated in the range of 5.29-5.60 during the first loading cycle (Fig. 5.63). At the end of the second loading cycle, the observed solution pH was 5.47. The solution pH in the third loading cycle fluctuated in the range of 5.06-5.45 for the entire duration while in the fourth loading cycle solution pH fluctuated in the range of 5.07-5.28. Since the solution pH was observed above 5.50 in the first loading cycle with B[Cu(0.15)+Pb(0.45)] combination, the removal of Cu(II) and Pb(II) metal ions from aqueous phase might be attributed to combined effects of precipitation and adsorption. However, in the second, third and fourth loading cycles, the solution pH was observed below 5.50, the removal of Cu(II) and Pb(II) metal ions from solution might be attributed to adsorption only. Further, under controlled pH conditions, pH of the solution during each loading cycle remained close to the initially buffered pH of 5.00 during course of the experimentation. Hence, the removal of Cu(II) and Pb(II) metal ions from solution might be attributed to adsorption only.

Under uncontrolled pH conditions of loading cycles, rapid Cu(II) and Pb(II) metal removal was observed up to 10-20 min. of the first loading cycle with B[Cu(0.15)+Pb(0.45)] combination [Fig. 5.63(b)&(c)]. The Cu(II) and Pb(II) metal removal was observed to be approximately 0.0075 meq/g and 0.0239 meq/g respectively at 20 min. of the first loading cycle. As the first loading cycle proceeded beyond 20 min., the removal of metal ions increased slowly with Cu(II) and Pb(II) removals of 0.0108 meq/g and 0.0347 meq/g respectively at the end of the cycle. During the second and third loading cycles with B[Cu(0.15)+Pb(0.45)] combination and the fourth loading cycle with B[Cu(0.45)+Pb(0.15)] combination, the solution pH varied but remained well below a value of 5.50, indicating

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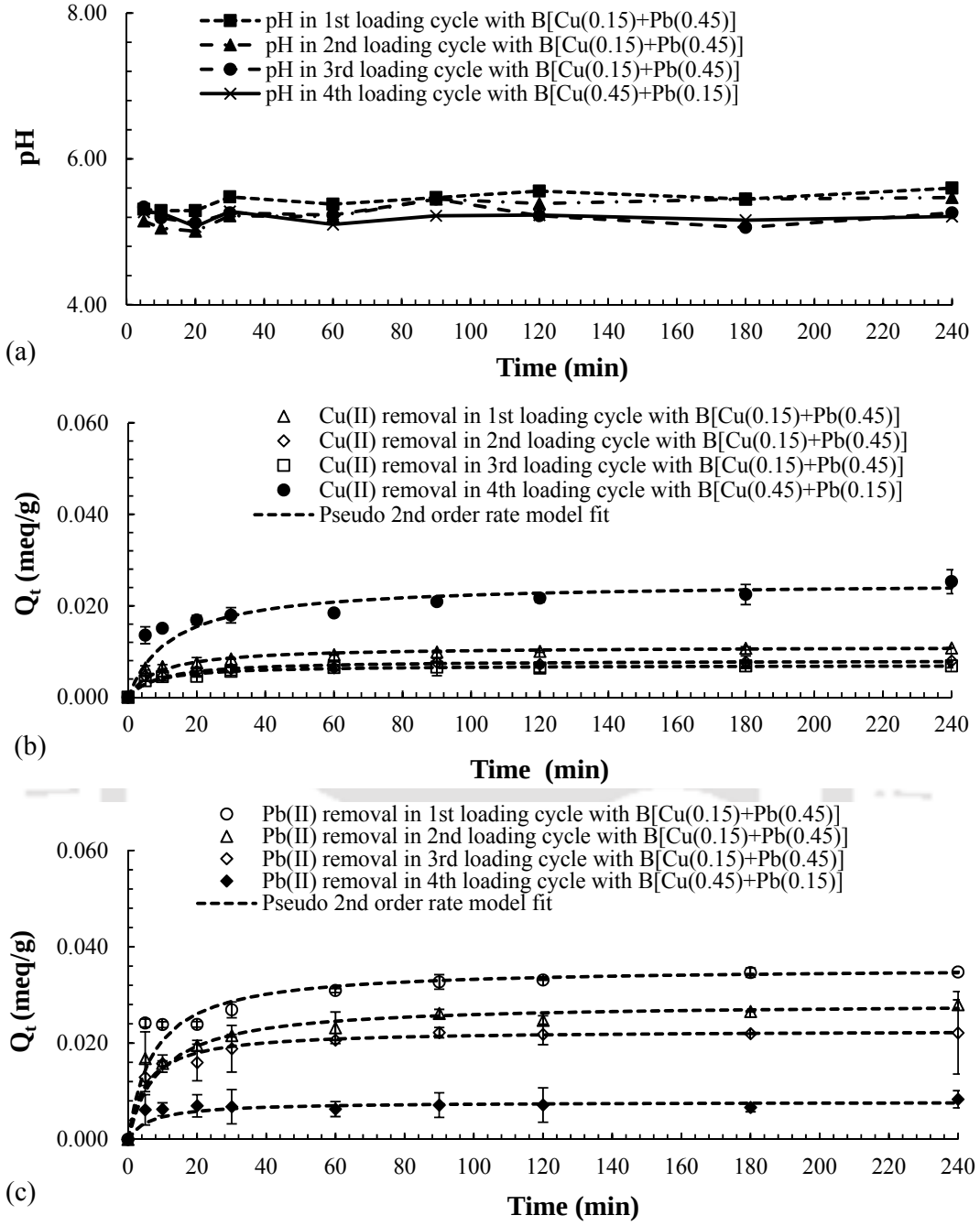

Fig. 5.63: Variation in (a) solution pH (b) Cu(II) and (c) Pb(II) metal removals in three loading cycles with B[Cu(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cu(0.45)+Pb(0.15)] combination under uncontrolled pH conditions {Initial metal conc. in B[Cu(0.15)+Pb(0.45)] combination = 0.15±0.01 meq/L of Cu(II) + 0.44±0.03 meq/L of Pb(II), B[Cu(0.45)+Pb(0.15)] combination = 0.45±0.03 meq/L of Cu(II) + 0.15±0.02 meq/L of Pb(II), Initial adjusted pH = 5.00±0.02, Temp. = 30±1 °C, GAA dose = 12 g/L, Mixing speed = 66 rpm} (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

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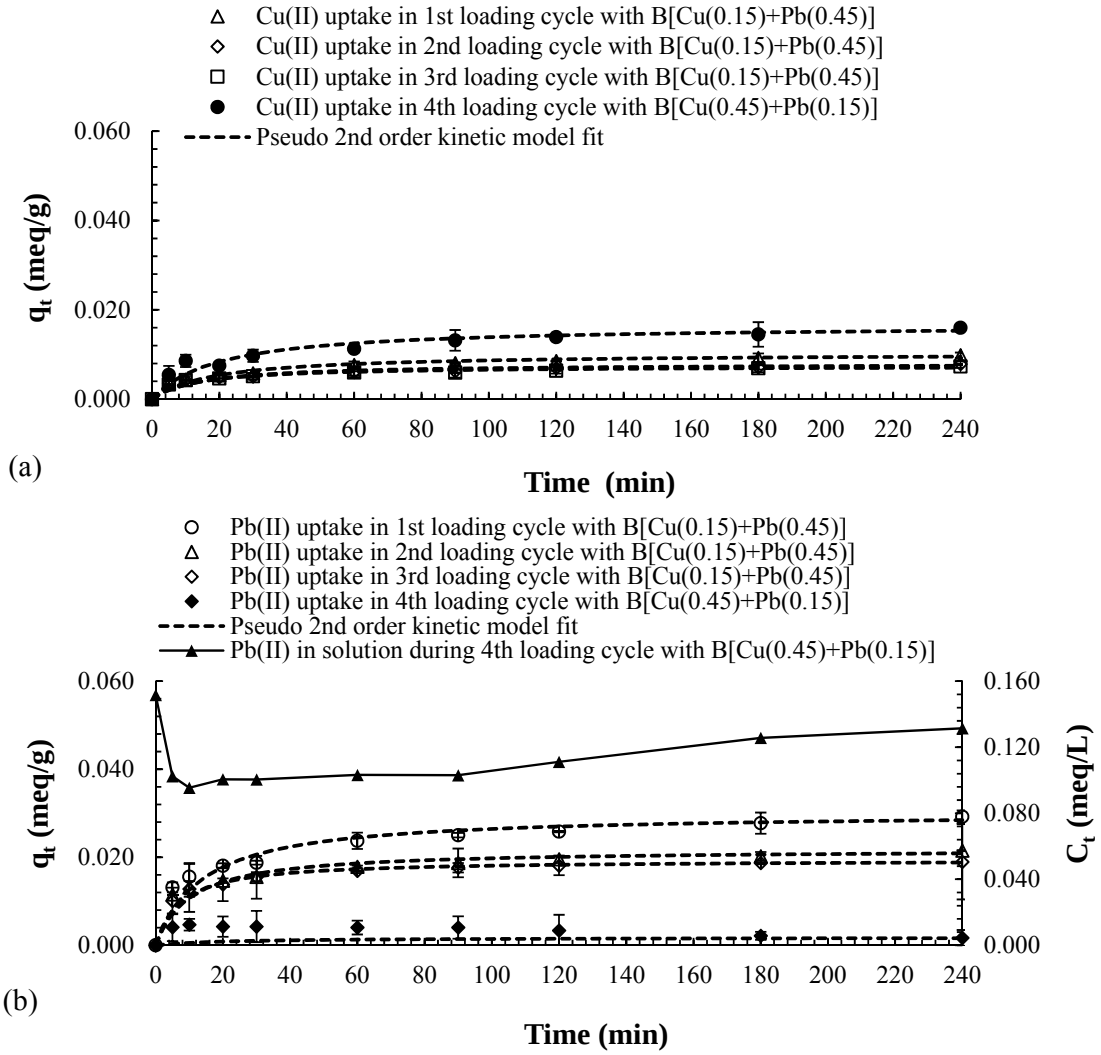

Fig. 5.64: Variation in (a) Cu(II) and (b) Pb(II) metal uptakes in three loading cycles with B[Cu(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cu(0.45)+Pb(0.15)] combination under controlled pH conditions {Initial metal ion conc. in B[Cu(0.15)+Pb(0.45)] combination: 0.15±0.02 meq/L of Cu(II) + 0.44±0.02 meq/L of Pb(II), B[Cu(0.45)+Pb(0.15)] combination: 0.45±0.01 meq/L of Cu(II) + 0.15±0.01 meq/L of Pb(II), Buffered pH = 4.90±0.10, Temp. = 30±1 ^{o}C, GAA dose = 12 g/L, Mixing speed = 66 rpm} (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

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metal removals from the solution due to adsorption. However, in order to compare results of the first loading cycle with results of other loading cycles, removals of Cu(II) and Pb(II) metal ions from the solution were estimated and represented rather than metal uptakes by GAA. When the GAA of the first loading cycle was again loaded with B[Cu(0.15)+Pb(0.45)] combination in the second loading cycle, the variation in Cu(II) metal removal during the second loading cycle were observed to overlap at 95% confidence intervals with the variation in Cu(II) metal removal observed during the first loading cycle. However, the variation in Pb(II) metal removals during the second loading cycle were observed to be lower than the variation in Pb(II) metal removals observed during the first loading cycle with no data points overlapping at 95% confidence intervals. At the end of the second loading cycle, approximately 0.0079 meq/g of Cu(II) and 0.0279 meq/g of Pb(II) metal removals were observed. Similarly, when the GAA of second loading cycle was again loaded with B[Cu(0.15)+Pb(0.45)] combination in the third loading cycle, the variation in Cu(II) and Pb(II) metal removals during the third loading cycle were observed to overlap at 95% confidence intervals with respective variation in Cu(II) and Pb(II) metal removals observed during the second loading cycle. The Cu(II) and Pb(II) metal removals were approximately 0.0069 meq/g and 0.0221 meq/g respectively at the end of the third loading cycle. In the fourth loading cycle, the GAA of the third loading cycle was exposed to B[Cu(0.45)+Pb(0.15)] combination. The variation in Cu(II) metal removal during the fourth loading cycle with B[Cu(0.45)+Pb(0.15)] combination was higher compared to previous three loading cycles with B[Cu(0.15)+Pb(0.45)] combination due to increased Cu(II) concentration in the bulk solution indicating Cu(II) metal concentration gradient towards the GAA surfaces. The Cu(II) and Pb(II) metal removals were 0.0253 meq/g and 0.0083 meq/g respectively at the end of the fourth loading cycle.

Under controlled pH conditions of the first loading cycle with B[Cu(0.15)+Pb(0.45)] combination (Fig. 5.64), Cu(II) and Pb(II) metal uptakes were observed up to first 30 min. of the cycle with Pb(II) metal uptake being rapid. Approximately 0.0098 meq/g of Cu(II) and 0.0292 meq/g of Pb(II) metal uptake was observed towards the end of the first loading cycle. The GAA of the first loading cycle was again loaded with B[Cu(0.15)+Pb(0.45)] combination in the second loading cycle. The variation in Cu(II) metal uptake during the second loading cycle were observed to overlap at 95% confidence interval with the variation in Cu(II) metal uptake observed during the first loading cycle. The variation in Pb(II) metal

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uptake during the second loading cycle were observed to be lower than the variation in Pb(II) metal uptake observed during the first loading cycle. At the end of the second loading cycle, approximately 0.0079 meq/g of Cu(II) and 0.0215 meq/g of Pb(II) metal uptake were observed. Similarly, when the GAA of the second loading cycle was again loaded with B[Cu(0.15)+Pb(0.45)] combination in the third loading cycle, the variation in Cu(II) and Pb(II) metal uptakes during the third loading cycle were observed to overlap at 95% confidence interval with respective variation in Cu(II) and Pb(II) metal uptakes observed during the second loading cycle. The Cu(II) and Pb(II) metal uptakes were approximately 0.0073 meq/g and 0.0190 meq/g respectively at the end of the third loading cycle. In the fourth loading cycle, the GAA of the third loading cycle was exposed to B[Cu(0.45)+Pb(0.15)] combination. In the previous three loading cycles, the GAA was exposed to lower initial concentration of Cu(II) and higher initial concentration of Pb(II) leading to accumulation of lower amounts of Cu(II) and higher amounts of Pb(II) on the surfaces of GAA. When the GAA was exposed to B[Cu(0.45)+Pb(0.15)] combination in the fourth loading cycle, the concentration of accumulated Cu(II) metal ions on the surface of the GAA might be lower than the concentration of Cu(II) metal ions in the bulk solution while the concentration of accumulated Pb(II) metal ions on the surface of the GAA might be higher than the concentration of Pb(II) metal ions in the bulk solution. This might be sufficient to induce concentration gradient of Cu(II) towards the GAA surface and consequently uptake of Cu(II) metal ions. On the other hand, the lower concentration of Pb(II) metal ions in the bulk solution might have failed to induce concentration gradient of Pb(II) metal ions towards the GAA surfaces with no significant Pb(II) metal uptake. The variation in residual Pb(II) metal ion concentration in the bulk solution is also presented in Fig. 5.64(b) indicating no or very little change in concentration levels. The Cu(II) metal uptake was approximately 0.0160 meq/g towards the end of the cycle.

Fig. 5.65 shows the variation in total metal removals (TQ_t) under uncontrolled pH conditions and total metal uptakes (Tq_t) under controlled pH conditions from each of the loading cycles. The variation in total metal removals (TQ_t) from three loading cycles with B[Cu(0.15)+Pb(0.45)] combination were observed to decrease with increase in number of loading cycles while total metal removal (TQ_t) from the fourth loading cycle with B[Cu(0.45)+Pb(0.15)] combination was observed to overlap at 95% confidence interval with most of the data points from the third loading cycle. Similarly, the variation in total metal

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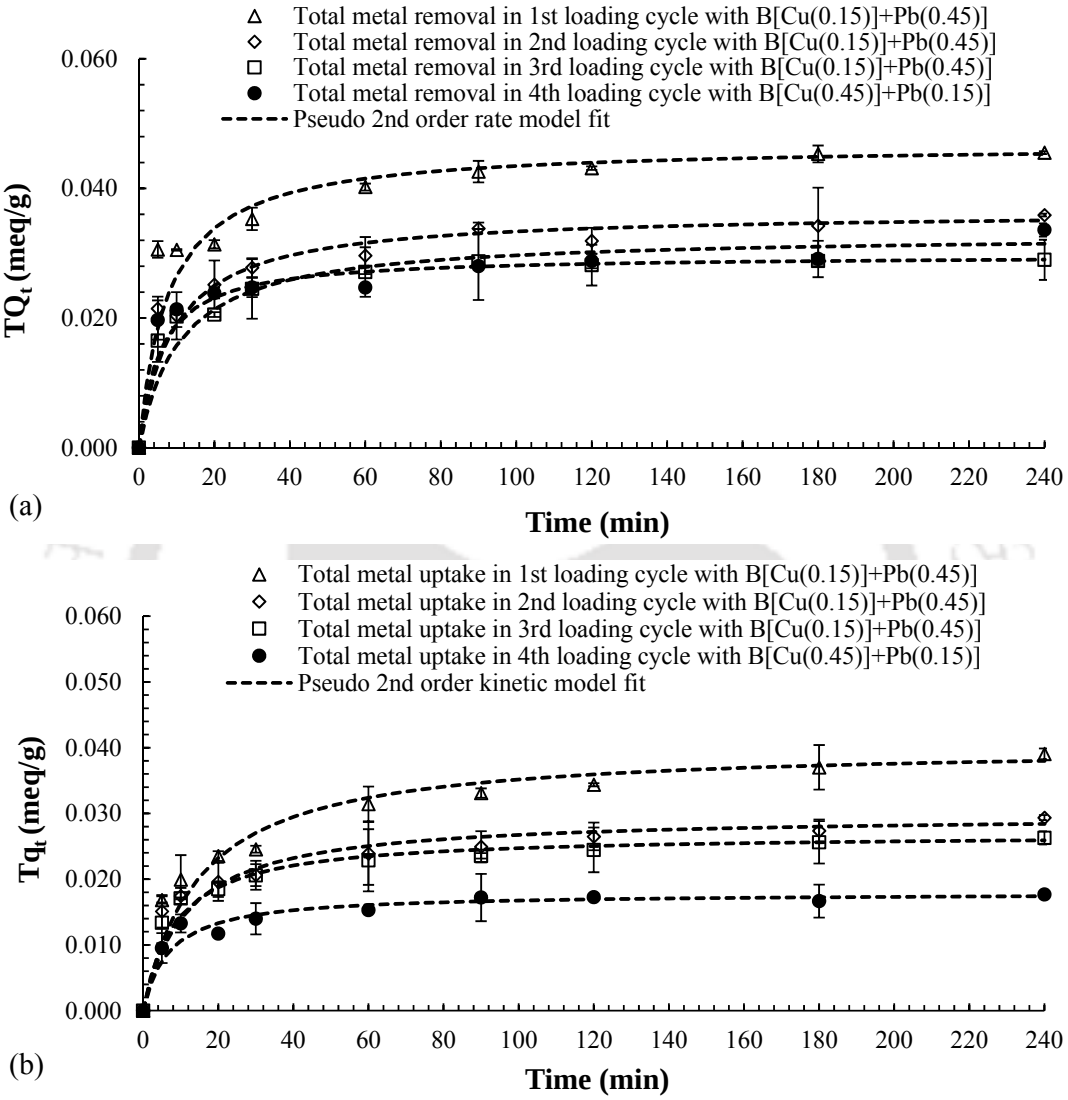

Fig. 5.65: Variation in (a) total metal removal under uncontrolled pH conditions and (b) total metal uptake under controlled pH conditions from three loading cycles with B[Cu(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cu(0.45)+Pb(0.15)] combination.

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uptakes (Tq_t) from second and third loading cycles were well below the variation observed in the first loading cycle and observed data points of second and third loading cycles overlapped at 95% confidence intervals with each other. Total metal uptake from the fourth loading cycle with B[Cu(0.45)+Pb(0.15)] combination was lower than the first three loading cycles with B[Cu(0.15)+Pb(0.45)] combination.

The variations in metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions carried out for four loading cycles were fitted to pseudo-first- and pseudo-second-order rate and kinetic models. The estimated rate and kinetic model parameters for experimental data obtained under uncontrolled and controlled pH conditions are presented in Table 5.31 and 5.32 respectively. The higher R^2 values for pseudo-second-order rate model indicated its suitability to describe metal removal under uncontrolled pH conditions and pseudo-second-order kinetic model for metal uptake under controlled pH conditions. The best fit plots of pseudo-second-order rate and kinetic models to experimental metal removal and metal uptake data are also presented in Fig. 5.63 and 5.64 respectively. An inspection of Table 5.31 and 5.32 revealed decreasing trend in values of $Q_{e,exp}$ and $q_{e,exp}$ as well as Q_{em} and q_{em} for Pb(II) metal with increase in number of loading cycles with B[Cu(0.15)+Pb(0.45)] combination. However, the values of $Q_{e,exp}$ and $q_{e,exp}$ as well as Q_{em} and q_{em} for Cu(II) metal in the fourth loading cycle with B[Cu(0.45)+Pb(0.15)] combination were higher compared to $Q_{e,exp}$ and $q_{e,exp}$ as well as Q_{em} and q_{em} values for Cu(II) metal obtained with the previous three loading cycles with B[Cu(0.15)+Pb(0.45)] combination. Similarly, the variations in total metal removals under uncontrolled pH conditions and total metal uptakes under controlled pH conditions carried out for four loading cycles were also fitted to pseudo-first- and pseudo-second-order rate and kinetic models. The estimated rate and kinetic model parameters for experimental data obtained under uncontrolled and controlled pH conditions are presented in Table 5.33. The higher R^2 values for pseudo-second-order rate model indicated its suitability to describe total metal removal under uncontrolled pH conditions and pseudo-second-order kinetic model for total metal uptake under controlled pH conditions. An inspection of Table 5.33 revealed decreasing trend in values of $TQ_{e,exp}$ and Q_{em} up to three loading cycles with B[Cu(0.15)+Pb(0.45)] combination while increase in values of $TQ_{e,exp}$ and Q_{em} in the fourth loading cycle with B[Cu(0.45)+Pb(0.15)] combination. However, decreasing trend in values of $Tq_{e,exp}$ and q_{em} were observed with increase in number of loading cycles under controlled pH conditions of

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Table 5.31: Summary of estimated pseudo-first- and pseudo-second-order rate models parameters for three loading cycles with B[Cu(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cu(0.45)+Pb(0.15)] combination under uncontrolled pH conditions.

Metal ion combinations	Loading cycle	Metal with initial conc. (meq/L)	$Q_{e,exp}$ (meq/g)	Pseudo-first-order rate model			Pseudo-second-order rate model		
				K_1 (1/min)	Q_{em} (meq/g)	R^2	K_2 (g/meq.min)	Q_{em} (meq/g)	R^2
B[Cu(0.15)+Pb(0.45)]	1st	Pb(II) = 0.44±0.03	0.0347	0.0781	0.0330	0.824	3.8224	0.0357	0.999
		Cu(II) = 0.15±0.01	0.0108	0.0909	0.0099	0.900	10.5943	0.0111	0.998
	2nd	Pb(II) = 0.44±0.03	0.0279	0.0780	0.0256	0.888	3.8583	0.0283	0.996
		Cu(II) = 0.15±0.01	0.0079	0.0842	0.0071	0.898	14.1094	0.0081	0.997
	3rd	Pb(II) = 0.44±0.03	0.0221	0.1170	0.0214	0.936	8.5155	0.0227	0.999
		Cu(II) = 0.15±0.01	0.0069	0.1103	0.0063	0.935	19.8465	0.0070	0.998
B[Cu(0.45)+Pb(0.15)]	4th	Pb(II) = 0.15±0.02	0.0083	0.3324	0.0069	0.936	19.3277	0.0078	0.977
		Cu(II) = 0.45±0.03	0.0253	0.1120	0.0205	0.880	3.2072	0.0251	0.990

$Q_{e,exp}$ = experimental metal removal at equilibrium, Q_{em} = metal removal at equilibrium calculated using rate models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with two independent data points.

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Table 5.32: Summary of estimated pseudo-first- and pseudo-second-order kinetic models parameters for three loading cycles with B[Cu(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cu(0.45)+Pb(0.15)] combination under controlled pH conditions.

Metal ion combinations	Loading cycle	Metal with initial conc. (meq/L)	$q_{e,exp}$ (meq/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
				k_1 (1/min)	q_{em} (meq/g)	R^2	k_2 (g/meq.min)	q_{em} (meq/g)	R^2
B[Cu(0.15)+Pb(0.45)]	1st	Pb(II) = 0.44±0.02	0.0292	0.0710	0.0254	0.909	2.4210	0.0301	0.996
		Cu(II) = 0.15±0.02	0.0098	0.0513	0.0078	0.927	5.3783	0.0103	0.994
	2nd	Pb(II) = 0.44±0.02	0.0215	0.1011	0.0188	0.908	4.4901	0.0218	0.997
		Cu(II) = 0.15±0.02	0.0079	0.0823	0.0061	0.890	8.7878	0.0080	0.992
	3rd	Pb(II) = 0.44±0.02	0.0190	0.1221	0.0172	0.949	7.1822	0.0194	0.999
		Cu(II) = 0.15±0.02	0.0073	0.0946	0.0063	0.913	10.4093	0.0075	0.994
B[Cu(0.45)+Pb(0.15)]	4th	Pb(II) = 0.15±0.01	0.0017	-	-	-	25.7665	0.0018	0.926
		Cu(II) = 0.45±0.01	0.0160	0.0613	0.0131	0.879	3.0994	0.0166	0.991

$q_{e,exp}$ = experimental metal uptake capacity at equilibrium, q_{em} = metal uptake capacity at equilibrium calculated using kinetic models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with two independent data points.

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Table 5.33: Summary of estimated kinetic parameters for total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions from three loading cycles with B[Cu(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cu(0.45)+Pb(0.15)] combination.

				Pseudo-first-order rate model			Pseudo-second-order rate model		
Uncontrolled pH conditions	Metal ion combinations	Loading cycle	$TQ_{e,exp}$ (meq/g)	K_1 (1/min)	Q_{em} (meq/g)	R^2	K_2 (g/meq.min)	Q_{em} (meq/g)	R^2
	B[Cu(0.15)+Pb(0.45)]	1st	0.0455	0.0833	0.0432	0.847	2.8147	0.0468	0.999
		2nd	0.0359	0.0788	0.0330	0.890	3.0303	0.0364	0.997
		3rd	0.0290	0.1124	0.0276	0.936	5.9856	0.0297	0.999
	B[Cu(0.45)+Pb(0.15)]	4th	0.0336	0.1456	0.0275	0.891	2.8237	0.0329	0.988
				Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Controlled pH conditions	Metal ion combinations	Loading cycle	$Tq_{e,exp}$ (meq/g)	k_1 (1/min)	q_{em} (meq/g)	R^2	k_2 (g/meq.min)	q_{em} (meq/g)	R^2
	B[Cu(0.15)+Pb(0.45)]	1st	0.0391	0.0655	0.0336	0.913	1.6823	0.0404	0.996
		2nd	0.0294	0.0964	0.0249	0.904	2.9924	0.0298	0.996
		3rd	0.0263	0.1134	0.0238	0.941	4.3193	0.0269	0.998
	B[Cu(0.45)+Pb(0.15)]	4th	0.0177	0.1205	0.0158	0.905	8.1206	0.0179	0.997

$TQ_{e,exp}$ = experimental total metal removal at equilibrium, $Tq_{e,exp}$ = experimental total metal uptake at equilibrium Q_{em} = total metal removal at equilibrium calculated using rate models, q_{em} = total metal uptake at equilibrium calculated using kinetic models.

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experimentation.

In addition, the variations in cumulative metal mass removed as well as cumulative metal mass adsorbed during the four loading cycles have been presented in Fig. 5.66 and 5.67 respectively. It appeared that the GAA had ability to remove additional amount of Cu(II) and Pb(II) metal ions under uncontrolled pH conditions and to uptake additional amount of Cu(II) and Pb(II) metal ions under controlled pH conditions during first three loading cycles. The cumulative Cu(II) and Pb(II) metal removal and cumulative Cu(II) and Pb(II) metal uptake in the fourth loading cycle were relatively higher than the cumulative Cu(II) and Pb(II) metal removal and cumulative Cu(II) and Pb(II) metal uptake in the third loading cycle. The cumulative Cu(II), Pb(II) and total metal removal under uncontrolled pH conditions were 0.0305 meq, 0.0559 meq and 0.0864 meq respectively while cumulative Cu(II), Pb(II) and total metal uptake under controlled pH conditions were 0.0246 meq, 0.0428 meq and 0.0674 meq respectively up to fourth loading cycle (Fig. 5.66 and 5.67).

5.5.5 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for four loading cycles with binary-metal ion system comprising of Cr(III) and Pb(II) ions

The kinetic studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions by GAA from binary-metal ion systems comprising of Cr(III) and Pb(II) ions were investigated. The studies were carried out in the first set by exposing virgin GAA to consecutive three loading cycles with B[Cr(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cr(0.15)+Pb(0.45)] combination and in the second set, three loading cycles with B[Cr(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination. The results are presented in following sub-sections.

5.5.5.1 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for three loading cycles with B[Cr(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cr(0.15)+Pb(0.45)] combination

The variation in solution pH and metal removals during three loading cycles with B[Cr(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cr(0.15)+Pb(0.45)] combination under uncontrolled pH conditions are shown in Fig. 5.68

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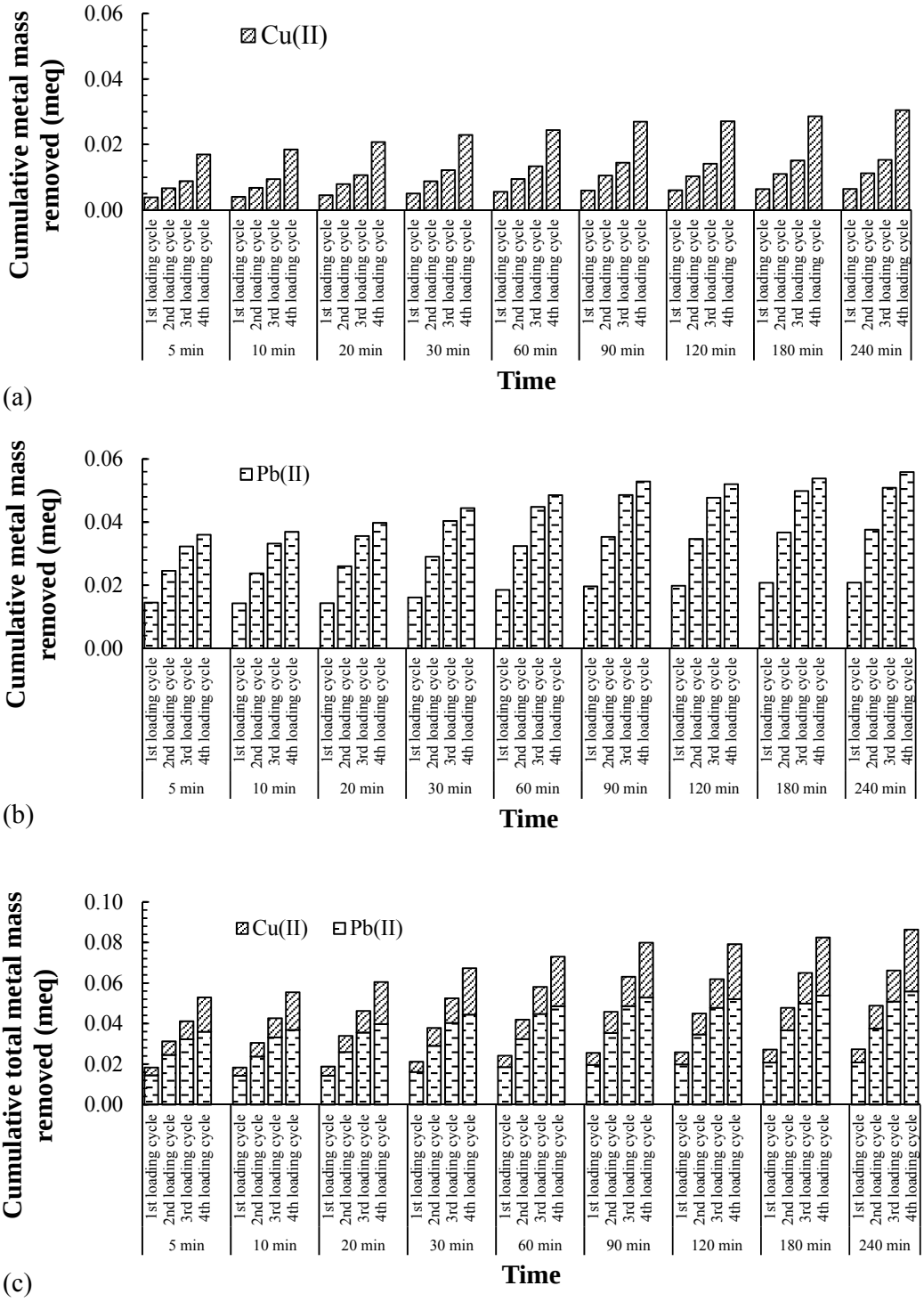

Fig. 5.66: Variation in cumulative (a) Cu(II), (b) Pb(II) and (c) total metal mass removed under uncontrolled pH conditions by GAA with three loading cycles with B[Cu(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cu(0.45)+Pb(0.15)] combination (Each data represents an average of two independent experimental values).

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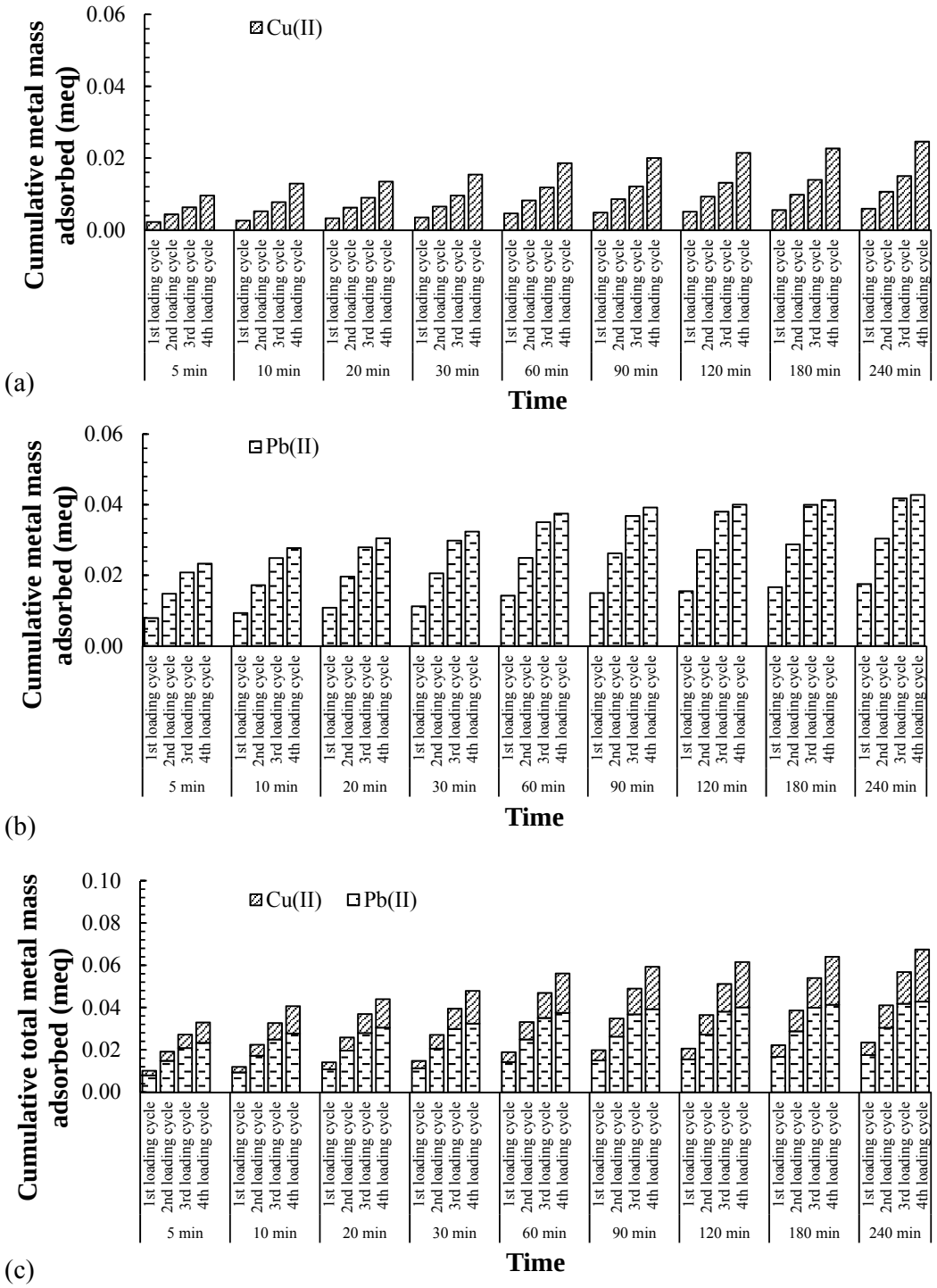

Fig. 5.67: Variation in cumulative (a) Cu(II), (b) Pb(II) and (c) total metal mass adsorbed under controlled pH conditions by GAA with three loading cycles with B[Cu(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cu(0.45)+Pb(0.15)] combination (Each data represents an average of two independent experimental values).

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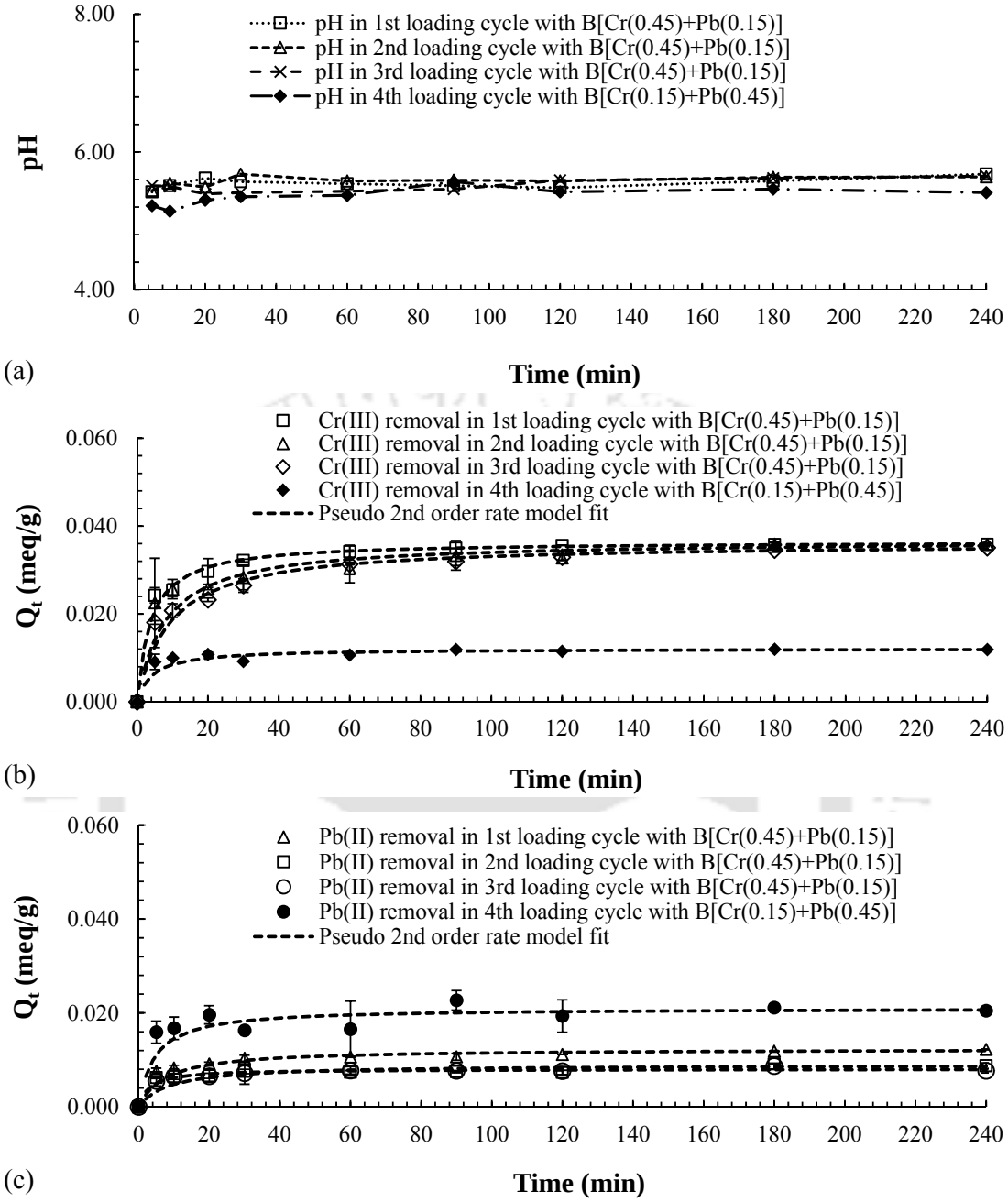

Fig. 5.68: Variation in (a) solution pH (b) Cr(III) and (c) Pb(II) metal removals in three loading cycles with B[Cr(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cr(0.15)+Pb(0.45)] combination under uncontrolled pH conditions {Initial metal conc. in B[Cr(0.45)+Pb(0.15)] combination = 0.46±0.01 meq/L of Cr(III) + 0.16±0.02 meq/L of Pb(II), B[Cr(0.15)+Pb(0.45)] combination = 0.15±0.01 meq/L of Cr(III) + 0.46±0.01 meq/L of Pb(II), Initial adjusted pH = 5.00±0.10; Temp. = 30±1 °C, GAA dose = 12 g/L, Mixing speed = 66 rpm} (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

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while metal uptakes under controlled pH conditions with similar loading cycles are shown in Fig. 5.69.

Under uncontrolled pH conditions of loading cycles, solution pH fluctuated in the range of 5.41-5.68 during the first three loading cycles with B[Cr(0.45)+Pb(0.15)] combination (Fig. 5.68). In the fourth loading cycle with B[Cr(0.15)+Pb(0.45)] combination, solution pH increased to 5.30 during initial 20 min. of the loading cycle. Further it reached to a pH value of 5.57 at 90 min. of the loading cycle and thereafter decreased to 5.41 at the end of the cycle. Since the solution pH increased beyond 5.50 in the first three loading cycles with B[Cr(0.45)+Pb(0.15)] combination and in the fourth loading cycle with B[Cr(0.15)+Pb(0.45)] combination, the removal of Cr(III) and Pb(II) metal ions from aqueous phase might be attributed to combined effects of precipitation and adsorption. However, under controlled pH conditions, pH of the solution during each of the loading cycles remained very close to the initially buffered pH of 5.00 during course of the experimentation. Hence, the removal of Cr(III) and Pb(II) metal ions from solution might be attributed to adsorption only.

Under uncontrolled pH conditions of loading cycles, Cr(III) and Pb(II) metal removals were observed to be fast up to 20 min. of the first loading cycle with B[Cr(0.45)+Pb(0.15)] combination [Fig. 5.68(b)&(c)]. The Cr(III) and Pb(II) metal removals were observed to be approximately 0.0297 meq/g and 0.0091 meq/g respectively at 20 min. of the first loading cycle. As the first loading cycle proceeded beyond 20 min., the removal of Cr(III) and Pb(II) metal ions increased slowly and observed removal was 0.0359 meq/g of Cr(III) and 0.0122 meq/g of Pb(II) at the end of the cycle. The GAA of the first loading cycle was again loaded with B[Cr(0.45)+Pb(0.15)] combination in the second loading cycle. The variation in Cr(III) metal removal during the second loading cycle was observed to overlap at 95% confidence interval with the same from the first loading cycle. Whereas the variation in Pb(II) metal removal during the second loading cycle was slightly lower than the variation in Pb(II) metal removal observed during the first loading cycle with a few data points overlapping at 95% confidence interval in the first 30 min. At the end of the second loading cycle, approximately 0.0358 meq/g of Cr(III) and 0.0088 meq/g of Pb(II) metal removals were observed. Similarly, when the GAA of the second loading cycle was again loaded with B[Cr(0.45)+Pb(0.15)] combination in the third loading cycle, the variation in Cr(III) metal removal during the third

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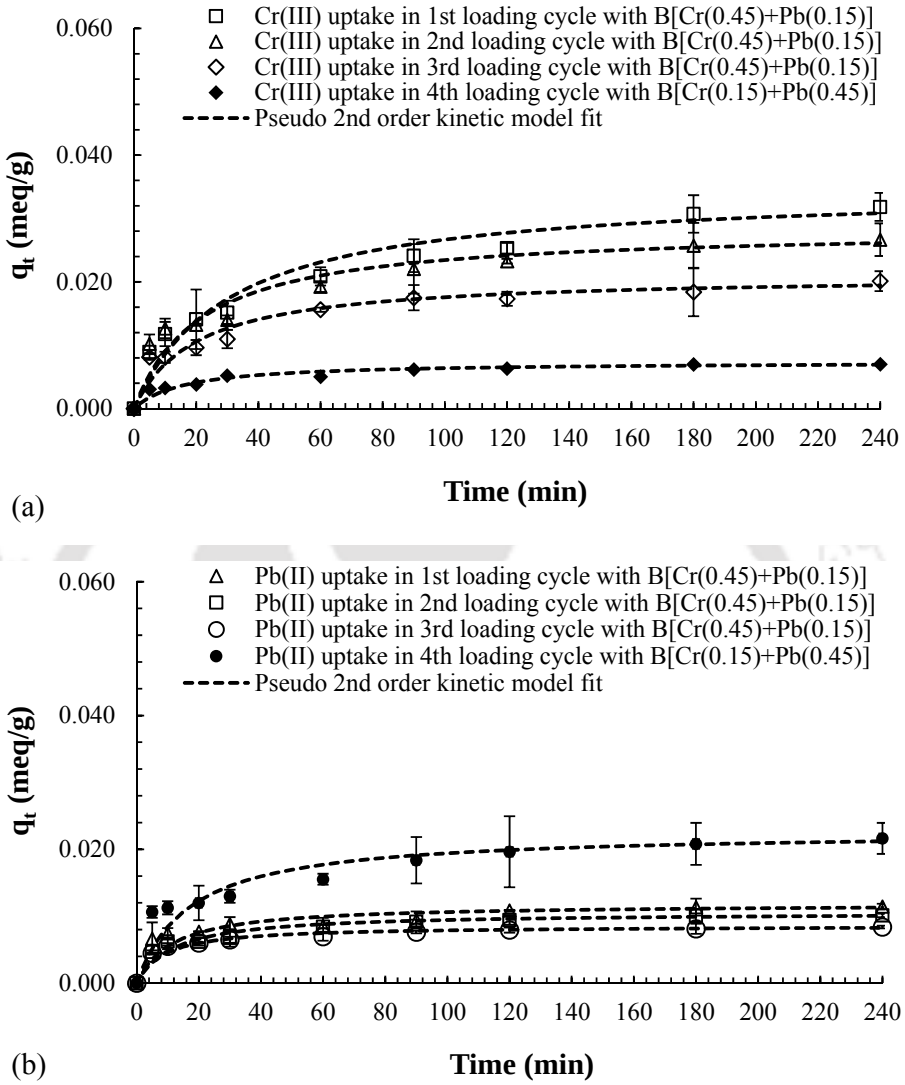

Fig. 5.69: Variation in (a) Cr(III) and (b) Pb(II) metal uptakes in three loading cycles with B[Cr(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cr(0.15)+Pb(0.45)] combination under controlled pH conditions {Initial metal ion conc. in B[Cr(0.45)+Pb(0.15)] combination: 0.45±0.01 meq/L of Cr(III) + 0.15±0.01 meq/L of Pb(II), B[Cr(0.15)+Pb(0.45)] combination: 0.15±0.02 meq/L of Cr(III) + 0.44±0.02 meq/L of Pb(II), Buffered pH = 4.90±0.10, Temp. = 30±1 ^{o}C, GAA dose = 12 g/L, Mixing speed = 66 rpm} (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

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loading cycle was observed to overlap at 95% confidence interval with the variation in Cr(III) metal removal observed during the first and second loading cycles. The variation in Pb(II) metal removal during the third loading cycle was observed to overlap at 95% confidence interval with the variation in Pb(II) metal removal observed during the second loading cycle. The Cr(III) and Pb(II) metal removals were approximately 0.0351 meq/g and 0.0077 meq/g respectively at the end of the third loading cycle. The GAA was able to remove relatively higher amounts of Cr(III) metal ions in comparison to amounts of Pb(II) metal ions from the solution up to third loading cycle. In the fourth loading cycle, the GAA of the third loading cycle was exposed to B[Cr(0.15)+Pb(0.45)] combination. The observed Pb(II) metal removal during the fourth loading cycle was higher than the observed Pb(II) metal removal during the first three loading cycles. The observed Cr(III) metal removal during the fourth loading cycle was lower than the observed Cr(III) metal removal during the previous three loading cycles. The Cr(III) and Pb(II) metal removals were 0.0119 meq/g and 0.0205 meq/g respectively at the end of the fourth loading cycle.

Under controlled pH conditions of the first loading cycle with B[Cr(0.45)+Pb(0.15)] combination (Fig. 5.69), faster Cr(III) and Pb(II) metal uptakes were observed up to the first 20 min. of the cycle while approximately 0.0318 meq/g of Cr(III) and 0.0115 meq/g of Pb(II) metal uptake were observed towards the end of the cycle. The GAA of the first loading cycle was again loaded with B[Cr(0.45)+Pb(0.15)] combination in the second loading cycle. The variation in Cr(III) and Pb(II) metal uptakes during the second loading cycle were observed to overlap at 95% confidence interval with the variation in Cr(III) and Pb(II) metal uptakes observed during the first loading cycle. At the end of the second loading cycle, approximately 0.0267 meq/g of Cr(III) and 0.0101 meq/g of Pb(II) metal uptakes were observed. Similarly, when the GAA of the second loading cycle was again loaded with B[Cr(0.45)+Pb(0.15)] combination in the third loading cycle, the variation in Cr(III) metal uptake was observed to be lower than the variation in Cr(III) metal uptake observed during the first and second loading cycles while the variation in Pb(II) metal uptake was observed to overlap at 95% confidence interval with the variation in Pb(II) metal uptake observed during the first and second loading cycles. The Cr(III) and Pb(II) metal uptakes were approximately 0.0201 meq/g and 0.0084 meq/g respectively at the end of the third loading cycle. In the fourth loading cycle, the GAA of the third loading cycle was exposed to B[Cr(0.15)+Pb(0.45)] combination. When the GAA was exposed to B[Cr(0.15)+Pb(0.45)] combination in the

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fourth loading cycle, the concentration of accumulated Cr(III) metal ions on surface of the GAA might be higher than the concentration of Cr(III) metal ions in the bulk solution while the concentration of accumulated Pb(II) metal ions on the surface of the GAA might be lower than the concentration of Pb(II) metal ions in the bulk solution. This might be able to induce concentration gradient of Pb(II) metal ions towards the GAA surfaces and consequently uptake of Pb(II) metal ions whereas lower concentration of Cr(III) in bulk solution might have induced lower migration of Cr(III) metal ions from the solution to GAA surfaces in the fourth loading cycles. The Cr(III) and Pb(II) metal uptakes under controlled pH conditions were approximately 0.0070 meq/g and 0.0216 meq/g respectively towards the end of the cycle.

Fig. 5.70 shows the variation in total metal removals (TQ_t) under uncontrolled pH conditions and total metal uptakes (Tq_t) under controlled pH conditions from each of the loading cycles. The variation in total metal removals (TQ_t) from second and third loading cycles under uncontrolled pH conditions were lower compared to first loading cycle and observed to overlap at 95% confidence intervals with each other. The variation in total metal removals (TQ_t) from the fourth loading cycle with B[Cr(0.15)+Pb(0.45)] combination were considerably lower compared to total metal removals (TQ_t) from the first three loading cycles. The total metal uptakes (Tq_t) from the first three loading cycles with B[Cr(0.45)+Pb(0.15)] combination were observed to decrease with increase in number of loading cycles. The total metal uptake (Tq_t) from the fourth loading cycle was observed to overlap at 95% confidence interval with the total metal uptake from the third loading cycle with B[Cr(0.45)+Pb(0.15)] combination.

The variations in metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions carried out for four loading cycles were fitted to pseudo-first- and pseudo-second-order rate and kinetic models. The estimated rate and kinetic model parameters are presented in Table 5.34 and 5.35 respectively. The higher R^2 values for pseudo-second-order rate model indicated its suitability to describe metal removal under uncontrolled pH conditions and pseudo-second-order kinetic model for metal uptake under controlled pH conditions. The best fit plots of pseudo-second-order rate and kinetic models to experimental metal removal and metal uptake data are also presented in Fig. 5.68 and 5.69.

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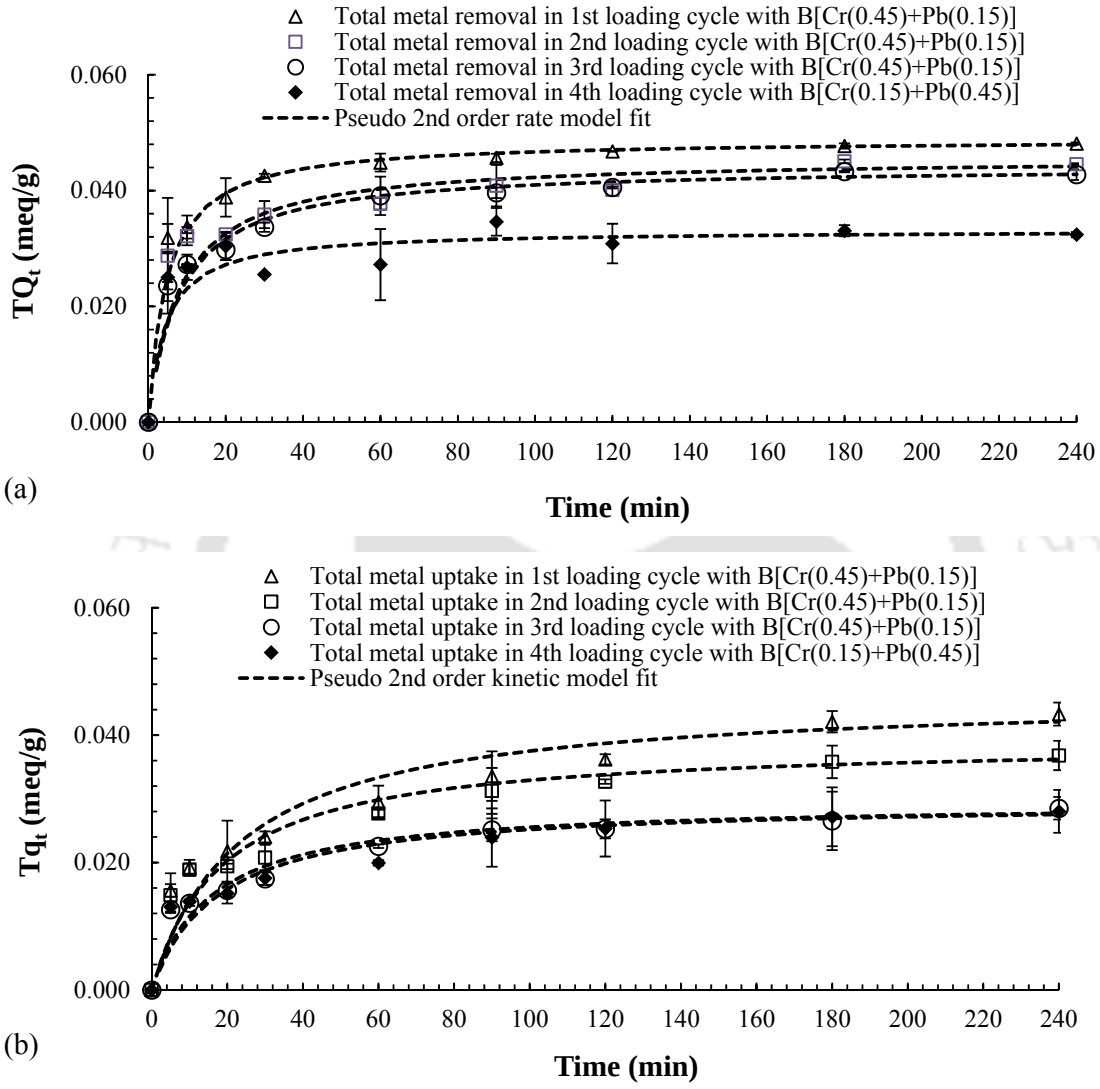

Fig. 5.70: Variation in (a) total metal removal under uncontrolled pH conditions and (b) total metal uptake under controlled pH conditions from three loading cycles with B[Cr(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cr(0.15)+Pb(0.45)] combination.

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Table 5.34: Summary of estimated pseudo-first and pseudo-second-order rate models parameters for three loading cycles with B[Cr(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cr(0.15)+Pb(0.45)] combination under uncontrolled pH conditions.

Metal ion combinations	Loading cycle	Metal with initial conc. (meq/L)	$Q_{e,exp}$ (meq/g)	Pseudo-first-order rate model			Pseudo-second-order rate model		
				K_1 (min^{-1})	Q_{em} (meq/g)	R^2	K_2 (g/meq.min)	Q_{em} (meq/g)	R^2
B[Cr(0.45)+Pb(0.15)]	1st	Pb(II) = 0.16±0.02	0.0122	0.1383	0.0108	0.932	10.8491	0.0124	0.997
		Cr(III) = 0.46±0.01	0.0359	0.1421	0.0345	0.949	7.2189	0.0365	0.999
	2nd	Pb(II) = 0.15±0.01	0.0088	0.1258	0.0079	0.849	13.0910	0.0089	0.988
		Cr(III) = 0.46±0.00	0.0358	0.1256	0.0326	0.897	3.4764	0.0367	0.998
	3rd	Pb(II) = 0.15±0.02	0.0077	0.1662	0.0077	0.940	42.5535	0.0081	0.993
		Cr(III) = 0.45±0.01	0.0351	0.0837	0.0323	0.928	2.9831	0.0362	0.997
B[Cr(0.15)+Pb(0.45)]	4th	Pb(II) = 0.46±0.01	0.0205	0.1041	0.0209	0.772	10.6361	0.0210	0.993
		Cr(III) = 0.15±0.01	0.0119	0.1752	0.0111	0.901	19.3280	0.0121	0.998

$Q_{e,exp}$ = experimental metal removal at equilibrium, Q_{em} = metal removal at equilibrium calculated using rate models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with two independent data points.

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Table 5.35: Summary of estimated pseudo-first and pseudo-second-order kinetic models parameters for three loading cycles with B[Cr(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cr(0.15)+Pb(0.45)] combination under controlled pH conditions.

Metal ion combinations	Loading cycle	Metal with initial conc. (meq/L)	$q_{e,exp}$ (meq/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
				k_1 (min^{-1})	q_{em} (meq/g)	R^2	k_2 (g/meq.min)	q_{em} (meq/g)	R^2
B[Cr(0.45)+Pb(0.15)]	1st	Pb(II) = 0.15±0.01	0.0115	0.0905	0.0099	0.850	7.4004	0.0118	0.993
		Cr(III) = 0.46±0.01	0.0318	0.0346	0.0260	0.915	0.9575	0.0347	0.983
	2nd	Pb(II) = 0.16±0.01	0.0101	0.0773	0.0091	0.897	7.8711	0.0106	0.996
		Cr(III) = 0.45±0.01	0.0267	0.0437	0.0229	0.891	1.6525	0.0284	0.991
	3rd	Pb(II) = 0.15±0.00	0.0084	0.1159	0.0078	0.928	13.5108	0.0086	0.997
		Cr(III) = 0.45±0.01	0.0201	0.0358	0.0168	0.923	2.4003	0.0211	0.993
B[Cr(0.15)+Pb(0.45)]	4th	Pb(II) = 0.45±0.01	0.0216	0.0481	0.0187	0.856	2.6110	0.0227	0.990
		Cr(III) = 0.15±0.01	0.0070	0.0511	0.0590	0.909	8.5496	0.0074	0.994

$q_{e,exp}$ = experimental metal uptake capacity at equilibrium, q_{em} = metal uptake capacity at equilibrium calculated using kinetic models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with two independent data points.

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An inspection of Table 5.34 and 5.35 revealed approximately similar values of $Q_{e,exp}$ and Q_{em} for Cr(III) metal removal while decreasing trend in values of $q_{e,exp}$ and q_{em} for Cr(III) metal was observed with increase in number of loading cycles with B[Cr(0.45)+Pb(0.15)] combination. The values of $Q_{e,exp}$ and Q_{em} as well as values of $q_{e,exp}$ and q_{em} for Pb(II) metal showed decreasing trend with increase in number of loading cycles up to the third cycle. However, the values of $Q_{e,exp}$ and $q_{e,exp}$ as well as Q_{em} and q_{em} for Pb(II) metal in the fourth loading cycle with B[Cr(0.15)+Pb(0.45)] combination were higher compared to similar values obtained with the previous three loading cycles with B[Cr(0.45)+Pb(0.15)] combination. Similarly, the variations in total metal removals under uncontrolled pH conditions and metal uptakes under controlled pH conditions carried out for four loading cycles were also fitted to pseudo-first- and pseudo-second-order rate and kinetic models. The estimated rate and kinetic model parameters are presented in Table 5.36. The higher R^2 values for pseudo-second-order rate model indicated its suitability to describe total metal removal under uncontrolled pH conditions and pseudo-second-order kinetic model for total metal uptake under controlled pH conditions. An inspection of Table 5.36 revealed decreasing trend in values of $TQ_{e,exp}$ and Q_{em} as well as $Tq_{e,exp}$ and q_{em} with increase in number of loading cycles.

In addition, variations in cumulative metal mass removed under uncontrolled pH conditions and cumulative metal mass adsorbed under controlled pH conditions by GAA with three loading cycles with B[Cr(0.45)+Pb(0.15)] combination followed with fourth loading cycle with B[Cr(0.15)+Pb(0.45)] combination have been presented in Fig. 5.71 and 5.72 respectively. It appeared that the GAA had ability to remove additional amount of Cr(III) and Pb(II) metal ions under uncontrolled pH conditions and to uptake additional amount of Cr(III) and Pb(II) metal ions under controlled pH conditions during the first three loading cycles. The cumulative Cr(III) and Pb(II) metal removal and cumulative Cr(III) and Pb(II) metal uptake in the fourth loading cycle were relatively higher than the cumulative Cr(III) and Pb(II) metal removal and cumulative Cr(III) and Pb(II) metal uptake in the third loading cycle. The cumulative Cr(III), Pb(II) and total metal removal under uncontrolled pH conditions were 0.0721 meq, 0.0295 meq and 0.1016 meq respectively while cumulative Cr(III), Pb(II) and total metal uptake under controlled pH conditions were 0.0522 meq, 0.0310 meq and 0.0832 meq respectively up to fourth loading cycle (Fig. 5.71 and 5.72).

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Table 5.36: Summary of estimated kinetic parameters for total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions from three loading cycles with B[Cr(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cr(0.15)+Pb(0.45)] combination.

				Pseudo-first-order rate model			Pseudo-second-order rate model		
Uncontrolled pH conditions	Metal ion combinations	Loading cycle	$TQ_{e,exp}$ (meq/g)	K_1 (1/min)	Q_{em} (meq/g)	R^2	K_2 (g/meq.min)	Q_{em} (meq/g)	R^2
	B[Cr(0.45)+Pb(0.15)]	1st	0.0481	0.1426	0.0456	0.948	4.3769	0.0488	0.999
		2nd	0.0446	0.1307	0.0406	0.895	2.7548	0.0457	0.996
		3rd	0.0428	0.0952	0.0399	0.927	2.8575	0.0442	0.999
	B[Cr(0.15)+Pb(0.45)]	4th	0.0324	0.1280	0.0313	0.831	6.9490	0.0332	0.995
				Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Controlled pH conditions	Metal ion combinations	Loading cycle	$Tq_{e,exp}$ (meq/g)	k_1 (1/min)	q_{em} (meq/g)	R^2	k_2 (g/meq.min)	q_{em} (meq/g)	R^2
	B[Cr(0.45)+Pb(0.15)]	1st	0.0433	0.0453	0.0375	0.888	0.9385	0.0462	0.987
		2nd	0.0368	0.0513	0.0312	0.889	1.4012	0.0389	0.994
		3rd	0.0285	0.0512	0.0254	0.913	2.1797	0.0295	0.995
	B[Cr(0.15)+Pb(0.45)]	4th	0.0280	0.0478	0.0251	0.878	1.9668	0.0295	0.993

$TQ_{e,exp}$ = experimental total metal removal at equilibrium, $Tq_{e,exp}$ = experimental total metal uptake at equilibrium Q_{em} = total metal removal at equilibrium calculated using rate models, q_{em} = total metal uptake at equilibrium calculated using kinetic models.

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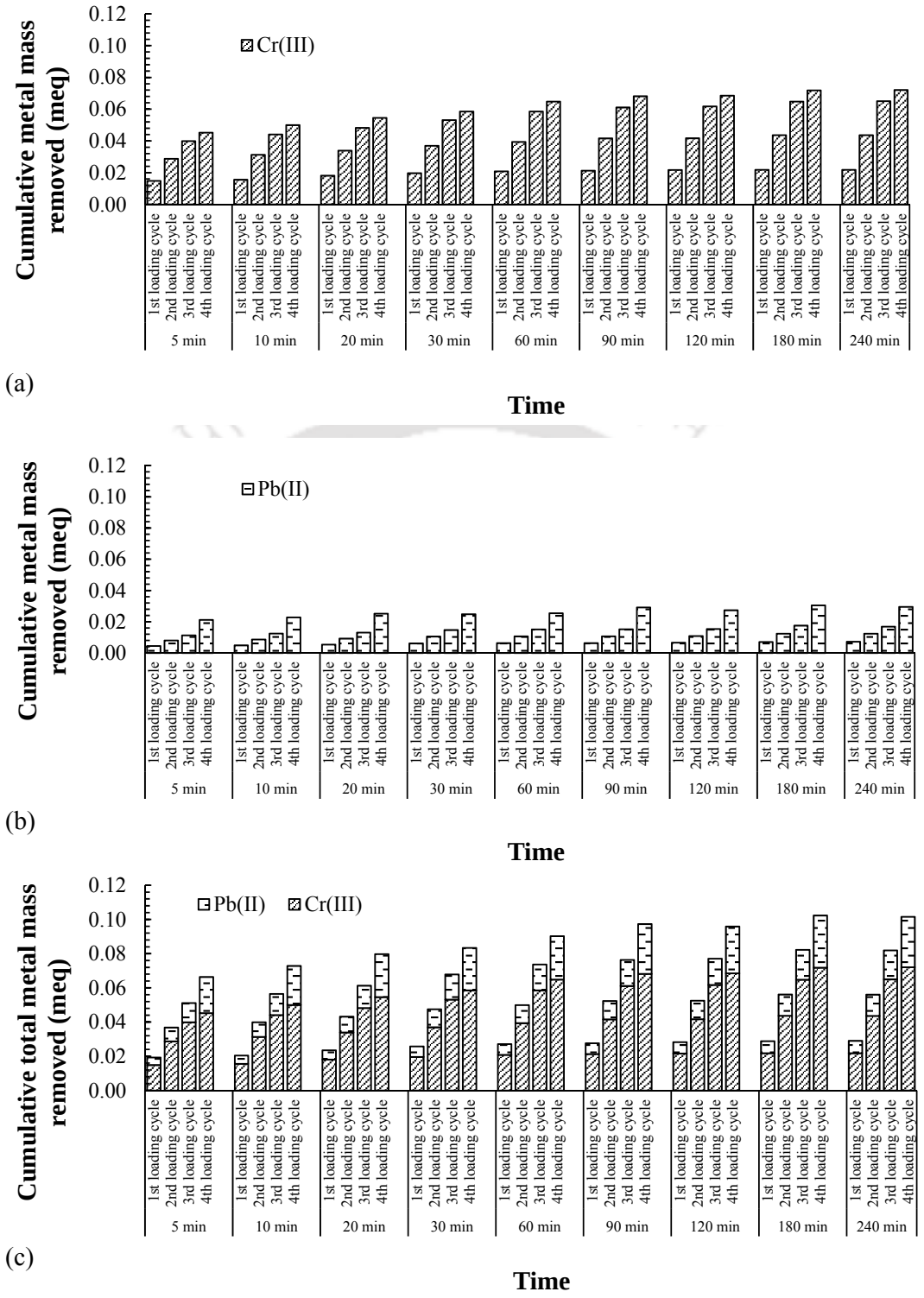

Fig. 5.71: Variation in cumulative (a) Cr(III), (b) Pb(II) and (c) total metal mass removed under uncontrolled pH conditions by GAA with three loading cycles with B[Cr(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cr(0.15)+Pb(0.45)] combination (Each data represents an average of two independent experimental values).

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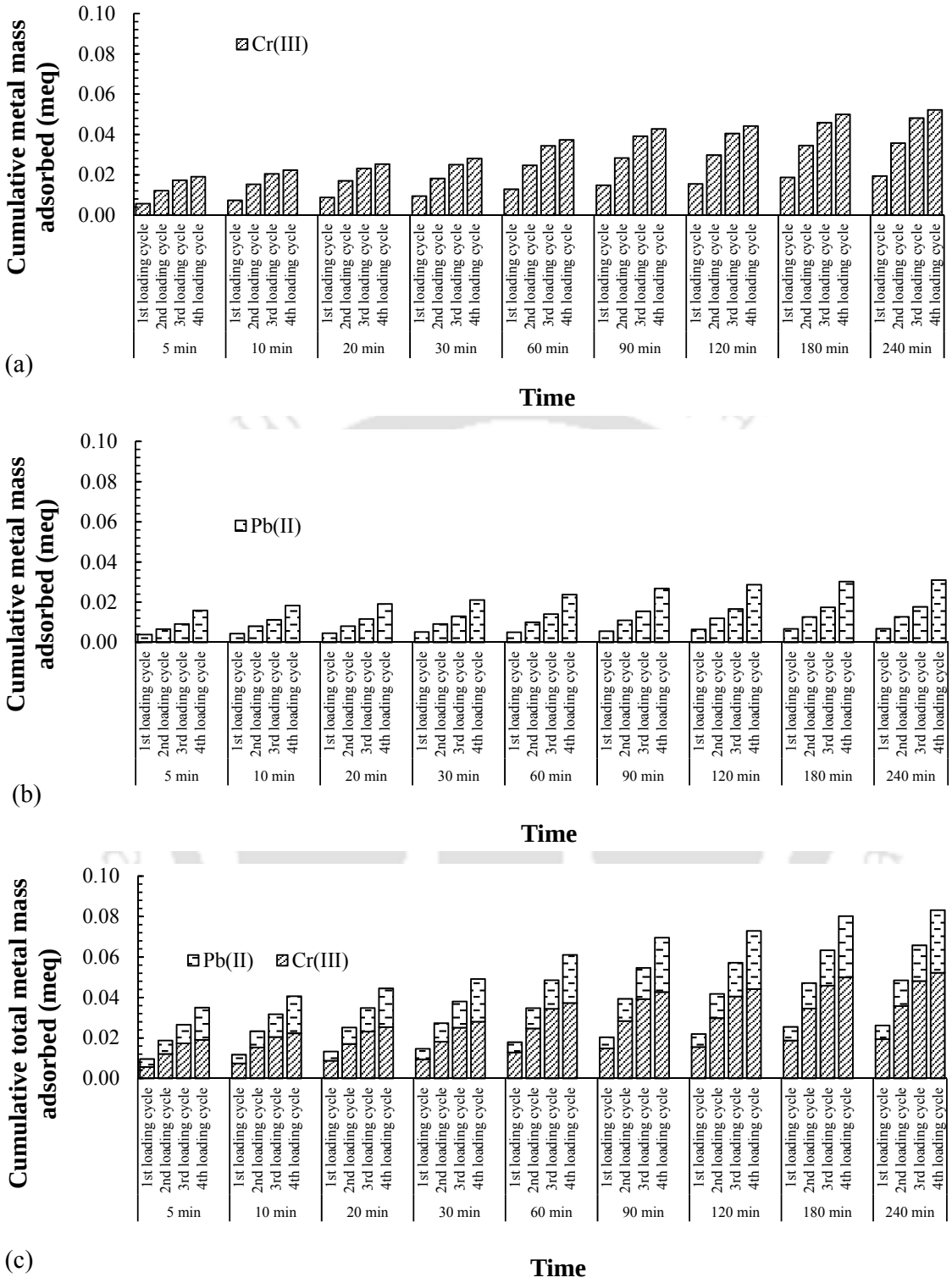

Fig. 5.72: Variation in cumulative (a) Cr(III), (b) Pb(II) and (c) total metal mass adsorbed under controlled pH conditions by GAA with three loading cycles with B[Cr(0.45)+Pb(0.15)] combination followed by fourth loading cycle with B[Cr(0.15)+Pb(0.45)] combination (Each data represents an average of two independent experimental values).

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5.5.5.2 Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for three loading cycles with B[Cr(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination

The variation in solution pH and metal removals during three loading cycles with B[Cr(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination under uncontrolled pH conditions are shown in Fig. 5.73 while metal uptakes under controlled pH conditions with similar loading cycles are shown in Fig. 5.74.

Under uncontrolled pH conditions of loading cycles, the solution pH fluctuated in the range of 5.10-5.52 during the first loading cycle (Fig. 5.73). At the end of the second loading cycle, the observed solution pH was 5.62. The solution pH in the third loading cycle fluctuated in the range of 5.36-5.65 while in the fourth loading cycle solution pH fluctuated in the range of 5.25-5.81. Since the solution pH increased beyond 5.50 in the first three loading cycles with B[Cr(0.15)+Pb(0.45)] combination and in the fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination, the removal of Cr(III) and Pb(II) metal ions from aqueous phase might be attributed to combined effects of precipitation and adsorption. However, under controlled pH conditions, pH of the solution during each of the loading cycles remained very close to the initially buffered pH of 5.00 during course of the experimentation. Hence, the removal of Cr(III) and Pb(II) metal ions from solution might be attributed to adsorption only.

Under uncontrolled pH conditions of loading cycles, Cr(III) and Pb(II) metal removals were faster up to 10-20 min. of the first loading cycle with B[Cr(0.15)+Pb(0.45)] combination [Fig. 5.73(b)&(c)]. The Cr(III) and Pb(II) metal removals were observed to be approximately 0.0114 meq/g and 0.0226 meq/g respectively at 20 min. of the first loading cycle. As the first loading cycle proceeded beyond 20 min., removals of metal ions increased slowly and observed removals were 0.0125 meq/g and 0.0318 meq/g respectively at the end of the cycle. The GAA of the first loading cycle was again loaded with B[Cr(0.15)+Pb(0.45)] combination in the second loading cycle. The variation in Cr(III) metal removal during the second loading cycle was observed to overlap at 95% confidence interval with the same from the first loading cycle. Furthermore, the variation in Pb(II) metal removal during the second

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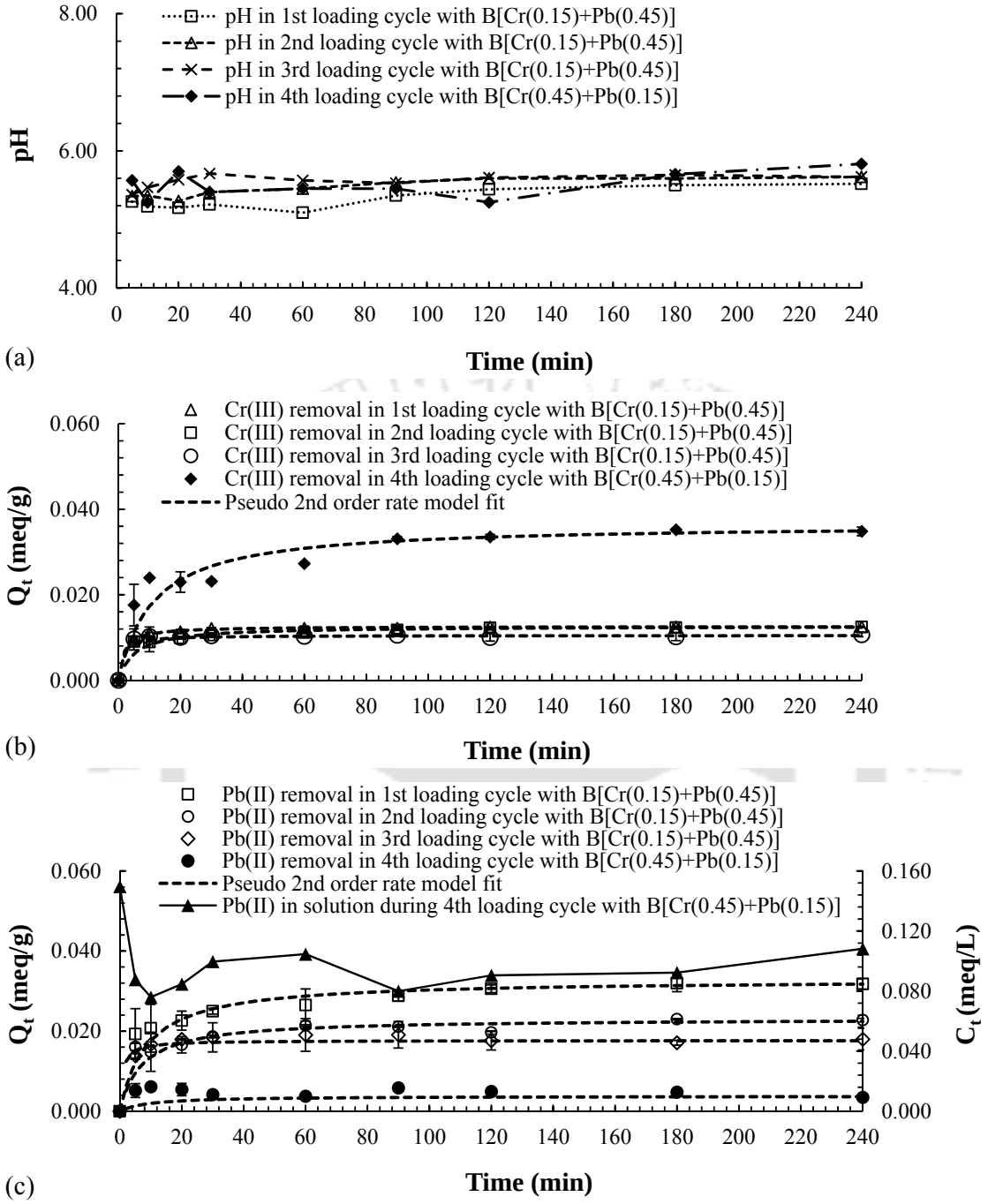

Fig. 5.73: Variation in (a) solution pH (b) Cr(III) and (c) Pb(II) metal removals in three loading cycles with B[Cr(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination under uncontrolled pH conditions {Initial metal conc. in B[Cr(0.15)+Pb(0.45)] combination = 0.15±0.02 meq/L of Cr(III) + 0.44±0.01 meq/L of Pb(II), B[Cr(0.45)+Pb(0.15)] combination = 0.45±0.02 meq/L of Cr(III) + 0.15±0.02 meq/L of Pb(II), Initial adjusted pH = 5.00±0.10, Temp. = 30±1 °C, GAA dose = 12 g/L, Mixing speed = 66 rpm} (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

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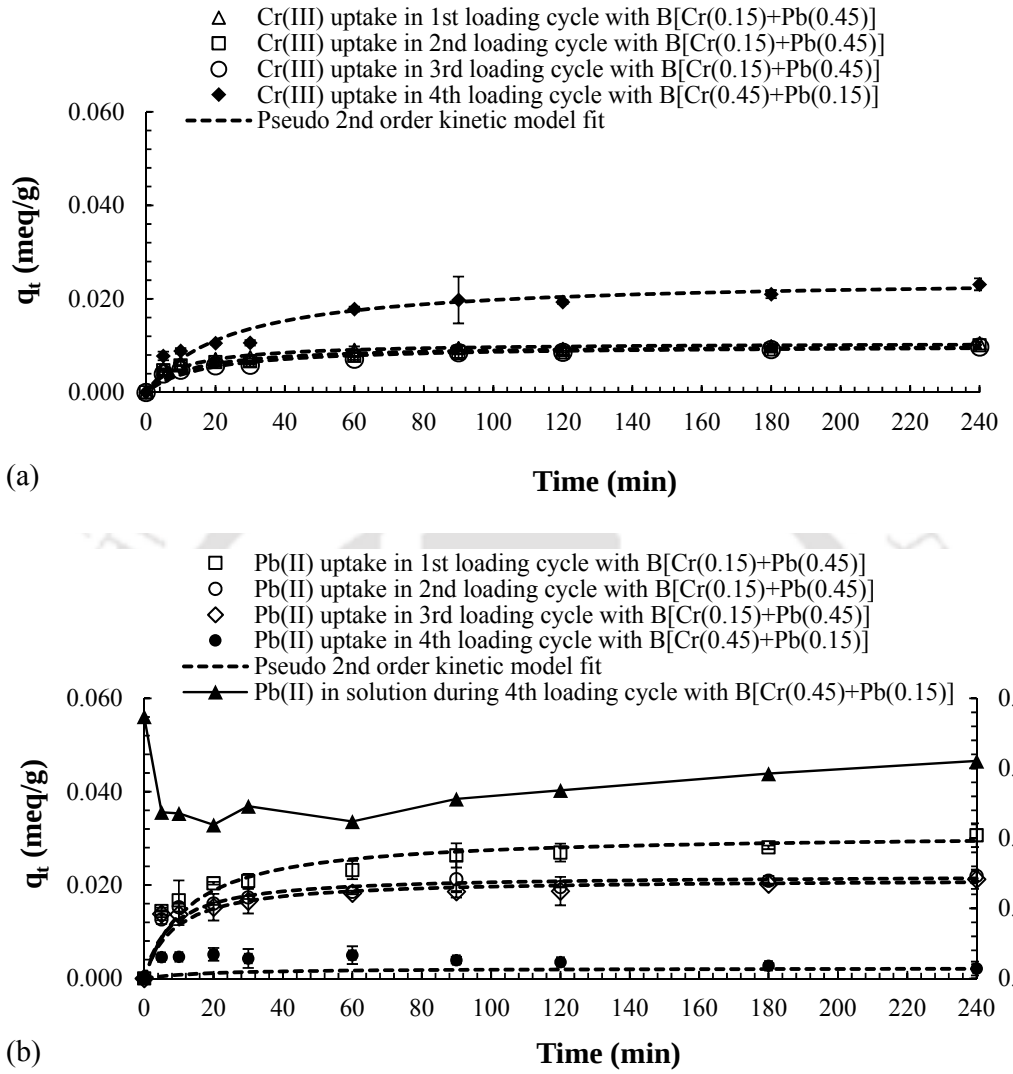

Fig. 5.74: Variation in (a) Cr(III) and (b) Pb(II) metal uptakes in three loading cycles with B[Cr(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination under controlled pH conditions {Initial metal ion conc. in B[Cr(0.15)+Pb(0.45)] combination: 0.16±0.01 meq/L of Cr(III) + 0.44±0.02 meq/L of Pb(II), B[Cr(0.45)+Pb(0.15)] combination: 0.46±0.02 meq/L of Cr(III) + 0.15±0.01 meq/L of Pb(II), Buffered pH = 4.90±0.10, Temp. = 30±1 ^{o}C, GAA dose = 12 g/L, Mixing speed = 66 rpm} (Each data represents an average of two independent experimental values with vertical bars representing 95% confidence interval).

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loading cycle was observed to be lower than the variation in Pb(II) metal removal observed during the first loading cycle and most of the data points did not overlap at 95% confidence interval except a few in the beginning. At the end of the second loading cycle, approximately 0.0125 meq/g of Cr(III) and 0.0228 meq/g of Pb(II) metal removals were observed. Similarly, when the GAA of the second loading cycle was again loaded with B[Cr(0.15)+Pb(0.45)] combination in the third loading cycle, the variation in Cr(III) metal removal during the third loading cycle was observed to overlap at 95% confidence interval with the variation in Cr(III) metal removal observed during the first and second loading cycles while the variation in Pb(II) metal removal during the third loading cycle overlapped at 95% confidence interval with the variation in Pb(II) metal removal observed during the second loading cycle. The Cr(III) and Pb(II) metal removals were approximately 0.0107 meq/g and 0.0180 meq/g respectively at the end of the third loading cycle. The GAA was able to remove relatively higher amounts of Pb(II) metal ions in comparison to amounts of Cr(III) metal ions from the solution up to third loading cycle. In the fourth loading cycle, the GAA of the third loading cycle was exposed to B[Cr(0.45)+Pb(0.15)] combination. The variation in Cr(III) metal removal during the fourth loading cycle was observed to be higher than the variation in Cr(III) metal removal observed during the first three loading cycles as none of the data points overlapped at 95% confidence intervals. However, there was little change in Pb(II) metal concentration in the solution indicating insignificant removal of Pb(II) metal ions. The Cr(III) and Pb(II) metal removals were 0.0348 meq/g and 0.0035 meq/g respectively at the end of the fourth loading cycle.

Under controlled pH conditions of the first loading cycle with B[Cr(0.15)+Pb(0.45)] combination (Fig. 5.74), rapid Cr(III) and Pb(II) metal uptakes were observed up to first 10-20 min. of the cycle and then it increased slowly to 0.0105 meq/g and 0.0307 meq/g respectively towards the end of the cycle. The GAA of the first loading cycle was again loaded with B[Cr(0.15)+Pb(0.45)] combination in the second loading cycle. The variation in Cr(III) metal uptake during the second loading cycle was observed to overlap at 95% confidence interval with the same from the first loading cycle while the variation in Pb(II) metal uptake was lower than the same from the first loading cycle with no overlap of data points at 95% confidence intervals. At the end of the second loading cycle, approximately 0.0101 meq/g of Cr(III) and 0.0220 meq/g of Pb(II) metal uptakes were observed. Similarly, when the GAA of second loading cycle was again loaded with B[Cr(0.15)+Pb(0.45)]

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combination in the third loading cycle, the variation in Cr(III) and Pb(II) metal uptakes during the third loading cycle were observed to overlap at 95% confidence interval with respective variation in Cr(III) and Pb(II) metal uptakes observed during the second loading cycle. The Cr(III) and Pb(II) metal uptakes were approximately 0.0097 meq/g and 0.0212 meq/g respectively at the end of the third loading cycle. In the fourth loading cycle, the GAA of the third loading cycle was exposed to B[Cr(0.45)+Pb(0.15)] combination. The variation in Cr(III) metal uptake during the fourth loading cycle was observed to be higher than the variation in Cr(III) metal uptake observed during the first three loading cycles as no data points overlapped at 95% confidence intervals. However, there was little change in Pb(II) metal concentration in the solution indicating insignificant uptake of Pb(II) metal ions. The Cr(III) and Pb(II) metal uptakes were approximately 0.0231 meq/g and 0.0021 meq/g respectively towards the end of the cycle.

Fig. 5.75 shows the variation in total metal removals (TQ_t) under uncontrolled pH conditions and total metal uptakes (Tq_t) under controlled pH conditions from each of the loading cycles. The variation in total metal removals (TQ_t) were observed to decrease with increase in number of loading cycles with B[Cr(0.15)+Pb(0.45)] combination while the total metal removal (TQ_t) from the fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination was higher than the total metal removals from second and third loading cycles with B[Cr(0.15)+Pb(0.45)] combination. The total metal uptakes (Tq_t) from the second and third loading cycles were lower than the first loading cycles with B[Cr(0.15)+Pb(0.45)] combination and overlapped at 95% confidence intervals with each other. The total metal uptake (Tq_t) from the fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination was lower than the total metal uptakes from the third loading cycle with B[Cr(0.15)+Pb(0.45)] combination.

The variations in metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions carried out for four loading cycles were fitted to pseudo-first- and pseudo-second-order rate and kinetic models. The estimated rate and kinetic model parameters obtained under uncontrolled and controlled pH conditions are presented in Table 5.37 and 5.38 respectively. The higher R^2 values for pseudo-second-order rate model indicated its suitability to describe metal removal under uncontrolled pH conditions and pseudo-second-order kinetic model for metal uptake under controlled pH conditions. The best

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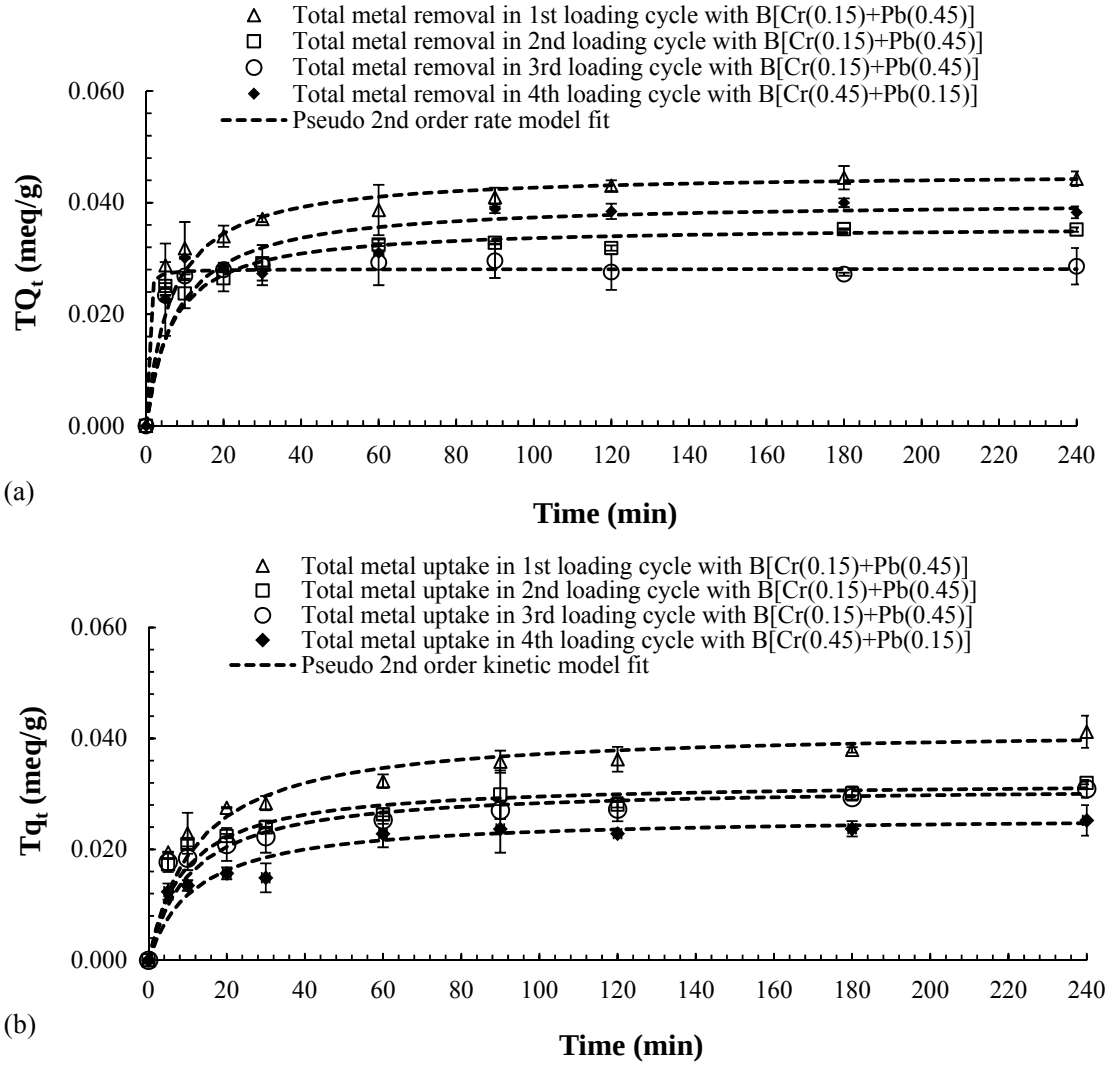

Fig. 5.75: Variation in (a) total metal removal under uncontrolled pH conditions and (b) total metal uptake under controlled pH conditions from three loading cycles with B[Cr(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination.

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Table 5.37: Summary of estimated pseudo-first and pseudo-second-order rate models parameters for three loading cycles with B[Cr(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination under uncontrolled pH conditions.

Metal ion combinations	Loading cycle	Metal with initial conc. (meq/L)	$Q_{e.exp}$ (meq/g)	Pseudo-first-order rate model			Pseudo-second-order rate model		
				K_1 (min^{-1})	Q_{em} (meq/g)	R^2	K_2 (g/meq.min)	Q_{em} (meq/g)	R^2
B[Cr(0.15)+Pb(0.45)]	1st	Pb(II) = 0.44±0.01	0.0318	0.0973	0.0292	0.891	3.5473	0.0329	0.998
		Cr(III) = 0.15±0.02	0.0125	0.3635	0.0121	0.988	47.7481	0.0126	1.000
	2nd	Pb(II) = 0.45±0.00	0.0228	0.0819	0.0222	0.835	6.1349	0.0232	0.994
		Cr(III) = 0.15±0.01	0.0125	0.1258	0.0120	0.891	15.0613	0.0127	0.999
	3rd	Pb(II) = 0.46±0.01	0.0180	0.3059	0.0184	0.987	67.5326	0.0177	0.998
		Cr(III) = 0.15±0.01	0.0107	0.9951	0.0104	0.993	86.0046	0.0105	0.999
B[Cr(0.45)+Pb(0.15)]	4th	Pb(II) = 0.14±0.01	0.0035	-	-	-	28.4249	0.00381	0.948
		Cr(III) = 0.45±0.02	0.0348	0.0855	0.0320	0.856	2.4720	0.0366	0.995

$Q_{e,exp}$ = experimental metal removal at equilibrium, Q_{em} = metal removal at equilibrium calculated using rate models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with two independent data points.

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Table 5.38: Summary of estimated pseudo-first and pseudo-second-order kinetic models parameters for three loading cycles with B[Cr(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination under controlled pH conditions.

Metal ion combinations	Loading cycle	Metal with initial conc. (meq/L)	$q_{e,exp}$ (meq/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
				k_1 (min^{-1})	q_{em} (meq/g)	R^2	k_2 (g/meq.min)	q_{em} (meq/g)	R^2
B[Cr(0.15)+Pb(0.45)]	1st	Pb(II) = 0.46±0.00	0.0307	0.0872	0.0252	0.906	2.5048	0.0310	0.994
		Cr(III) = 0.16±0.01	0.0105	0.0969	0.0093	0.931	9.3244	0.0107	0.997
	2nd	Pb(II) = 0.45±0.01	0.0220	0.1869	0.0193	0.926	6.1013	0.0221	0.996
		Cr(III) = 0.15±0.02	0.0101	0.0938	0.0085	0.898	7.5824	0.0101	0.992
	3rd	Pb(II) = 0.44±0.01	0.0212	0.1100	0.0191	0.881	5.4854	0.0214	0.995
		Cr(III) = 0.15±0.02	0.0097	0.0589	0.0085	0.902	5.9400	0.0101	0.991
B[Cr(0.45)+Pb(0.15)]	4th	Pb(II) = 0.16±0.01	0.0021	-	-	-	23.9674	0.0022	0.948
		Cr(III) = 0.46±0.02	0.0231	0.0334	0.0210	0.934	1.6968	0.0245	0.987

$q_{e,exp}$ = experimental metal uptake capacity at equilibrium, q_{em} = metal uptake capacity at equilibrium calculated using kinetic models. Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with two independent data points.

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fit plots of pseudo-second-order rate and kinetic models to experimental metal removal and metal uptake data are also presented in Fig. 5.73 and 5.74. An inspection of Table 5.37 and 5.38 revealed decreasing trends in values of $Q_{e,exp}$ and $q_{e,exp}$ as well as Q_{em} and q_{em} for Pb(II) metal with increase in number of loading cycles with B[Cr(0.15)+Pb(0.45)] combination. The values of $Q_{e,exp}$ and $q_{e,exp}$ as well as Q_{em} and q_{em} for Cr(III) metal varied in a narrow range with increase in number of loading cycles with B[Cr(0.15)+Pb(0.45)] combination. However, the values of $Q_{e,exp}$ and $q_{e,exp}$ as well as Q_{em} and q_{em} for Cr(III) metal in the fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination were higher compared to similar values obtained with the previous three loading cycles with B[Cr(0.15)+Pb(0.45)] combination. Similarly, the variations in total metal removals under uncontrolled pH conditions and total metal uptakes under controlled pH conditions carried out for four loading cycles were also fitted to pseudo-first- and pseudo-second-order rate and kinetic models. The estimated rate and kinetic model parameters are presented in Table 5.39. The higher R^2 values for pseudo-second-order rate model indicated its suitability to describe total metal removal under uncontrolled pH conditions and pseudo-second-order kinetic model for total metal uptake under controlled pH conditions. An inspection of Table 5.39 revealed decreasing trend in values of $TQ_{e,exp}$ and Q_{em} up to third loading cycles with B[Cr(0.15)+Pb(0.45)] combination while in the fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination the obtained values of $TQ_{e,exp}$ and Q_{em} were higher than the second and third loading cycles. However the values of $q_{e,exp}$ and q_{em} were decreasing with increase in number of loading cycles.

In addition, variations in cumulative metal mass removed under uncontrolled pH conditions and cumulative metal mass adsorbed under controlled pH conditions by GAA with three loading cycles with B[Cr(0.15)+Pb(0.45)] combination followed with fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination have been presented in Fig. 5.76 and 5.77 respectively. It appeared that the GAA had ability to remove additional amount of Cr(III) and Pb(II) metal ions under uncontrolled pH conditions and to uptake additional amount of Cr(III) and Pb(II) metal ions under controlled pH conditions during first three loading cycles. The cumulative Cr(III) and Pb(II) metal removal and cumulative Cr(III) and Pb(II) metal uptake in the fourth loading cycle were relatively higher than the cumulative Cr(III) and Pb(II) metal removal and cumulative Cr(III) and Pb(II) metal uptake in the third loading cycle. The cumulative Cr(III), Pb(II) and total metal removal under uncontrolled pH conditions were 0.0422 meq, 0.0465 meq and 0.0887 meq respectively while cumulative

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Table 5.39: Summary of estimated kinetic parameters for total metal removal under uncontrolled pH conditions and total metal uptake under controlled pH conditions from three loading cycles with B[Cr(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination.

				Pseudo-first-order rate model			Pseudo-second-order rate model		
Uncontrolled pH conditions	Metal ion combinations	Loading cycle	$TQ_{e,exp}$ (meq/g)	K_1 (1/min)	Q_{em} (meq/g)	R^2	K_2 (g/meq.min)	Q_{em} (meq/g)	R^2
	B[Cr(0.15)+Pb(0.45)]	1st	0.0443	0.1381	0.0413	0.924	3.4865	0.0454	0.999
		2nd	0.0352	0.0979	0.0337	0.861	4.3751	0.0358	0.997
		3rd	0.0286	0.4265	0.0284	0.989	221.4950	0.0281	0.998
	B[Cr(0.45)+Pb(0.15)]	4th	0.0383	0.1010	0.0366	0.839	3.1921	0.0403	0.995
				Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Controlled pH conditions	Metal ion combinations	Loading cycle	$Tq_{e,exp}$ (meq/g)	k_1 (1/min)	q_{em} (meq/g)	R^2	k_2 (g/meq.min)	q_{em} (meq/g)	R^2
	B[Cr(0.15)+Pb(0.45)]	1st	0.0412	0.0894	0.0347	0.915	1.9727	0.0417	0.995
		2nd	0.0320	0.1196	0.0272	0.913	3.4344	0.0322	0.996
		3rd	0.0309	0.0907	0.0265	0.885	2.9946	0.0314	0.996
	B[Cr(0.45)+Pb(0.15)]	4th	0.0252	0.0564	0.0230	0.894	3.2294	0.0260	0.995

$TQ_{e,exp}$ = experimental total metal removal at equilibrium, $Tq_{e,exp}$ = experimental total metal uptake at equilibrium Q_{em} = total metal removal at equilibrium calculated using rate models, q_{em} = total metal uptake at equilibrium calculated using kinetic models.

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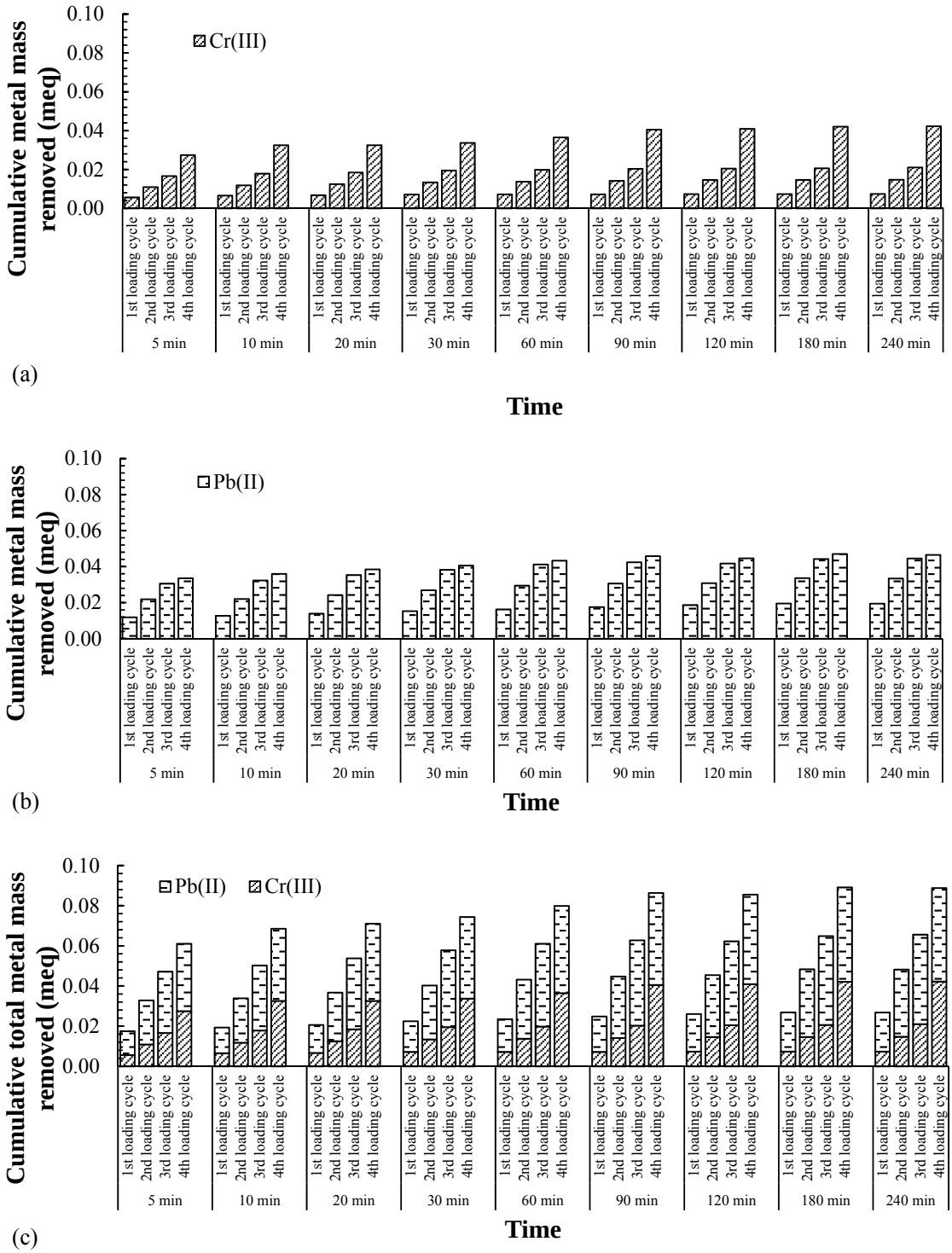

Fig. 5.76: Variation in cumulative (a) Cr(III), (b) Pb(II) and (c) total metal mass removed under uncontrolled pH conditions by GAA with three loading cycles with B[Cr(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination (Each data represents an average of two independent experimental values).

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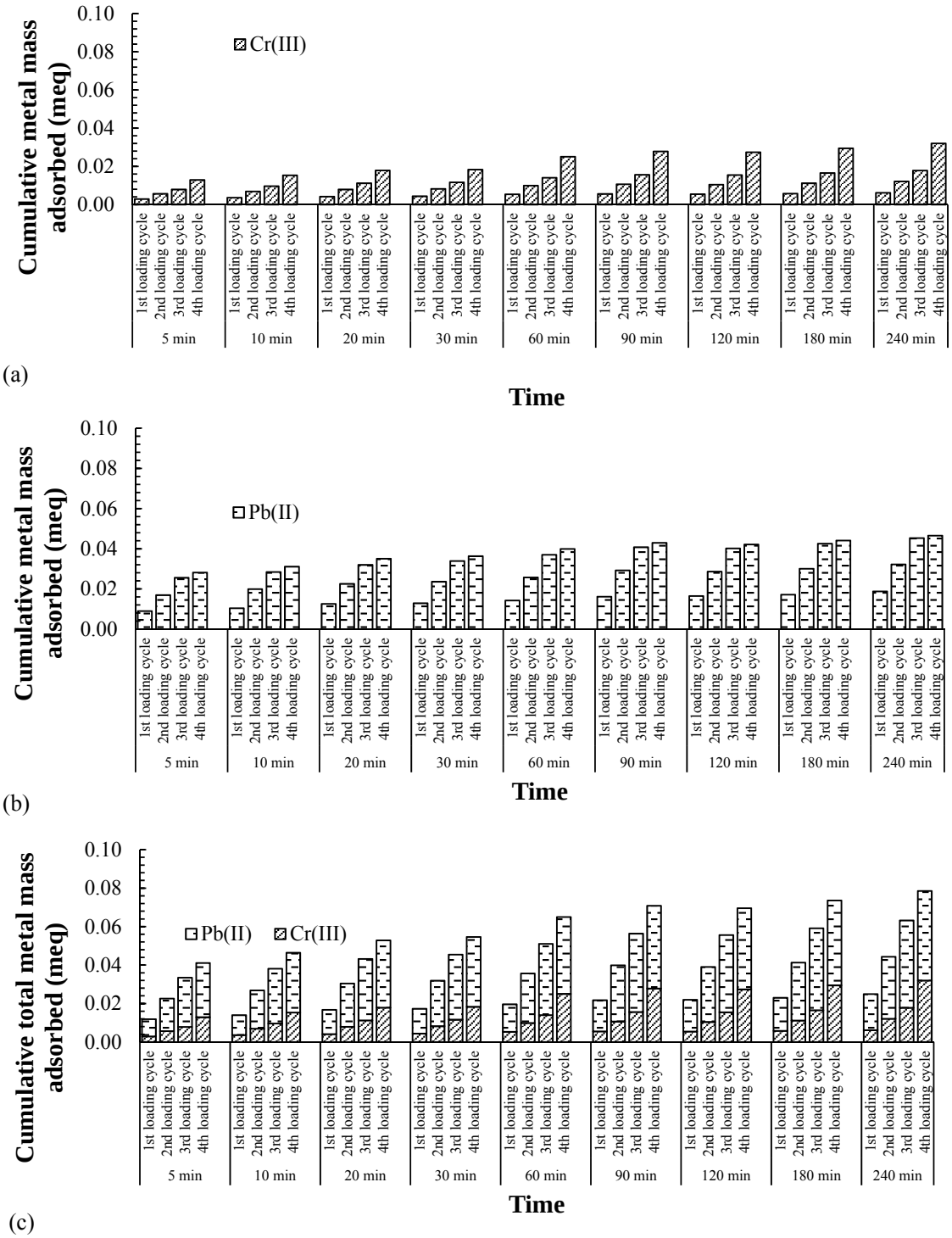

Fig. 5.77: Variation in cumulative (a) Cr(III), (b) Pb(II) and (c) total metal mass adsorbed under controlled pH conditions by GAA with three loading cycles with B[Cr(0.15)+Pb(0.45)] combination followed by fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination (Each data represents an average of two independent experimental values).

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Cr(III), Pb(II) and total metal uptake under controlled pH conditions were 0.0320 meq, 0.0465 meq and 0.0785 meq respectively up to fourth loading cycle (Fig. 5.76 and 5.77).

5.5.6 Summary

The kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions by GAA were investigated with consecutive three loading cycles of a combination of binary-metal ion system followed by fourth loading cycle of another combination of binary-metal ion system comprising of Cu(II), Pb(II) and Cr(III) metals. The combination of binary-metal ion system contained the same metal ions but its concentrations were interchanged in the fourth loading cycles compared to the first three loading cycles. During the first three loading cycles with a combination of binary-metal ion system, metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for the metal ions with higher concentration in the combination decreased with increase in number of loading cycles {except for Cr(III) metal removal under uncontrolled pH condition from B[Cr(0.45)+Pb(0.15)] combination}. When GAA loaded with first three loading cycles of a combination of binary-metal ion system was exposed to another combination in the fourth loading cycle, the metal ion having lower concentration in combination had insignificant removal under uncontrolled pH conditions and insignificant uptake under controlled pH conditions {except for Pb(II) metal removal under uncontrolled pH conditions from B[Cu(0.45)+Pb(0.15)] combination and Cr(III) metal removal and metal uptake from B[Cr(0.15)+Pb(0.45)] combination} while the metal ion having higher concentration in combination had shown higher removal under uncontrolled pH conditions and higher uptake under controlled pH conditions compared to its removal and uptake from previous three loading cycles. The higher metal uptake might be due to higher concentration gradient induced from bulk solution to GAA surface during the fourth loading cycle. The variation in total metal removals under uncontrolled pH conditions and total metal uptakes under controlled pH conditions generally decreased with increase in number of loading cycles except for the fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination wherein total metal removals from the cycle were higher than that obtained during the second and third loading cycles with B[Cr(0.15)+Pb(0.45)] combination. The cumulative metal removal under uncontrolled pH conditions and cumulative metal uptake under controlled pH conditions increased with number of loading cycles indicating additional metal removal and additional metal uptake potential of GAA.

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5.6 Equilibrium studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from mono-, binary- and ternary-metal ions systems

The adsorption isotherm is the equilibrium relationship between concentration of the solute (or adsorbate) in the fluid phase and concentration of the solute (or adsorbate) on the adsorbent particles at a given temperature. Several mathematical relationships have been developed to describe the equilibrium distribution of solute (or adsorbate) between the solid and liquid phases and thus aid in interpretation of adsorption equilibrium data. In published literatures, equilibrium studies data have been frequently analyzed using the most popular isotherm models – Langmuir and Freundlich. The Langmuir adsorption isotherm was originally developed to describe gas-solid phase adsorption on activated carbon. This model is based upon two assumptions: (i) the forces of interaction between adsorbed molecules are negligible and (ii) once a molecule occupies a site, no further sorption takes place on the same site. In its derivation, Langmuir isotherm refers to homogeneous adsorption, with no transmigration of the adsorbate in the plane of the surface. Essentially the Langmuir model is about the surface phenomena of solute (or adsorbate) adsorption and its parameters q_m and b represent the maximum capacity of the adsorbent to accommodate the adsorbate and free energy of adsorption respectively. Similarly, the Freundlich isotherm is the earliest known relationship describing non-ideal and reversible adsorption, not restricted to formation of the monolayer. The development of Freundlich isotherm was based on the assumption that the adsorbent had a heterogeneous surface composed of different classes of adsorption sites, with adsorption on each class of site following the Langmuir isotherm (Sheindorf et al., 1981). The Freundlich isotherm parameter k is a constant indicative of the relative adsorption capacity of the adsorbent and n is a constant indicative of the intensity of adsorption. Therefore, isotherm parameters namely q_m and k mainly represent capacity of the adsorbent to retain the adsorbate on to surface and do not account for the removal of metal ions from the bulk phase by precipitation due to rise in solution pH. However most of the published literatures have not taken into account the rise in solution pH during equilibrium studies leading to removal of a part of metal ions by precipitation (Srivastava et al., 2006; Tien, 2008). However, all the metal ions removed from the solution phase had been inadvertently attributed to adsorption in most of the available literature. These equilibrium data had been fitted to the Langmuir and Freundlich isotherm models ignoring the obvious that equilibrium data depended upon the equilibrium condition and not the initial state (Tien, 2008). Since pH

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of the solution at the equilibrium conditions might be different and higher from initially adjusted pH of the solution, the precipitation might had also contributed in removal of a part of metal ions along with adsorption of metal ions. Therefore, the estimated values of the Langmuir and Freundlich isotherm parameters might had given grossly wrong assessment as far as the capacity of the adsorbent was concerned. In the present investigation, the removal of Cu(II), Pb(II) and Cr(III) metal ions from mono-, binary- and ternary-metal ion systems under uncontrolled pH conditions had been attributed to combined effects of precipitation and adsorption due to rise in solution pH leading to precipitation of a part of metal ions. Since the Langmuir and Freundlich isotherm parameters namely q_m and k represented the amount of the metal ions adsorbed on to the surface of the adsorbent and didn't account for the amount of metal ions removed by precipitation from the bulk solution, application of these models to describe experimental equilibrium data obtained under uncontrolled pH conditions of equilibrium studies were possibly not justifiable. Hence in the present work, the experimental equilibrium data obtained under uncontrolled pH conditions have not been fitted to any of the well known adsorption isotherms. But attempts have been made to establish a mathematical relationship between amount of metal ions removed from the solution per unit mass of adsorbent (Q_e) (since mass of adsorbent played an important role in affecting the solution pH) with the equilibrium residual metal ion concentration (C_e) using curve fitting techniques (mainly power and polynomial equations). Whereas, data obtained under controlled pH conditions have been fitted to the Langmuir and Freundlich adsorption isotherm models since pH of the solution at equilibrium was well below the precipitation pH value of respective metal ions. The experimental data of equilibrium studies have been used to estimate equilibrium metal removal from the solution phase under uncontrolled pH conditions using

$$Q_e = \frac{V(C_o - C_e)}{1000\, m} \tag{5.6}$$

while equilibrium metal uptake by the adsorbent under controlled pH conditions using

$$q_e = \frac{V(C_o - C_e)}{1000\, m} \tag{5.7}$$

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where Q_e is equilibrium metal removal from the solution (meq/g), q_e is equilibrium metal uptake by adsorbent (meq/g), V is solution volume in (mL), C_o is initial metal concentration in solution (meq/L), C_e is equilibrium metal concentration in solution (meq/L) and m is mass of adsorbent used (g).

In the present work, equilibrium studies have been carried out under uncontrolled and controlled pH conditions from mono-, binary- and ternary-metal ion systems by maintaining a fixed total initial metal ion concentration in the solution.

5.6.1 Equilibrium studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from mono-metal ion systems of Cu(II), Pb(II) and Cr(III) ions

The equilibrium studies have been carried out under uncontrolled and controlled pH conditions for mono-metal ion systems of M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] with a fixed initial metal ion concentration of approximately 0.60 meq/L while adsorbent GAA doses varied in the range of 4-32 g/L. The results obtained under uncontrolled pH conditions along with variation in solution pH at equilibrium (pH_e) are shown in Fig. 5.78 while results obtained under controlled pH conditions are presented in Fig. 5.79.

The variations in solution pH obtained under uncontrolled pH conditions are plotted with the residual equilibrium concentration of metal ions from M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] systems and shown in Fig. 5.78(a). In general, the solution pH increased with decrease in residual equilibrium metal concentration. This might be due to higher doses of GAA used for obtaining lower values of equilibrium concentration of metal ions. Since the solution pH increased beyond 5.50 in all the three mono-metal ion systems investigated, the removal of Cu(II), Pb(II) and Cr(III) metal ions might be attributed to combined effects of precipitation and adsorption. However, under controlled pH conditions, solution pH in M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] systems were observed in the range of 5.01-5.14. Hence, the removal of Cu(II), Pb(II) and Cr(III) metal ions from solution under controlled pH conditions might be attributed to adsorption only.

Adsorption isotherm plots for M[Pb(0.60)] and M[Cr(0.60)] systems were observed to overlap at 95% confidence intervals for most of the data points while isotherm plot for

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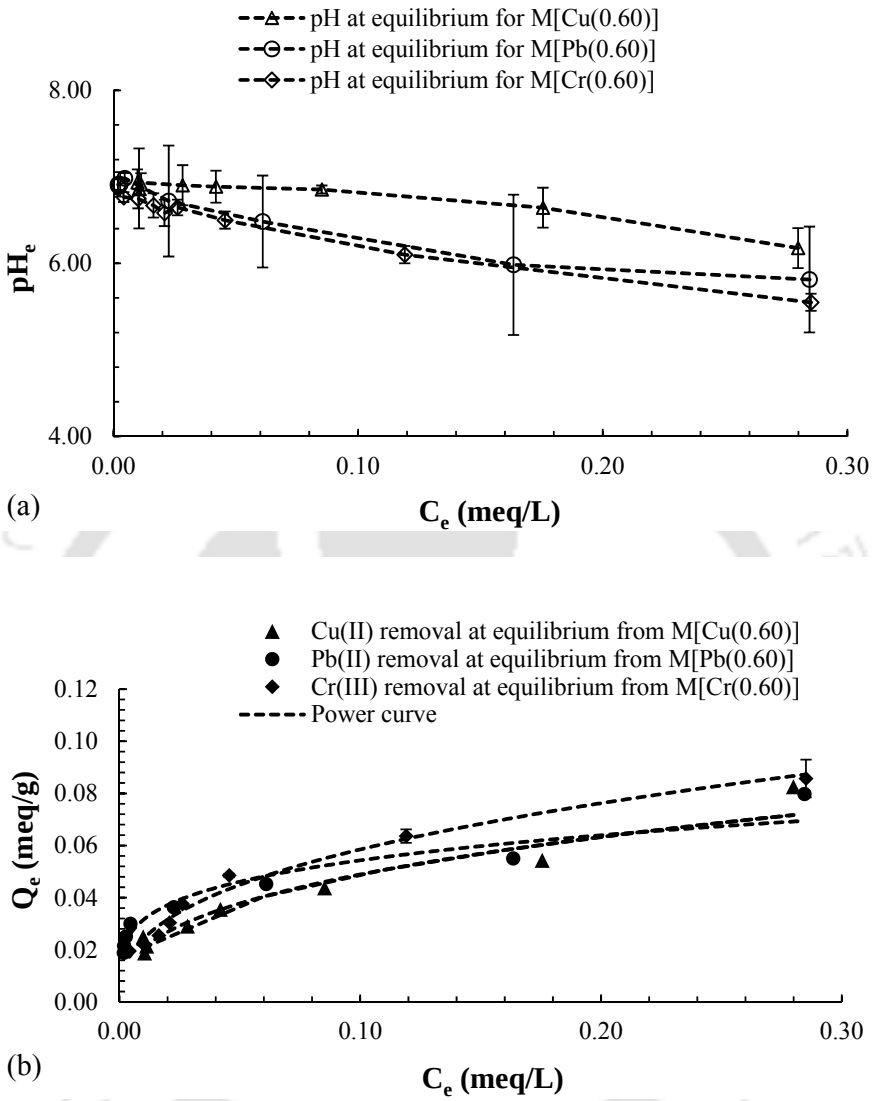

Fig. 5.78: Variation in (a) solution pH at equilibrium (b) equilibrium metal removal obtained for M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] systems under uncontrolled pH conditions {Initial metal conc. in M[Cu(0.60)] = 0.61±0.01 meq/L, M[Pb(0.60)] = 0.60±0.01 meq/L, M[Cr(0.60)] = 0.63±0.02 meq/L, Initial adjusted pH = 5.00±0.02, Shaking speed = 66 rpm, Reaction volume = 50 mL, GAA dose = 4 to 32 g/L, Mixing time = 180 min., Temp. = 30±2 °C} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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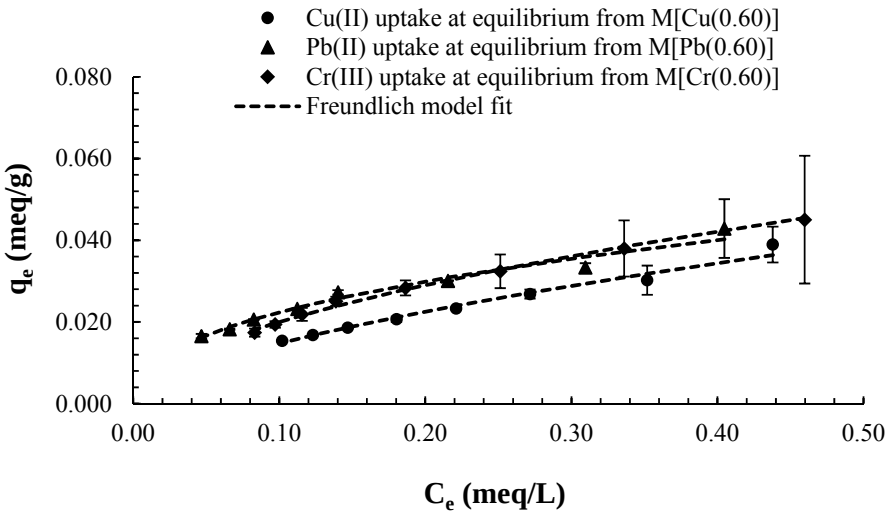

Fig. 5.79: Adsorption isotherm plots for M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] systems investigated under controlled pH conditions {Initial metal conc. in M[Cu(0.60)] = 0.59±0.03 meq/L, M[Pb(0.60)] = 0.58±0.09 meq/L, M[Cr(0.60)] = 0.64±0.00 meq/L, Buffered pH = 5.00±0.02, Shaking speed = 66 rpm, Reaction volume = 50 mL, GAA dose = 4 to 32 g/L, Mixing time = 180 min., Temp. = 30±2 °C} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

M[Cu(0.60)] system didn't overlap at 95% confidence interval with the other two isotherms even though estimated adsorption capacities (*k* values) for M[Cu(0.60)] and M[Pb(0.60)] systems were approximately similar while it was higher for M[Cr(0.60)] system. It was observed that the adsorption intensity constant (*n*) for Pb(II) metal ions were higher than that of Cu(II) and Cr(III) metal ions indicating Pb(II) would be more attracted to higher energy sites (Table 5.40). The variation in Q_e (obtained under uncontrolled pH conditions) and q_e (obtained under controlled pH conditions) with C_e are shown in Fig. 5.78(b) and 5.79 respectively. The mathematical relationship established between values of Q_e with C_e as presented in Fig. 5.78(b) using curve fitting techniques are presented in Table 5.40. Closer R^2 values for both power and polynomial equations fitted indicated its suitability to describe experimental equilibrium metal removal data obtained under uncontrolled pH conditions. Whereas, the Langmuir and Freundlich isotherm models have been applied to data presented in Fig. 5.79 and estimated model parameters are presented in Table 5.40. Higher values of R^2 for Freundlich adsorption isotherm model indicated its applicability to describe the equilibrium uptake data of Cu(II), Pb(II) and Cr(III) metal ions.

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Table 5.40: Established mathematical relationships for equilibrium metal removal under uncontrolled pH conditions and estimated adsorption isotherm model parameters under controlled pH conditions for M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] systems.

Uncontrolled pH conditions	Metal ion system with initial conc. (meq/L)	Fitted Curve					
		Power			Polynomial		
		Equation		R^2	Equation		R^2
	M[Cu(0.60)] = 0.61±0.01	$Q_e = 0.115C_e^{0.371}$		0.950	$Q_e = -0.050C_e^2+0.227C_e+0.021$		0.968
	M[Pb(0.60)] = 0.60±0.01	$Q_e = 0.093C_e^{0.235}$		0.956	$Q_e = -0.246C_e^2+0.257C_e+0.024$		0.942
	M[Cr(0.60)] = 0.63±0.02	$Q_e = 0.140C_e^{0.381}$		0.966	$Q_e = -0.105C_e^2+0.530C_e+0.019$		0.971
Controlled pH conditions	Metal ion system with initial conc. (meq/L)	Langmuir adsorption isotherm model			Freundlich adsorption isotherm model		
		q_m (meq/g)	b (L/meq)	R^2	k [(meq/g)/(meq/L)$^{1/n}$]	$1/n$	R^2
	M[Cu(0.60)] = 0.59±0.03	0.0684	2.5286	0.898	0.0603	0.611	0.986
	M[Pb(0.60)] = 0.58±0.09	0.0513	7.9902	0.954	0.0589	0.420	0.979
	M[Cr(0.60)] = 0.64±0.00	0.0669	4.1162	0.987	0.0692	0.539	0.993

Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with three independent data points, Q_e expressed in meq/g and C_e in meq/L.

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5.6.2 Equilibrium studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from binary-metal ion systems comprising of Cu(II) and Pb(II) ions

Equilibrium studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from binary-metal ion systems comprising of Cu(II) and Pb(II) metal ions have been carried out for four selected combinations: B[Cu(0.15)+Pb(0.45)], B[Cu(0.30)+Pb(0.30)], B[Cu(0.45)+Pb(0.15)] and B[Cu(0.60)+Pb(0.60)]. In the first three combinations, the initial metal ion concentration of individual metals have been selected in such a way to have the total initial metal ion concentrations near to 0.60 meq/L thereby exposing the adsorbent GAA with the same total initial metal ion concentrations. However, in the fourth combination, the initial metal ion concentration of the two metal ions were kept the same (i.e. 0.60 meq/L each) leading to the total initial metal ion concentration close to 1.20 meq/L – thereby exposing the adsorbent GAA with almost double of the total initial metal ion concentrations compared to total initial metal ion concentration in the first three combinations. The encouragement for selection of the fourth combination with doubled total initial metal ion concentration came from published literature (Hawari & Mulligan, 2007; Srivastava et al., 2006) wherein the selected initial metal ion concentrations of individual metal ions in mono- and binary-metal ion systems were kept the same. It led to a situation where the adsorbent was exposed to double the total initial metal ion concentration in the binary-metal ion system compared to the initial metal ion concentration in the mono-metal ion systems. The results of such studies from binary-metal ion systems have been used to understand the competitive equilibrium uptake of a metal ion in presence of the influencing metal ion (other than the metal being adsorbed) and vice-versa without keeping a track of change in solution pH values at equilibrium. Also attempts were made to compare the results obtained for competitive metal uptakes from the binary-metal ion system with the metal uptakes from the mono-metal ion systems even though the experimental conditions in terms of total initial metal ion concentrations in both the systems (i.e. mono- and binary-metal ion systems) were entirely different. Therefore, in the present equilibrium studies, efforts have been made to understand metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from binary-metal ion systems comprising of Cu(II) and Pb(II) by maintaining (a) total initial metal ion concentrations of 0.60 meq/L in the first three combinations with three different proportion of

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individual metal ions, and (b) total initial metal ion concentration of 1.20 meq/L in the fourth combination by having an initial concentration near to 0.60 meq/L for each of the metal ions.

The results of equilibrium studies obtained under uncontrolled pH conditions have been shown in Fig. 5.80 as variation in metal removals at equilibrium (Q_e) with residual metal concentrations at equilibrium (C_e). This figure also shows the variation in equilibrium solution pH (pH_e). In order to understand and compare the competitive removal of a metal ion at equilibrium under the influence of the other metal ion present in a combination of the binary-metal ion system, the variation in Q_e values of two metal ions having same level of initial metal ion concentrations have been plotted against respective C_e values ensuring that the initial concentration of the influencing metal ions was also having same levels – either similar or different than the initial concentration of the metals being removed. The metal ion undergoing competitive removal is termed as the target metal ion while the influencing metal ion present in the solution is termed as the non-target metal ion in this work for the presentation of results. For example, the initial concentrations of Cu(II) in B[Cu(0.15)+Pb(0.45)] combination and Pb(II) in B[Cu(0.45)+Pb(0.15)] combination were approximately 0.15 meq/L while the initial concentrations of non-target metal ions Pb(II) in B[Cu(0.15)+Pb(0.45)] combination and Cu(II) in B[Cu(0.45)+Pb(0.15)] combination were approximately 0.45 meq/L (higher than the metal being removed) as shown in Fig. 5.80(a). An inspection of Fig. 5.80 indicated average equilibrium pH of solutions in the range of 5.45-5.79 at higher C_e values which increased to average equilibrium pH values of 6.56-6.92 at lower C_e values. The increase in average equilibrium pH values at lower C_e values was attributed to use of higher amounts of GAA. Since the average equilibrium pH values of solutions were well above precipitation pH values of 5.50 for both the metal ions, the metal removals from the solutions were mainly due to processes of precipitation as well as adsorption taking place simultaneously. The variations in Q_e values for Cu(II) and Pb(II) metal ion removals with C_e appeared to follow similar trends close to each other for initial metal ion concentrations of 0.15 meq/L, 0.30 meq/L and 0.45 meq/L in the combinations studied, whereas the trend in variations of Q_e with C_e were different for initial metal ion concentration of 0.60 meq/L yielding higher removals for Pb(II) metal ions compared to Cu(II) metal ions without any overlap in data points at 95% confidence intervals. However, the residual equilibrium concentrations of Pb(II) metal ions were observed to be little lower compared with residual equilibrium concentrations of Cu(II) for the same amount of GAA

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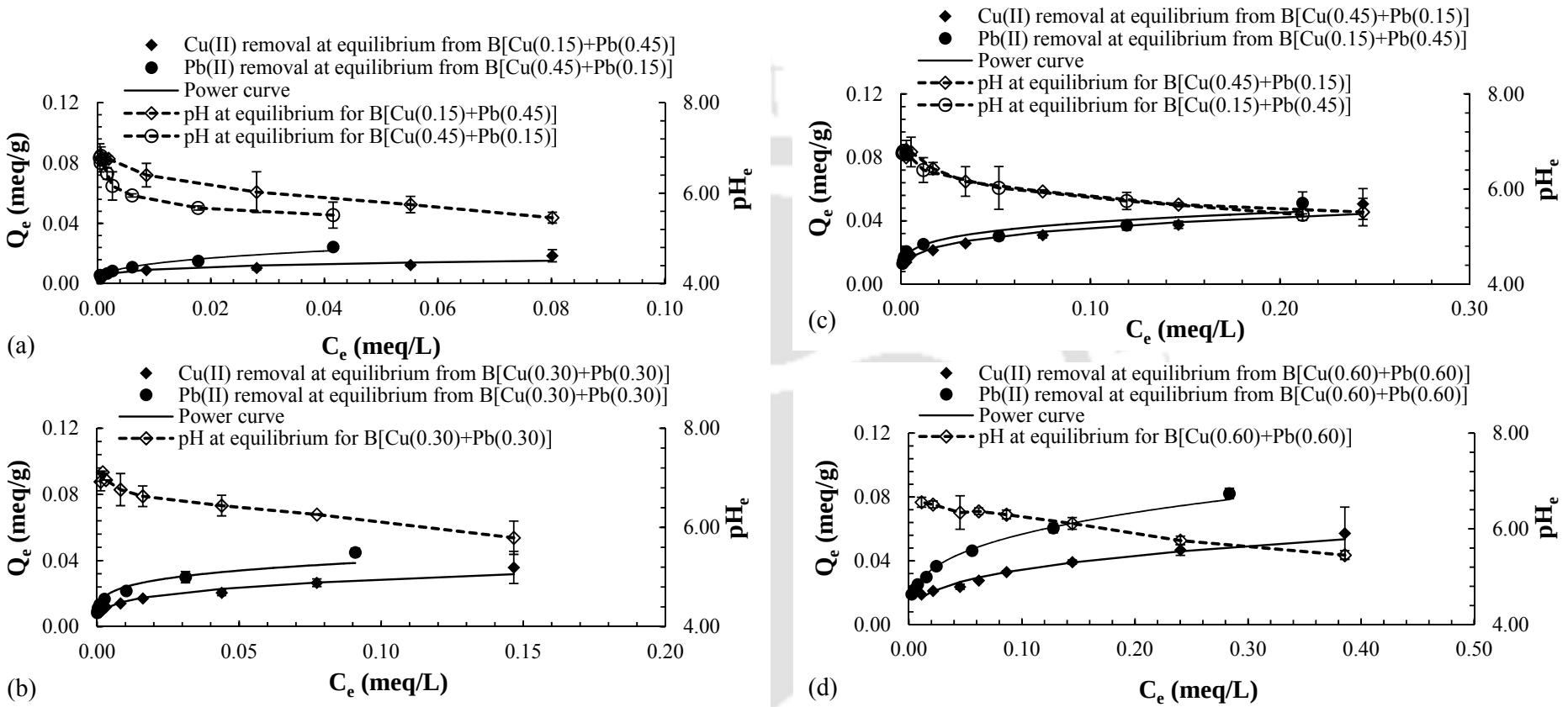

Fig. 5.80: Variations in target metal removals and solution pH at equilibrium from binary-metal ion systems comprising of Cu(II) and Pb(II) under uncontrolled pH conditions for metal ions having initial concentrations: (a) 0.15 meq/L (b) 0.30 meq/L (c) 0.45 meq/L and (d) 0.60 meq/L {Initial metal conc. in combinations B[Cu(0.45)+Pb(0.15)] = 0.45±0.00 meq/L of Cu(II) + 0.14±0.00 meq/L of Pb(II), B[Cu(0.30)+Pb(0.30)] = 0.29±0.00 meq/L of Cu(II) + 0.27±0.02 meq/L of Pb(II), B[Cu(0.15)+Pb(0.45)] = 0.15±0.00 meq/L of Cu(II) + 0.42±0.00 meq/L of Pb(II), B[Cu(0.60)+Pb(0.60)] = 0.61±0.00 meq/L of Cu(II) + 0.61±0.00 meq/L of Pb(II), Initial adjusted pH = 5.00±0.02, Shaking speed = 66 rpm, Reaction volume = 50 mL, GAA dose = 4 to 32 g/L, Mixing time = 180 min., Temp. = 30±2 °C} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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used. The established mathematical relationships between Q_e and C_e (in terms of power and polynomial curves) for the removal of each of the metal ions from combinations of the binary-metal ion systems without considering the impact of non-target metal ion on the removals are tabulated in Table 5.41. The R^2 values for power and polynomial curves were close to each other indicating either of the two mathematical relationships could be used to predict Q_e value for any of the C_e values within the range. The power curves have also been plotted in Fig. 5.80.

The results of equilibrium studies obtained under controlled pH conditions have been shown in Fig. 5.81 as variation in target metal uptakes at equilibrium (q_e) with residual metal concentrations at equilibrium (C_e). In order to understand and compare the competitive uptake of a metal ion at equilibrium under the influence of the other metal ion present in a combination of the binary-metal ion system, the variations in q_e values of metal ions having same level of initial metal ion concentrations have been plotted against respective C_e values ensuring that the initial concentration of the influencing metal was having same levels – either similar or different than the initial concentration of the metals being adsorbed. The metal ion undergoing competitive uptake is termed as the target metal ion while the influencing metal ion present in the solution is termed as the non-target metal ion in this work for presentation of the results. For example, the initial concentrations of target Pb(II) metal in B[Cu(0.15)+Pb(0.45)] combination and target Cu(II) metal in B[Cu(0.45)+Pb(0.15)] combination were approximately 0.45 meq/L while the initial concentrations of non-target Cu(II) metal in B[Cu(0.15)+Pb(0.45)] combination and non-target Pb(II) metal in B[Cu(0.45)+Pb(0.15)] combination were approximately 0.15 meq/L (lower than the target metal being adsorbed) as shown in Fig. 5.81(c). The variations in q_e values for Cu(II) and Pb(II) metal ions with C_e appeared to follow similar trends but data points did not overlap at 95% confidence intervals for the initial metal ion concentrations of 0.15 meq/L, 0.30 meq/L, 0.45 meq/L and 0.60 meq/L in the combinations studied. However, for all the initial metal ion concentrations, the uptake of Pb(II) was observed to be higher than the uptake of Cu(II) throughout the range of C_e values and no overlap was observed at 95% confidence interval. The equilibrium data of target metal uptakes were fitted to Langmuir and Freundlich isotherm models without considering the impact of non-target metal ion on the uptakes and estimated model parameters are presented in Table 5.41. The higher R^2 values obtained for Freundlich

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Table 5.41: Summary of established mathematical relationships for target metal removal at equilibrium under uncontrolled pH conditions and adsorption isotherm model parameters for target metal uptake at equilibrium under controlled pH conditions for binary-metal ion system comprising of Cu(II) and Pb(II) ions.

	Binary-metal ion combinations	Non-target metal with initial conc. (meq/L)	Fitted Curve					
			Target metal with initial conc. (meq/L)	Power		Polynomial		
				Equation	R^2	Equation		R^2
Uncontrolled pH conditions	B[Cu(0.15)+Pb(0.45)]	Pb(II) = 0.42±0.00	Cu(II) = 0.15±0.00	$Q_e = 0.027C_e^{0.225}$	0.924	$Q_e = 0.339C_e^2+0.118C_e+0.006$		0.926
		Cu(II) = 0.15±0.00	Pb(II) = 0.42±0.00	$Q_e = 0.063C_e^{0.212}$	0.963	$Q_e = -0.346C_e^2+0.229C_e+0.017$		0.935
	B[Cu(0.30)+Pb(0.30)]	Pb(II) = 0.27±0.02	Cu(II) = 0.29±0.00	$Q_e = 0.053C_e^{0.268}$	0.978	$Q_e = -0.629C_e^2+0.262C_e+0.010$		0.978
		Cu(II) = 0.29±0.00	Pb(II) = 0.27±0.02	$Q_e = 0.064C_e^{0.214}$	0.977	$Q_e = -4.603C_e^2+0.784C_e+0.011$		0.968
	B[Cu(0.45)+Pb(0.15)]	Pb(II) = 0.14±0.00	Cu(II) = 0.45±0.00	$Q_e = 0.063C_e^{0.248}$	0.968	$Q_e = -0.250C_e^2+0.197C_e+0.017$		0.970
		Cu(II) = 0.45±0.00	Pb(II) = 0.14±0.00	$Q_e = 0.066C_e^{0.349}$	0.957	$Q_e = -6.500C_e^2+0.725C_e+0.005$		0.975
	B[Cu(0.60)+Pb(0.60)]	Pb(II) = 0.61±0.00	Cu(II) = 0.61±0.00	$Q_e = 0.073C_e^{0.325}$	0.968	$Q_e = -0.183C_e^2+0.172C_e+0.017$		0.993
		Cu(II) = 0.61±0.00	Pb(II) = 0.61±0.00	$Q_e = 0.116C_e^{0.311}$	0.994	$Q_e = -0.758C_e^2+0.425C_e+0.022$		0.980
Controlled pH conditions	Binary-metal ion combinations	Non-target metal with initial conc. (meq/L)	Target metal with initial conc. (meq/L)	Langmuir isotherm model			Freundlich isotherm model		
				q_m (meq/g)	b (L/meq)	R^2	k [(meq/g)/(meq/L)$^{1/n}$]	$1/n$	R^2
	B[Cu(0.15)+Pb(0.45)]	Pb(II) = 0.46±0.01	Cu(II) = 0.16±0.01	0.0164	9.2575	0.879	0.0321	0.612	0.969
		Cu(II) = 0.16±0.01	Pb(II) = 0.46±0.01	0.0389	8.4532	0.934	0.0466	0.426	0.984
	B[Cu(0.30)+Pb(0.30)]	Pb(II) = 0.32±0.02	Cu(II) = 0.28±0.02	0.0290	6.3302	0.900	0.0408	0.571	0.981
		Cu(II) = 0.28±0.02	Pb(II) = 0.32±0.02	0.0359	17.1148	0.927	0.0547	0.418	0.981
	B[Cu(0.45)+Pb(0.15)]	Pb(II) = 0.15±0.01	Cu(II) = 0.44±0.01	0.0390	2.9719	0.850	0.0373	0.593	0.962
		Cu(II) = 0.44±0.01	Pb(II) = 0.15±0.01	0.0173	35.0121	0.936	0.0398	0.451	0.984
	B[Cu(0.60)+Pb(0.60)]	Pb(II) = 0.56±0.03	Cu(II) = 0.59±0.01	0.0477	2.7757	0.976	0.0418	0.560	0.995
		Cu(II) = 0.59±0.01	Pb(II) = 0.56±0.03	0.0441	8.1057	0.986	0.0500	0.406	0.996

Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with three independent data points.

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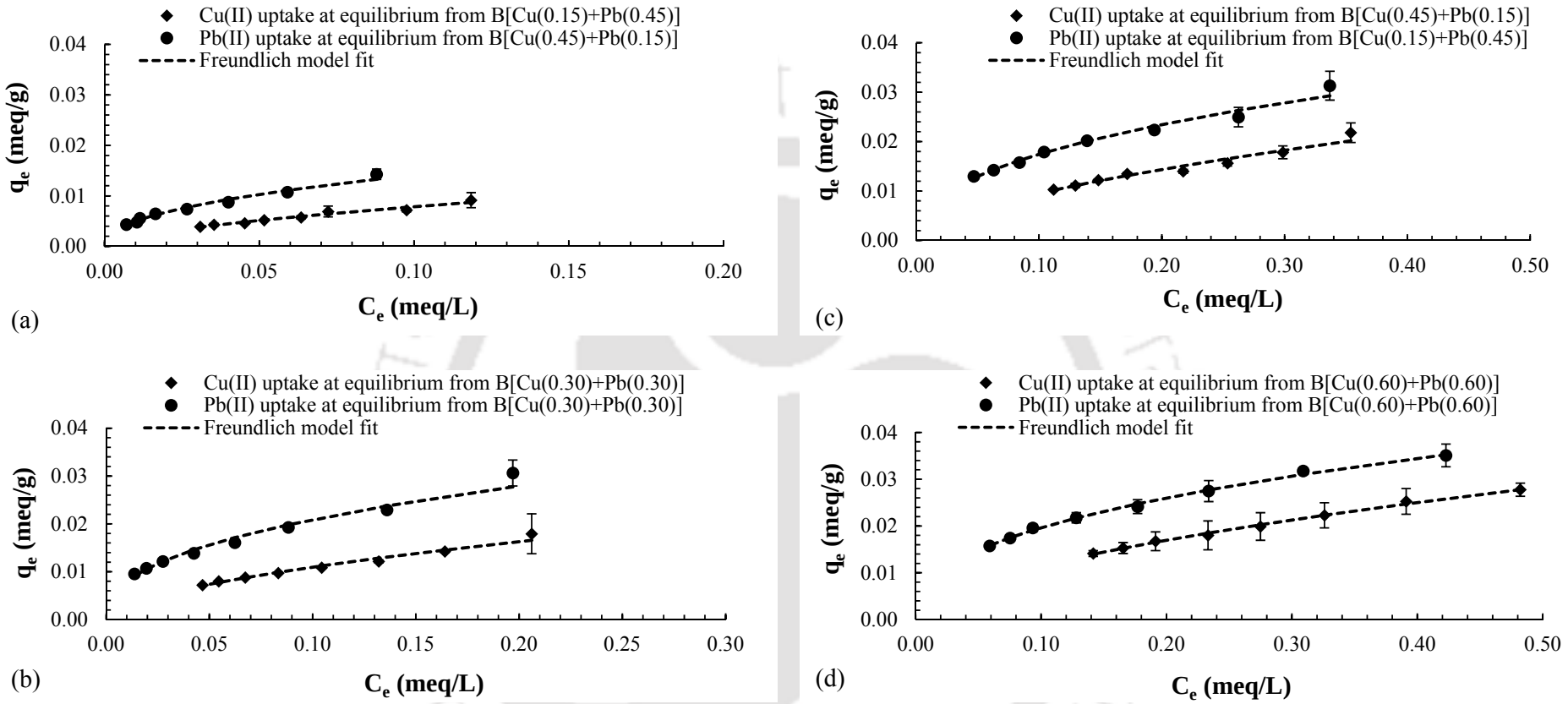

Fig. 5.81: Variations in target metal uptakes at equilibrium from binary-metal ion systems comprising of Cu(II) and Pb(II) under controlled pH conditions for metal ions having initial concentrations: (a) 0.15 meq/L (b) 0.30 meq/L (c) 0.45 meq/L and (d) 0.60 meq/L {Initial metal conc. in combinations B[Cu(0.45)+Pb(0.15)] = 0.44±0.01 meq/L of Cu(II) + 0.15±0.01 meq/L of Pb(II), B[Cu(0.30)+Pb(0.30)] = 0.28±0.02 meq/L of Cu(II) + 0.32±0.02 meq/L of Pb(II), B[Cu(0.15)+Pb(0.45)] = 0.16±0.01 meq/L of Cu(II) + 0.46±0.01 meq/L of Pb(II), B[Cu(0.60)+Pb(0.60)] = 0.59±0.01 meq/L of Cu(II) + 0.56±0.03 meq/L of Pb(II), Buffered pH = 5.00±0.02, Shaking speed = 66 rpm, Reaction volume = 50 mL, GAA dose = 4 to 32 g/L, Mixing time = 180 min., Temp. = 30±2 °C} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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isotherm model indicated its better suitability to represent the experimental equilibrium metal uptake data. The fitted curves have also been included in Fig. 5.81.

A careful examination of target metal removals at equilibrium under uncontrolled pH conditions and target metal uptakes at equilibrium under controlled pH conditions as presented in Fig. 5.80 and 5.81 respectively indicated simultaneous removal and uptake of non-target metals as well under uncontrolled and controlled pH conditions. For example, Fig. 5.80(a) shows target Cu(II) metal removals from B[Cu(0.15)+Pb(0.45)] combination while Fig. 5.80(c) shows non-target Pb(II) metal removals from the same binary-metal ion combination. Similarly, target Pb(II) metal uptakes from B[Cu(0.45)+Pb(0.15)] combination is shown in Fig. 5.81(a) while Fig. 5.81(c) shows non-target Cu(II) metal uptakes from the same binary-metal ion combination. Therefore, it appeared that both the metal ions i.e. target as well as non-target were getting removed from the solutions simultaneously under uncontrolled pH conditions and simultaneously migrating to the surface of GAA under controlled pH conditions from the binary-metal ion system studied. Hence, it appeared to be interesting to look into total metal removals at equilibrium under uncontrolled pH conditions and total metal uptakes at equilibrium under controlled pH conditions from the binary-metal ion system. For this purpose, experimental metal removals data under uncontrolled pH conditions and experimental metal uptakes data under controlled pH conditions have been used to plot variations in total metal removals at equilibrium (TQ_e) and total metal uptakes at equilibrium (Tq_e) with total residual metal concentration at equilibrium (TC_e) and the plots have been presented in Fig. 5.82. In the course of experiments, a set of eight specimen tubes contained the same amounts of total initial metal ion concentrations in a binary-metal ion combination (i.e. 0.60 meq/L in the first three combination of binary-metal ion system and 1.20 meq/L in the fourth combination of binary-metal ion system), added with the fixed amounts of GAA in each of the eight specimen tubes (in the range of 4 to 32 g/L) and mixed up to the equilibrium time of 180 min. under uncontrolled and controlled pH conditions. After completion of mixing time, the solid and liquid portions were separated and residual metal ion concentrations were estimated. Hence, each of the specimen tube data from a set were used to estimate total metal removals at equilibrium (TQ_e) under uncontrolled pH conditions and total metal uptakes at equilibrium (Tq_e) under controlled pH conditions along with the total residual metal concentration in solution at equilibrium (TC_e).

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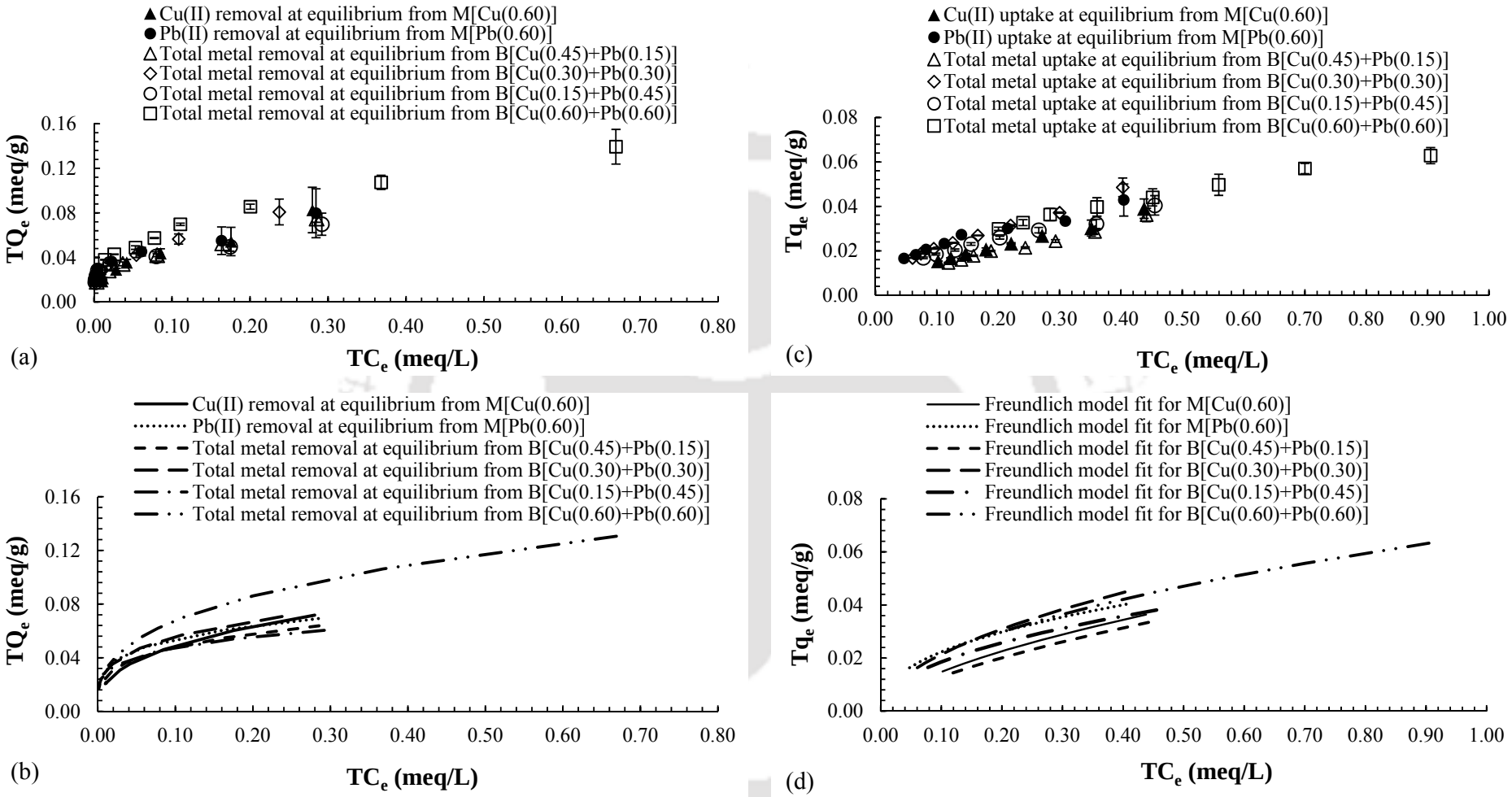

Fig. 5.82: Variations in (a) total metal removals and (b) fitted power curves to total metal removals under uncontrolled pH conditions; and (c) total metal uptakes (d) fitted Freundlich model to total metal uptakes under controlled pH conditions from mono- and binary-metal ion systems comprising of Cu(II) and Pb(II) ions.

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The variation in total metal removals at equilibrium (TQ_e) data points with total residual metal concentration at equilibrium (TC_e) obtained under uncontrolled pH conditions from the four selected binary-metal ion combinations namely B[Cu(0.15)+Pb(0.45)], B[Cu(0.30)+Pb(0.30)], B[Cu(0.45)+Pb(0.15)] and B[Cu(0.60)+Pb(0.60)] are presented in Fig. 5.82(a). The variations in TQ_e data points for B[Cu(0.15)+Pb(0.45)], B[Cu(0.30)+Pb(0.30)] and B[Cu(0.45)+Pb(0.15)] combinations with TC_e appeared to overlap at 95% confidence intervals. However, the variations in TQ_e data points for B[Cu(0.60)+Pb(0.60)] combination with TC_e appeared to be higher and not overlapping at 95% confidence intervals with other three binary combinations having total initial metal concentration of approximately 0.60 meq/L. The established mathematical relationships between TQ_e and TC_e (in terms of power and polynomial curves) for all the combinations of the binary-metal ion systems are tabulated in Table 5.42 while the power curves are also drawn and shown in Fig. 5.82(b). The R^2 values for power and polynomial curves are close to each other indicating either of the two mathematical relationships could be used to predict TQ_e value for any of the TC_e value within the range. Since the equilibrium studies with mono-metal ion systems namely M[Cu(0.60)] and M[Pb(0.60)] were also carried out with initial metal ion concentration of approximately 0.60 meq/L, therefore, the variation in experimental metal removals under uncontrolled pH conditions have also been plotted in Fig. 5.82(a). The variations in metal removals from M[Cu(0.60)] and M[Pb(0.60)] appeared to overlap at 95% confidence intervals to variations with metal removals from the first three combinations of binary-metal ion systems having total initial metal ion concentrations approximately to 0.60 meq/L. The best fit curves for metal removals under uncontrolled pH conditions from mono- and binary-metal ion systems are separately plotted in Fig. 5.82(b). All the curves with an exception for B[Cu(0.60)+Pb(0.60)] combination appeared to be very close to each other. These results clearly suggested that the total metal removals at equilibrium were similar and fairly independent of proportion of initial metal ion concentrations present in selected combinations of binary-metal ion systems as long as total initial metal ion concentration was approximately the same, i.e. 0.60 meq/L even though ionic radius as well as atomic weight of the metal ions were different from each other.

The variation in total metal uptakes at equilibrium (Tq_e) data points with total residual metal concentration at equilibrium (TC_e) obtained under controlled pH conditions from the four selected binary-metal ion combinations namely B[Cu(0.15)+Pb(0.45)],

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Table 5.42: Summary of established mathematical relationships for total metal removal at equilibrium under uncontrolled pH conditions and estimated overall adsorption isotherm model parameters for total metal uptake at equilibrium under controlled pH conditions for binary-metal ion system comprising of Cu(II) and Pb(II) ions.

Uncontrolled pH conditions	Binary-metal ion combinations	Fitted Curve					
		Power			Polynomial		
		Equation		R^2	Equation		R^2
	B[Cu(0.45)+Pb(0.15)]	$TQ_e = 0.090(TC_e)^{0.274}$		0.964	$TQ_e = -0.221(TC_e)^2+0.246(TC_e)+0.021$		0.977
	B[Cu(0.30)+Pb(0.30)]	$TQ_e = 0.105(TC_e)^{0.275}$		0.980	$TQ_e = -0.718(TC_e)^2+0.419(TC_e)+0.021$		0.982
	B[Cu(0.15)+Pb(0.45)]	$TQ_e = 0.079(TC_e)^{0.218}$		0.955	$TQ_e = -0.149(TC_e)^2+0.197(TC_e)+0.023$		0.936
	B[Cu(0.60)+Pb(0.60)]	$TQ_e = 0.150(TC_e)^{0.345}$		0.977	$TQ_e = -0.171(TC_e)^2+0.266(TC_e)+0.036$		0.992
Controlled pH conditions	Binary-metal ion combinations	Langmuir isotherm model*			Freundlich isotherm model*		
		q_m (meq/g)	b (L/meq)	R^2	k [(meq/g)/(meq/L)$^{1/n}$]	$1/n$	R^2
	B[Cu(0.45)+Pb(0.15)]	0.0697	2.0592	0.850	0.0566	0.643	0.976
	B[Cu(0.30)+Pb(0.30)]	0.0694	4.4040	0.916	0.0728	0.531	0.987
	B[Cu(0.15)+Pb(0.45)]	0.0542	4.8796	0.951	0.0533	0.474	0.986
	B[Cu(0.60)+Pb(0.60)]	0.0930	2.1840	0.986	0.0666	0.498	0.997

*Model parameters estimated using Tq_e and TC_e values of combinations of binary-metal ion systems.

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B[Cu(0.30)+Pb(0.30)], B[Cu(0.45)+Pb(0.15)] and B[Cu(0.60)+Pb(0.60)] are presented in Fig. 5.82(c). The variations in Tq_e data points for B[Cu(0.15)+Pb(0.45)], B[Cu(0.30)+Pb(0.30)] and B[Cu(0.45)+Pb(0.15)] combinations with TC_e appeared to vary in a narrow band (but might not be overlapping at 95% confidence intervals). Even, the variation in Tq_e data points for B[Cu(0.60)+Pb(0.60)] combination with TC_e appeared to be within the same narrow band and overlapping at 95% confidence intervals with some of the other binary combinations having total initial metal concentration of approximately 0.60 meq/L. The equilibrium data of total metal uptakes were fitted to Langmuir and Freundlich isotherm models and estimated model parameters are presented in Table 5.42. The higher R^2 value obtained for Freundlich isotherm model indicated its better suitability to represent the experimental equilibrium total metal uptake data. Since the equilibrium studies with mono-metal ion systems namely M[Cu(0.60)] and M[Pb(0.60)] were also carried out with initial metal ion concentration of approximately 0.60 meq/L, therefore, the variation in experimental metal uptakes under controlled pH conditions have also been plotted in Fig. 5.82(c). The variations in metal uptakes from M[Cu(0.60)] and M[Pb(0.60)] appeared to vary within the same narrow band and overlapping at 95% confidence intervals to variation with metal uptakes from some of the combinations of binary-metal ion systems having total initial metal ion concentrations of approximately 0.60 meq/L. The best fit curves for metal uptakes under controlled pH conditions from mono- and binary-metal ion systems are separately plotted in Fig. 5.82(d). These results clearly suggested that the total metal uptakes at equilibrium was similar and fairly independent of proportion of initial metal ion concentrations present in selected combinations of binary-metal ion systems as long as total initial metal ion concentration was approximately the same, i.e. 0.60 meq/L even though ionic radius as well as atomic weight of the metal ions were different from each other.

5.6.3 Equilibrium studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from binary-metal ion systems comprising of Cr(III) and Pb(II) ions

Equilibrium studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from binary-metal ion systems comprising of Cr(III) and Pb(II) metal ions have been carried out for four selected combinations: B[Cr(0.45)+Pb(0.15)], B[Cr(0.30)+Pb(0.30)], B[Cr(0.15)+Pb(0.45)] and B[Cr(0.60)+Pb(0.60)]. In the first three combinations, the initial metal ion concentration of

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individual metals have been selected to have the total initial metal ion concentrations near to 0.60 meq/L thereby exposing the adsorbent GAA with the same total initial metal ion concentration. However, in the fourth combination, the initial metal ion concentration of the two metal ions were kept the same (i.e. 0.60 meq/L each) leading to the total initial metal ion concentration close to 1.20 meq/L – thereby exposing the adsorbent GAA with almost double of the total initial metal ion concentrations compared to total initial metal ion concentration in the first three combinations.

The results of equilibrium studies obtained under uncontrolled pH conditions have been shown in Fig. 5.83 as variation in metal removals at equilibrium (Q_e) with residual metal concentrations at equilibrium (C_e). This figure also shows the variation in equilibrium solution pH (pH_e). In order to understand and compare the target metal removal at equilibrium under the influence of the non-target metal ion present in a combination of the binary-metal ion system, the variation in Q_e values of metal ions having same level of initial metal ion concentrations have been plotted against respective C_e values ensuring that the initial concentration of the non-target metal was also having same levels – either similar or different than the initial concentration of the target metal ions being removed. An inspection of Fig. 5.83 indicated average equilibrium pH of solutions in the range of 5.03-5.02 at higher C_e values which increased to average equilibrium pH values of 5.88-5.95 at lower C_e values. The increase in average equilibrium pH values at lower C_e values was attributed to use of higher amounts of GAA. Since the average equilibrium pH values of solutions were well above precipitation pH values of 5.50 for both the metal ions, the metal removals from solutions were mainly due to precipitation as well as adsorption taking place simultaneously. The variations in Q_e values for target Cr(III) and target Pb(II) metal ion removals with C_e appeared to follow two distinctly different trends without any overlap of data points at 95% confidence intervals for the initial metal ion concentrations of 0.15 meq/L, 0.30 meq/L, 0.45 meq/L and 0.60 meq/L in the combinations studied. Also, higher removals for target Cr(III) metal ions were observed compared to target Pb(II) metal ions. The residual equilibrium concentrations of target Cr(III) metal ions were observed to be lower compared with residual equilibrium concentrations of target Pb(II) metal for the same amount of GAA used. The established mathematical relationships between Q_e and C_e (in terms of power and polynomial curves) for the removal of each of the target metal ions from combinations of the binary-metal ion systems without considering the impact of non-target metal removals are tabulated

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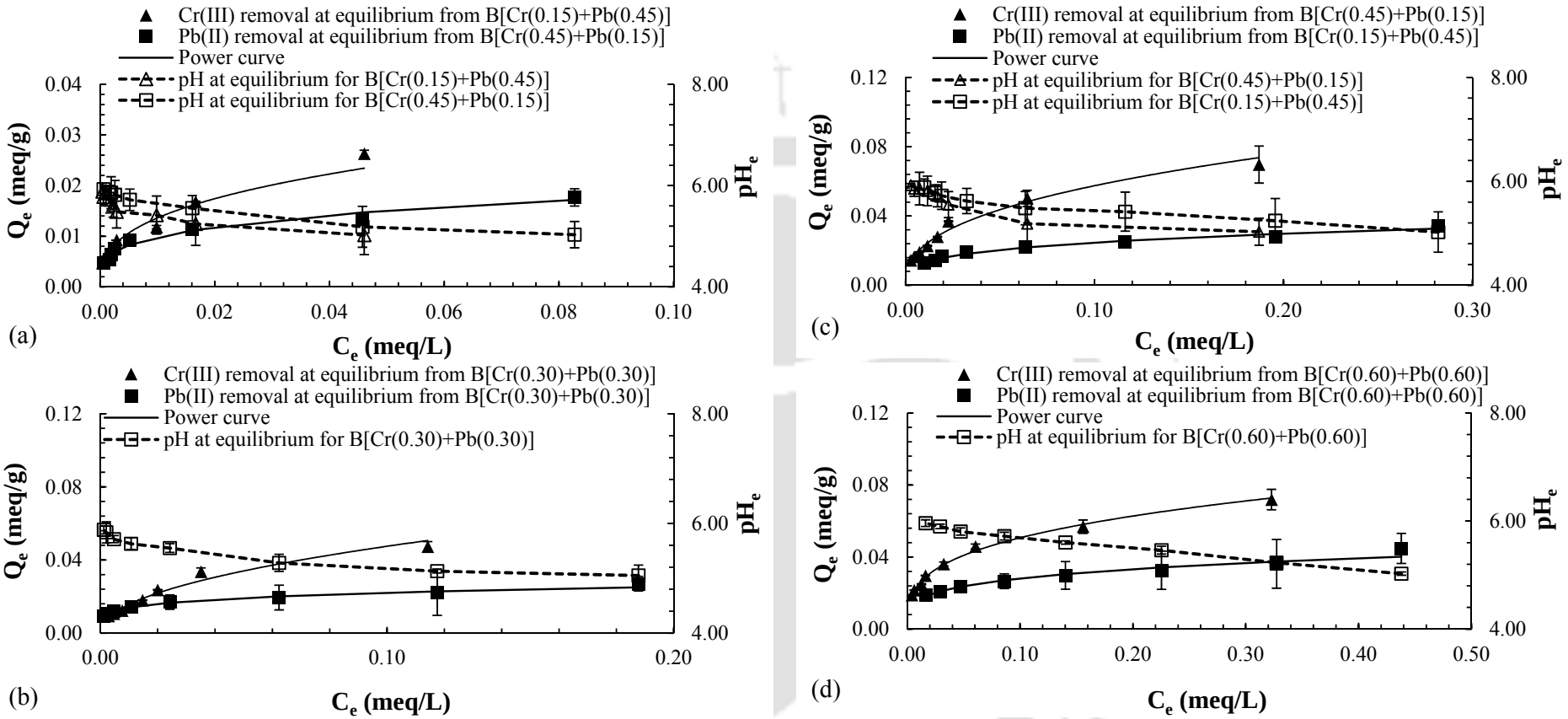

Fig. 5.83: Variations in target metal removals and solution pH at equilibrium from binary-metal ion systems comprising of Cr(III) and Pb(II) under uncontrolled pH conditions for metal ions having initial concentrations: (a) 0.15 meq/L (b) 0.30 meq/L (c) 0.45 meq/L and (d) 0.60 meq/L {Initial metal conc. in combinations B[Cr(0.45)+Pb(0.15)] = 0.47±0.10 meq/L of Cr(III) + 0.15±0.03 meq/L of Pb(II), B[Cr(0.30)+Pb(0.30)] = 0.30±0.06 meq/L of Cr(III) + 0.30±0.04 meq/L of Pb(II), B[Cr(0.15)+Pb(0.45)] = 0.15±0.01 meq/L of Cr(III) + 0.42±0.03 meq/L of Pb(II), B[Cr(0.60)+Pb(0.60)] = 0.61±0.00 meq/L of Cr(III) + 0.62±0.01 meq/L of Pb(II), Initial adjusted pH = 5.00±0.02, Shaking speed = 66 rpm, Reaction volume = 50 mL, GAA dose = 4 to 32 g/L, Mixing time = 180 min., Temp. = 30±2 °C} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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in Table 5.43 while the power curves have also been drawn and shown in Fig. 5.83. The R^2 values for power and polynomial curves were close to each other indicating either of the two mathematical relationships could be used to predict Q_e value for any of the C_e values within the range.

The results of equilibrium studies obtained under controlled pH conditions have been shown in Fig. 5.84 as variation in target metal uptakes at equilibrium (q_e) with residual metal concentrations at equilibrium (C_e). In order to understand and compare the target metal uptake at equilibrium under the influence of the non-target metal ion present in a combination of the binary-metal ion system, the variation in q_e values of metal ions having same level of initial metal ion concentrations have been plotted against respective C_e values ensuring that the initial concentration of the non-target metal was also having same levels – either similar or different than the initial concentration of the target metal being adsorbed. The variations in q_e values for target Cr(III) and target Pb(II) metal ion uptakes with C_e appeared to follow similar trends but the data points did not overlap at 95% confidence intervals for the initial metal ion concentrations of 0.15 meq/L, 0.30 meq/L, 0.45 meq/L and 0.60 meq/L in the combinations studied. However, for all the initial metal ion concentrations, the uptake of target Pb(II) metal was observed to be higher than the uptake of target Cr(III) metal throughout the range of C_e values and no overlap was observed at 95% confidence interval. The equilibrium data of target metal uptakes were fitted to Langmuir and Freundlich isotherm models without considering the impact of non-target metal ion on the uptakes and estimated model parameters are presented in Table 5.43. The higher R^2 values obtained for Freundlich isotherm model indicated its better suitability to represent the experimental equilibrium metal uptake data and the fitted curves have also been included in Fig. 5.84.

A careful examination of target metal removals under uncontrolled pH conditions and target metal uptakes under controlled pH conditions at equilibrium as presented in Fig. 5.83 and 5.84 respectively indicated removals and uptakes of non-target metals as well under uncontrolled and controlled pH conditions. Hence, the experimental metal removals data under uncontrolled pH conditions and experimental metal uptakes data under controlled pH conditions have been used to plot variations in total metal removals at equilibrium (TQ_e) and total metal uptakes at equilibrium (Tq_e) with total residual metal concentration at equilibrium (TC_e) and the plots have been presented in Fig. 5.85.

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Table 5.43: Summary of established mathematical relationship for target metal removal at equilibrium under uncontrolled pH conditions and adsorption isotherm model parameters for target metal uptake at equilibrium under controlled pH conditions for binary-metal ion system comprising of Cr(III) and Pb(II) ions.

	Binary-metal ion combinations	Non-target metal with initial conc. (meq/L)	Target metal with initial conc. (meq/L)	Fitted Curve					
				Power			Polynomial		
				Equation		R^2	Equation		R^2
Uncontrolled pH conditions	B[Cr(0.15)+Pb(0.45)]	Pb(II) = 0.42±0.03	Cr(III) = 0.15±0.01	$Q_e = 0.070C_e^{0.355}$		0.966	$Q_e = -7.862C_e^2+0.819C_e+0.005$		0.987
		Cr(III) = 0.15±0.01	Pb(II) = 0.42±0.03	$Q_e = 0.046C_e^{0.270}$		0.981	$Q_e = -0.248C_e^2+0.138C_e+0.013$		0.987
	B[Cr(0.30)+Pb(0.30)]	Pb(II) = 0.30±0.04	Cr(III) = 0.30±0.06	$Q_e = 0.144C_e^{0.482}$		0.971	$Q_e = -5.273C_e^2+0.965C_e+0.005$		0.997
		Cr(III) = 0.30±0.06	Pb(II) = 0.30±0.04	$Q_e = 0.035C_e^{0.200}$		0.992	$Q_e = -0.377C_e^2+0.152C_e+0.011$		0.939
	B[Cr(0.45)+Pb(0.15)]	Pb(II) = 0.15±0.03	Cr(III) = 0.42±0.03	$Q_e = 0.143C_e^{0.397}$		0.982	$Q_e = -2.488C_e^2+0.758C_e+0.014$		0.976
		Cr(III) = 0.42±0.03	Pb(II) = 0.15±0.03	$Q_e = 0.033C_e^{0.262}$		0.968	$Q_e = -1.442C_e^2+0.254C_e+0.006$		0.913
	B[Cr(0.60)+Pb(0.60)]	Pb(II) = 0.62±0.01	Cr(III) = 0.61±0.00	$Q_e = 0.103C_e^{0.308}$		0.994	$Q_e = -0.602C_e^2+0.347C_e+0.021$		0.962
		Cr(III) = 0.61±0.00	Pb(II) = 0.62±0.01	$Q_e = 0.049C_e^{0.241}$		0.970	$Q_e = -0.025C_e^2+0.065C_e+0.019$		0.969
Controlled pH conditions	Binary-metal ion combinations	Non-target metal with initial conc. (meq/L)	Target metal with initial conc. (meq/L)	Langmuir isotherm model			Freundlich isotherm model		
				q_m (meq/g)	b (L/meq)	R^2	k [(meq/g)/(meq/L)$^{1/n}$]	$1/n$	R^2
	B[Cr(0.15)+Pb(0.45)]	Pb(II) = 0.44±0.00	Cr(III) = 0.15±0.00	0.0129	10.8591	0.918	0.0246	0.565	0.976
		Cr(III) = 0.15±0.00	Pb(II) = 0.44±0.00	0.0302	7.1977	0.955	0.0339	0.419	0.979
	B[Cr(0.30)+Pb(0.30)]	Pb(II) = 0.29±0.00	Cr(III) = 0.29±0.02	0.0150	10.9890	0.995	0.0194	0.394	0.991
		Cr(III) = 0.29±0.02	Pb(II) = 0.29±0.00	0.0207	13.778	0.992	0.0296	0.408	0.996
	B[Cr(0.45)+Pb(0.15)]	Pb(II) = 0.15±0.01	Cr(III) = 0.46±0.02	0.0260	4.5808	0.991	0.0265	0.477	0.995
		Cr(III) = 0.46±0.02	Pb(II) = 0.15±0.01	0.0136	25.6883	0.983	0.0293	0.464	0.999
	B[Cr(0.60)+Pb(0.60)]	Pb(II) = 0.60±0.05	Cr(III) = 0.64±0.00	0.0429	1.6881	0.693	0.0295	0.593	0.885
		Cr(III) = 0.64±0.00	Pb(II) = 0.60±0.05	0.0608	2.2269	0.627	0.0480	0.582	0.881

Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with three independent data points.

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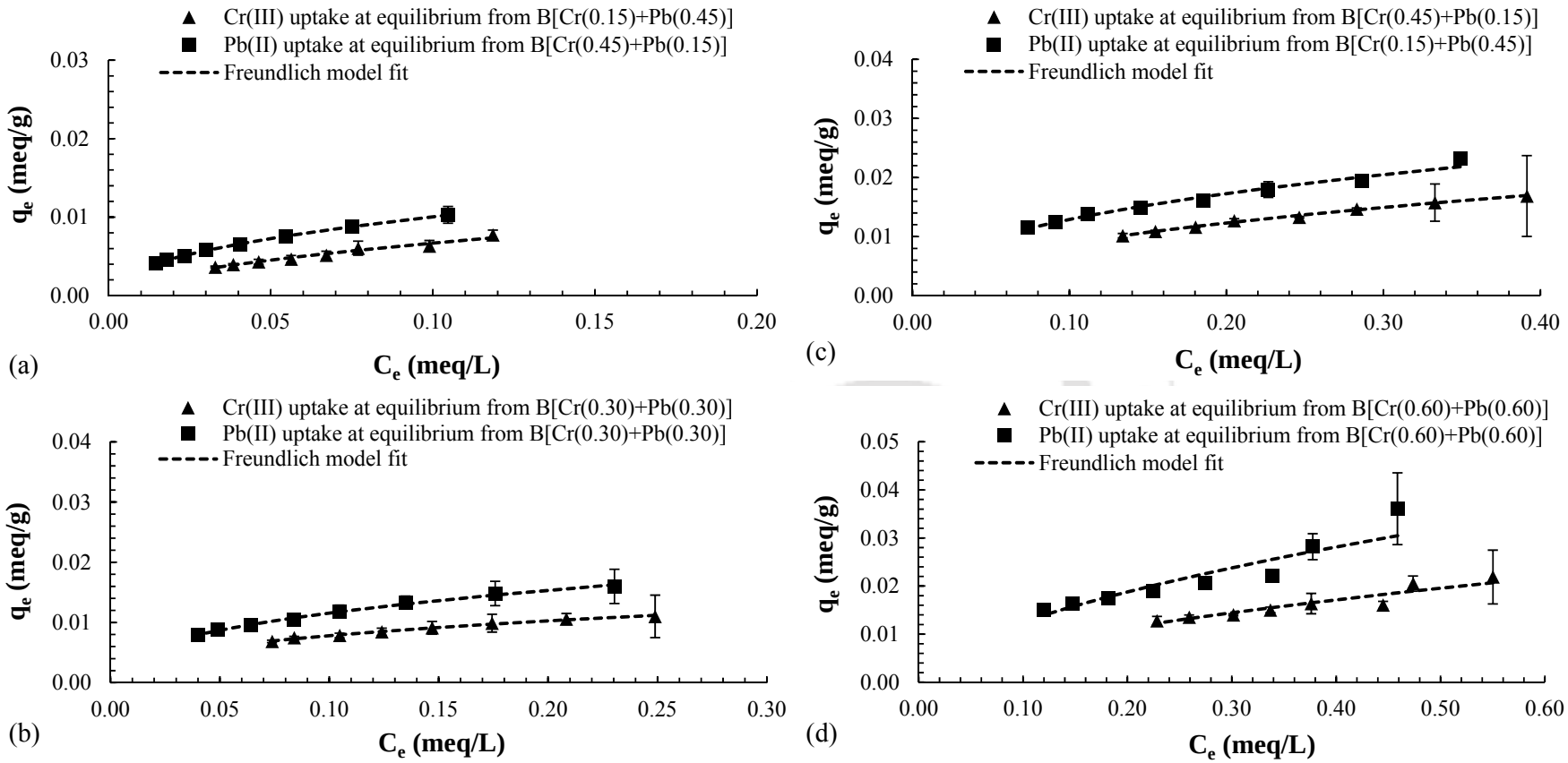

Fig. 5.84: Variations in target metal uptakes at equilibrium from binary-metal ion systems comprising of Cr(III) and Pb(II) under controlled pH conditions for metal ions having initial concentrations: (a) 0.15 meq/L (b) 0.30 meq/L (c) 0.45 meq/L and (d) 0.60 meq/L {Initial metal conc. in combinations B[Cr(0.45)+Pb(0.15)] = 0.46±0.02 meq/L of Cr(III) + 0.15±0.01 meq/L of Pb(II), B[Cr(0.30)+Pb(0.30)] = 0.29±0.02 meq/L of Cr(III) + 0.29±0.00 meq/L of Pb(II), B[Cr(0.15)+Pb(0.45)] = 0.15±0.00 meq/L of Cr(III) + 0.44±0.00 meq/L of Pb(II), B[Cr(0.60)+Pb(0.60)] = 0.64±0.00 meq/L of Cr(III) + 0.60±0.05 meq/L of Pb(II), Buffered pH = 5.00±0.02, Shaking speed = 66 rpm, Reaction volume = 50 mL, GAA dose = 4 to 32 g/L, Mixing time = 180 min., Temp. = 30±2 °C} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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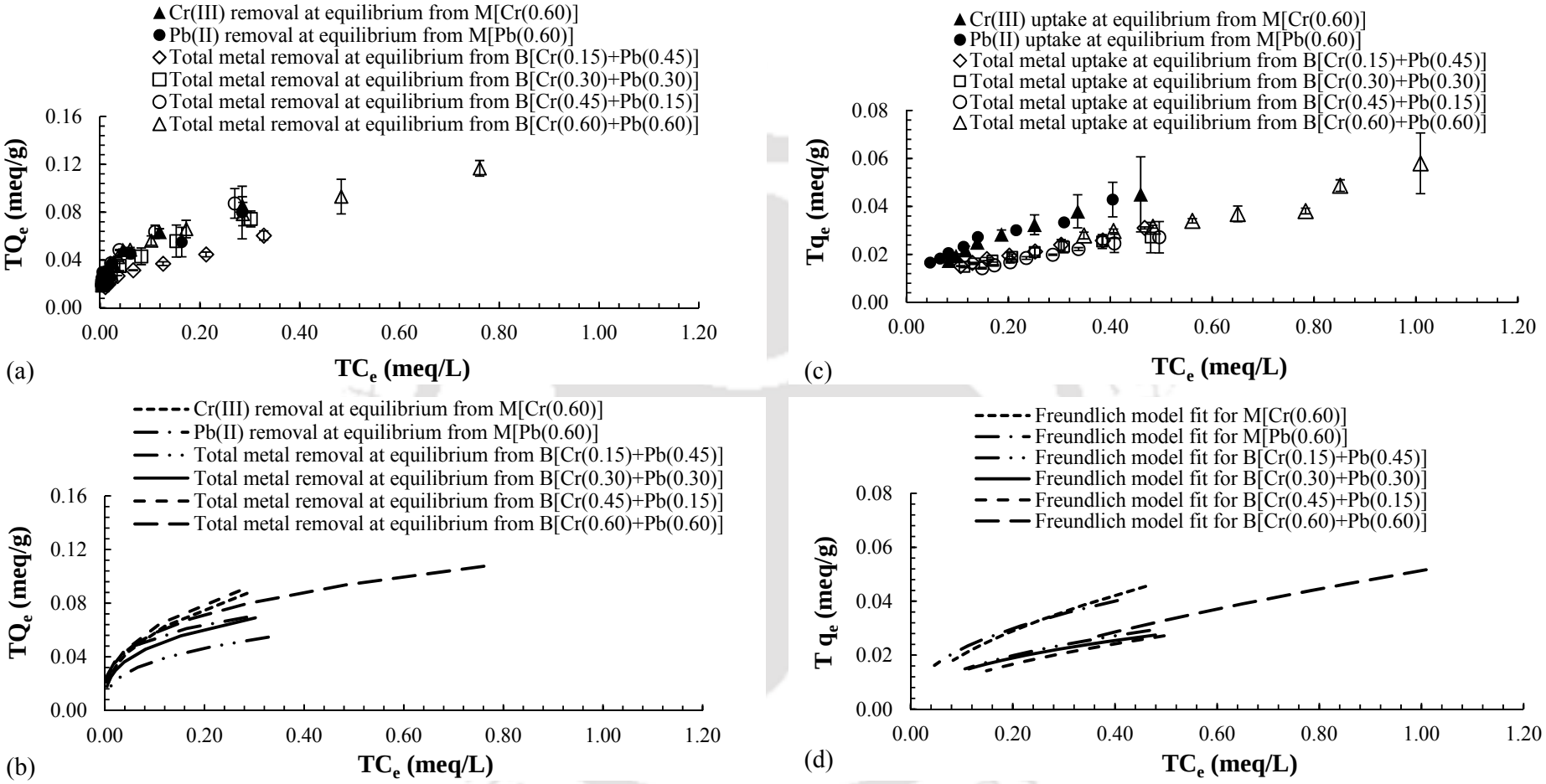

Fig. 5.85: Variations in (a) total metal removals and (b) fitted power curves under uncontrolled pH conditions; and (c) total metal uptakes (d) fitted Freundlich model under controlled pH conditions from mono- and binary-metal ion systems comprising of Cr(III) and Pb(II) ions.

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The variation in total metal removals at equilibrium (TQ_e) data points with total residual metal concentration at equilibrium (TC_e) obtained under uncontrolled pH conditions from the four selected binary-metal ion combinations namely B[Cr(0.15)+Pb(0.45)], B[Cr(0.30)+Pb(0.30)], B[Cr(0.45)+Pb(0.15)] and B[Cr(0.60)+Pb(0.60)] are presented in Fig. 5.85(a). The variations in TQ_e data points for B[Cr(0.15)+Pb(0.45)], B[Cr(0.30)+Pb(0.30)] and B[Cr(0.45)+Pb(0.15)] combinations with TC_e appeared to vary within a small band (but might not be overlapping at 95% confidence intervals). However, the variations in TQ_e data points for B[Cr(0.60)+Pb(0.60)] combination with TC_e appeared to be higher and few data points at lower TC_e values overlapped at 95% confidence intervals with one or two of the three binary combinations having total initial metal concentration of approximately 0.60 meq/L. The established mathematical relationships between TQ_e and TC_e (in terms of power and polynomial curves) for all the combinations of binary-metal ion systems are tabulated in Table 5.44 while the power curves have also been drawn and shown in Fig. 5.85(b). The R^2 values for power and polynomial curves were close to each other indicating either of the two mathematical relationships could be used to predict TQ_e value for any of the TC_e values within the range. Since the equilibrium studies with mono-metal ion systems namely M[Cr(0.60)] and M[Pb(0.60)] were also carried out with initial metal ion concentration of approximately 0.60 meq/L, therefore, the variation in experimental metal removals under uncontrolled pH conditions have also been plotted in Fig. 5.85(a). The variations in metal removals from M[Cr(0.60)] and M[Pb(0.60)] systems appeared to fall within the band and overlapped at 95% confidence intervals to variations with metal removals from the first three combinations of binary-metal ion systems having total initial metal ion concentrations of approximately 0.60 meq/L. The best fit curves for metal removals under uncontrolled pH conditions from mono- and binary-metal ion systems have been separately plotted in Fig. 5.85(b). All the curves appeared to be within the band. These results clearly suggested that the metal removals at equilibrium appeared to depend on the total initial metal ion concentration of Cr(III) and Pb(II) even though ionic radius, valence as well as atomic weight of the metal ions were different from each other.

The variations in total metal uptakes at equilibrium (Tq_e) data points with total residual metal concentration at equilibrium (TC_e) obtained under controlled pH conditions from the four selected binary-metal ion combinations namely B[Cr(0.15)+Pb(0.45)], B[Cr(0.30)+Pb(0.30)], B[Cr(0.45)+Pb(0.15)] and B[Cr(0.60)+Pb(0.60)] are presented

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Table 5.44: Summary of established mathematical relationships for total metal removal at equilibrium under uncontrolled pH conditions and estimated overall adsorption isotherm model parameters for total metal uptake at equilibrium under controlled pH conditions for binary-metal ion system comprising of Cr(III) and Pb(II) ions.

	Binary-metal ion combinations	Fitted Curve					
		Power			Polynomial		
Uncontrolled pH conditions		Equation		R^2	Equation		R^2
	B[Cr(0.45)+Pb(0.15)]	$TQ_e = 0.143(TC_e)^{0.360}$		0.992	$TQ_e = -1.133(TC_e)^2+0.547(TC_e)+0.021$		0.969
	B[Cr(0.30)+Pb(0.30)]	$TQ_e = 0.101(TC_e)^{0.317}$		0.991	$TQ_e = -0.447(TC_e)^2+0.312(TC_e)+0.020$		0.988
	B[Cr(0.15)+Pb(0.45)]	$TQ_e = 0.079(TC_e)^{0.330}$		0.981	$TQ_e = -0.089(TC_e)^2+0.153(TC_e)+0.018$		0.976
	B[Cr(0.60)+Pb(0.60)]	$TQ_e = 0.117(TC_e)^{0.306}$		0.987	$TQ_e = -0.075(TC_e)^2+0.158(TC_e)+0.038$		0.990
Controlled pH conditions	Binary-metal ion combinations	Langmuir isotherm model*			Freundlich isotherm model*		
		q_m (meq/g)	b (L/meq)	R^2	k [(meq/g)/(meq/L)$^{1/n}$]	$1/n$	R^2
	B[Cr(0.45)+Pb(0.15)]	0.0447	2.9876	0.987	0.0396	0.537	0.997
	B[Cr(0.30)+Pb(0.30)]	0.0370	5.4781	0.993	0.0376	0.425	0.995
	B[Cr(0.15)+Pb(0.45)]	0.0424	4.5804	0.951	0.0412	0.453	0.980
	B[Cr(0.60)+Pb(0.60)]	0.1179	0.7732	0.594	0.0514	0.639	0.887

* Model parameters estimated using Tq_e and TC_e values of combinations of binary-metal ion systems.

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in Fig. 5.85(c). The variations in Tq_e data points for B[Cr(0.15)+Pb(0.45)], B[Cr(0.30)+Pb(0.30)] and B[Cr(0.45)+Pb(0.15)] combinations with TC_e appeared to overlap at 95% confidence interval. Even, the variation in Tq_e data points for B[Cr(0.60)+Pb(0.60)] combination with TC_e appeared to be within the same narrow band and overlapped at 95% confidence intervals with some of the other binary combinations having total initial metal concentration of approximately 0.60 meq/L. The equilibrium data of total metal uptakes were fitted to Langmuir and Freundlich isotherm models and estimated model parameters are presented in Table 5.44. The higher R^2 values obtained for Freundlich isotherm model indicated its better suitability to represent the experimental equilibrium total metal uptake data. Since the equilibrium studies with mono-metal ion systems namely M[Cr(0.60)] and M[Pb(0.60)] were also carried out with initial metal ion concentration of approximately 0.60 meq/L, therefore, the variation in experimental metal uptakes under controlled pH conditions have also been plotted in Fig. 5.85(c). The variations in metal uptakes from M[Cr(0.60)] and M[Pb(0.60)] systems appeared to be higher and didn't overlap at 95% confidence intervals to variations in metal uptakes from the combination of binary-metal ion systems having total initial metal ion concentrations of approximately 0.60 meq/L. The best fit curves for metal uptakes under controlled pH conditions from mono- and binary-metal ion systems are separately plotted in Fig. 5.85(d). The variations in all the binary combinations curves appeared to be within a narrow band. The variations in both the mono-metal systems curves appeared to be higher compared to the binary-metal ion systems. These results clearly suggested that the metal uptakes at equilibrium appeared to depend on the total initial metal ion concentration of Cr(III) and Pb(II) even though ionic radius, valence as well as atomic weight of the metal ions were different from each other.

5.6.4 Equilibrium studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from binary-metal ion systems comprising of Cu(II) and Cr(III) ions

Equilibrium studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from binary-metal ion systems comprising of Cu(II) and Cr(III) metal ions have been carried out for four selected combinations: B[Cu(0.15)+Cr(0.45)], B[Cu(0.30)+Cr(0.30)], B[Cu(0.45)+Cr(0.15)] and B[Cu(0.60)+Cr(0.60)]. Since precipitation of Cu(II) and Cr(III) metal ions in B[Cu(0.30)+Cr(0.30)], B[Cu(0.45)+Cr(0.15)] and B[Cu(0.60)+Cr(0.60)] combinations were

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observed at solution pH of 5.00, the equilibrium study under uncontrolled pH conditions was restricted to B[Cu(0.15)+Cr(0.45)] combination only. However, equilibrium studies under controlled pH conditions have been carried out for all the four selected combinations.

The results of equilibrium studies obtained with B[Cu(0.15)+Cr(0.45)] combination under uncontrolled pH conditions have been shown in Fig. 5.86 as variation in metal removals at equilibrium (Q_e) with residual metal concentrations at equilibrium (C_e). This figure also shows the variation in equilibrium solution pH (pH_e). The average equilibrium pH of solutions were in the range of 5.99-6.06 at higher C_e values which increased to average equilibrium pH values of 6.50-6.70 at lower C_e values. The increase in average equilibrium pH values at lower C_e values was attributed to use of higher amounts of GAA. Since the average equilibrium pH values of solutions were well above precipitation pH values for both the metal ions, the metal removals from the solution was mainly due to precipitation as well as adsorption taking place simultaneously. The variation in Q_e values for Cu(II) and Cr(III) metal ion removals with C_e appeared to follow distinctly two different trends without overlap

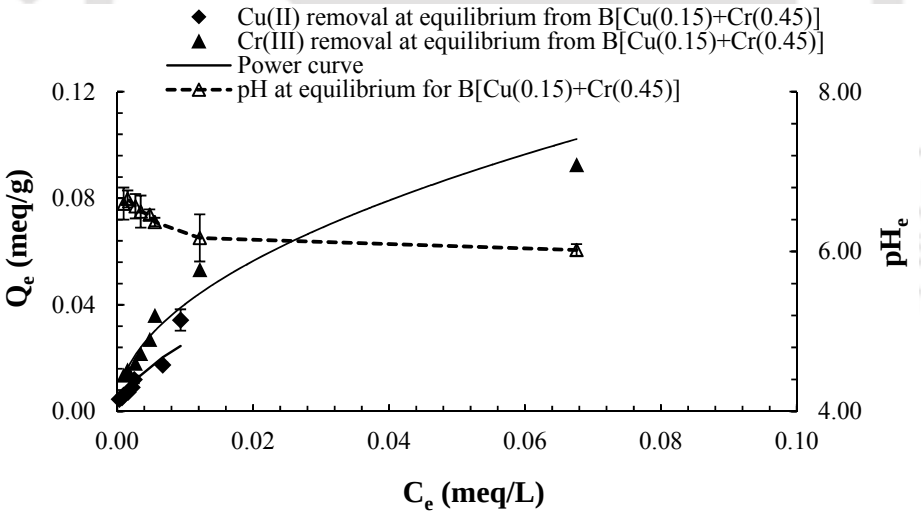

Fig. 5.86: Variations in metal removals and solution pH at equilibrium from binary-metal ion combination B[Cu(0.15)+Cr(0.45)] under uncontrolled pH conditions {Initial metal conc. in combination B[Cu(0.15)+Cr(0.45)] = 0.15±0.00 meq/L of Cu(II) + 0.44±0.01 meq/L of Cr(III), Initial adjusted pH = 5.00±0.02, Shaking speed = 66 rpm, Reaction volume = 50 mL, GAA dose = 4 to 32 g/L, Mixing time = 180 min., Temp. = 30±2 °C} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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in data points at 95% confidence intervals. The residual equilibrium concentrations of Cr(III) metal ions were observed to be higher compared with residual equilibrium concentrations of Cu(II) as concentration of Cr(III) in B[Cu(0.15)+Cr(0.45)] combination was higher. The established mathematical relationships between Q_e and C_e (in terms of power and polynomial curves) for removal of each of the metal ions from B[Cu(0.15)+Cr(0.45)] combination are tabulated in Table 5.45 while the power curves have also been drawn and shown in Fig. 5.86. The R^2 values for power and polynomial curves were close to each other indicating either of the two mathematical relationships could be used to predict Q_e value for any of the C_e values within the range.

The results of equilibrium studies obtained under controlled pH conditions have been shown in Fig. 5.87 as variation in metal uptakes at equilibrium (q_e) with residual metal concentrations at equilibrium (C_e). In order to understand and compare the uptake of target metal ion at equilibrium under the influence of the non-target metal ion present in a combinations of binary-metal ion system, the variations in q_e values of metal ions having same level of initial metal ion concentrations have been plotted against respective C_e values ensuring that the initial concentration of the non-target metal ion was also having same levels – either similar or different than the initial concentration of the target metal ions being adsorbed. The variations in q_e values for target Cu(II) and target Cr(III) metal ion uptakes with C_e appeared to follow similar trends and data points appeared to overlap at 95% confidence intervals for the initial metal ion concentrations of 0.15 meq/L, 0.30 meq/L, 0.45 meq/L and 0.60 meq/L. The equilibrium data of target metal uptakes were fitted to Langmuir and Freundlich isotherm models without considering the impact of non-target metal ion on the uptakes and estimated model parameters are presented in Table 5.45. The higher R^2 values obtained for Freundlich isotherm model indicated its better suitability to represent the experimental equilibrium metal uptake data and the fitted curves have also been included in Fig. 5.87.

A careful examination of target metal removals under uncontrolled pH conditions and target metal uptakes under controlled pH conditions at equilibrium as presented in Fig. 5.86 and 5.87 respectively indicated removals and uptakes of non-target metals as well under uncontrolled and controlled pH conditions. Hence, the experimental metal removals data under uncontrolled pH conditions and experimental metal uptakes data under controlled pH

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Table 5.45: Summary of established mathematical relationships for target metal removal at equilibrium under uncontrolled pH conditions and adsorption isotherm model parameters for target metal uptake at equilibrium under controlled pH conditions for binary-metal ion systems comprising of Cu(II) and Cr(III) ions.

			Fitted Curve						
Uncontrolled pH conditions	Binary-metal ion combinations	Non-target metal with initial conc. (meq/L)	Target metal with initial conc. (meq/L)	Power			Polynomial		
				Equation		R^2	Equation		R^2
	B[Cu(0.15)+Cr(0.45)]	Cr(III) = 0.44±0.01	Cu(II) = 0.15±0.00	$Q_e = 0.357C_e^{0.573}$		0.911	$Q_e = 240.3C_e^2+0.691C_e+0.005$		0.960
		Cu(II) = 0.15±0.00	Cr(III) = 0.44±0.01	$Q_e = 0.380C_e^{0.487}$		0.961	$Q_e = -44.92C_e^2+4.274C_e+0.008$		0.911
Controlled pH conditions	Binary-metal ion combinations	Non-target metal with initial conc. (meq/L)	Target metal with initial conc. (meq/L)	Langmuir isotherm model			Freundlich isotherm model		
				q_m (meq/g)	b (L/meq)	R^2	k [(meq/g)/(meq/L)$^{1/n}$]	$1/n$	R^2
	B[Cu(0.15)+Cr(0.45)]	Cr(III) = 0.48±0.01	Cu(II) = 0.15±0.00	0.0175	8.8601	0.840	0.0345	0.625	0.975
		Cu(II) = 0.15±0.00	Cr(III) = 0.48±0.01	0.0259	13.3092	0.993	0.0298	0.304	0.985
	B[Cu(0.30)+Cr(0.30)]	Cr(III) = 0.33±0.05	Cu(II) = 0.29±0.00	0.0367	9.4123	0.942	0.0597	0.547	0.993
		Cu(II) = 0.29±0.00	Cr(III) = 0.33±0.05	0.0382	12.1465	0.984	0.0628	0.502	0.996
	B[Cu(0.45)+Cr(0.15)]	Cr(III) = 0.16±0.01	Cu(II) = 0.45±0.00	0.0403	2.9749	0.875	0.0386	0.595	0.972
		Cu(II) = 0.45±0.00	Cr(III) = 0.16±0.01	0.0211	10.6592	0.982	0.0458	0.621	0.999
	B[Cu(0.60)+Cr(0.60)]	Cr(III) = 0.62±0.03	Cu(II) = 0.59±0.02	0.0713	3.2865	0.859	0.0685	0.572	0.974
		Cu(II) = 0.59±0.02	Cr(III) = 0.62±0.03	0.0614	5.7238	0.951	0.0661	0.468	0.991

Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with three independent data points.

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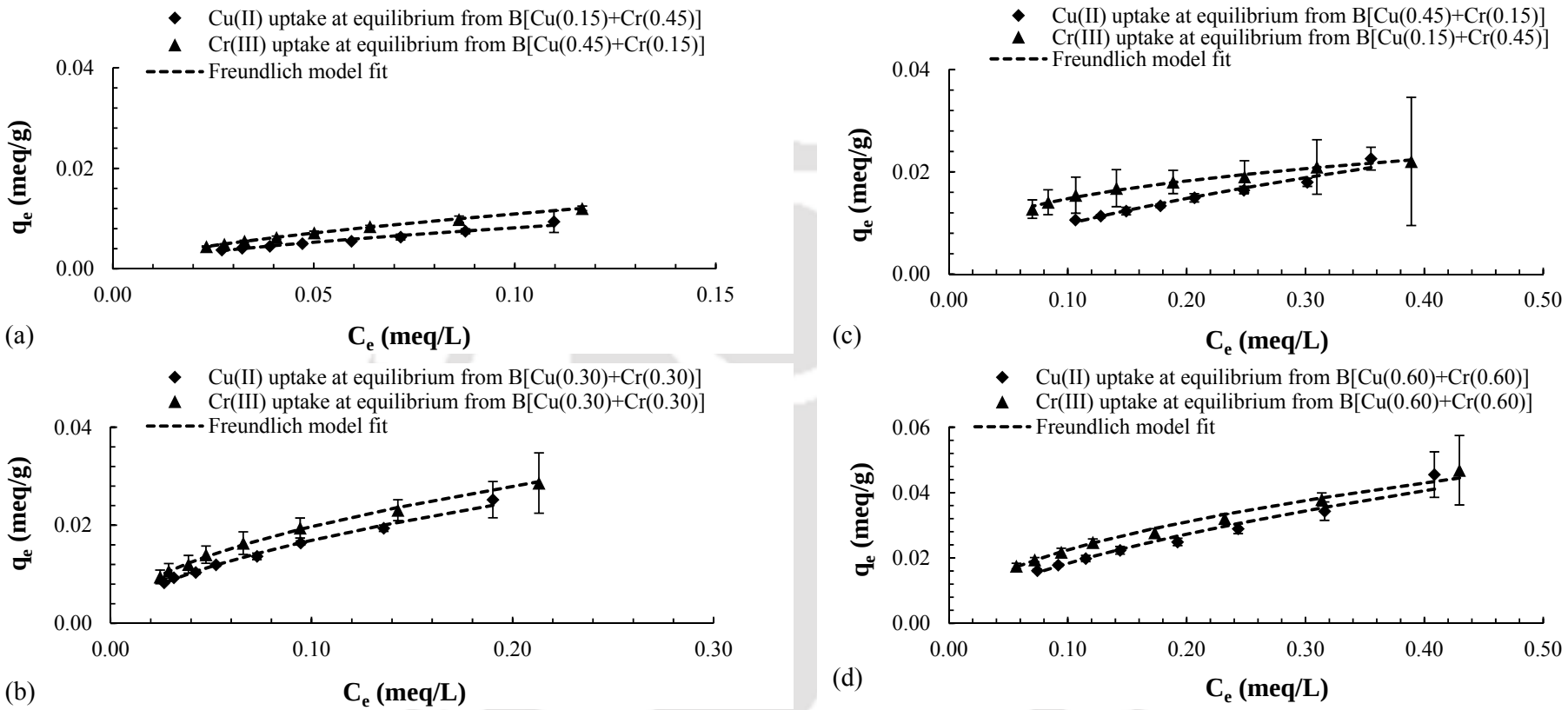

Fig. 5.87: Variations in target metal uptakes at equilibrium from binary-metal ion systems comprising of Cu(II) and Cr(III) under controlled pH conditions for metal ions having initial concentrations: (a) 0.15 meq/L (b) 0.30 meq/L (c) 0.45 meq/L and (d) 0.60 meq/L {Initial metal conc. in combinations B[Cu(0.45)+Cr(0.15)] = 0.45±0.00 meq/L of Cu(II) + 0.16±0.01 meq/L of Cr(III), B[Cu(0.30)+Cr(0.30)] = 0.29±0.00 meq/L of Cu(II) + 0.33±0.05 meq/L of Cr(III), B[Cu(0.15)+Cr(0.45)] = 0.15±0.00 meq/L of Cu(II) + 0.48±0.01 meq/L of Cr(III), B[Cu(0.60)+Cr(0.60)] = 0.59±0.02 meq/L of Cu(II) + 0.62±0.03 meq/L of Cr(III), Buffered pH = 5.00±0.02, Shaking speed = 66 rpm, Reaction volume = 50 mL, GAA dose = 4 to 32 g/L, Mixing time = 180 min., Temp. = 30±2 °C} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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conditions have been used to plot variations in total metal removals at equilibrium (TQ_e) and total metal uptakes at equilibrium (Tq_e) with total residual metal concentration at equilibrium (TC_e) and the plots have been presented in Fig. 5.88.

The variations in total metal removals at equilibrium (TQ_e) data points with total residual metal concentration at equilibrium (TC_e) obtained under uncontrolled pH conditions from B[Cu(0.15)+Cr(0.45)] combination is presented in Fig. 5.88(a). The established mathematical relationships between TQ_e and TC_e (in terms of power and polynomial curves) for the combination are tabulated in Table 5.46 while the power curve have also been drawn and shown in Fig. 5.88(a). The R^2 values for power and polynomial curves were close to each other indicating either of the two mathematical relationships could be used to predict TQ_e value for any of the TC_e values within the range. Since the equilibrium studies with mono-metal ion systems namely M[Cu(0.60)] and M[Cr(0.60)] were also carried out with initial metal ion concentration of approximately 0.60 meq/L, therefore, the variations in experimental metal removals under uncontrolled pH conditions have also been plotted in Fig. 5.88(a). The variations in metal removals from M[Cu(0.60)] and M[Cr(0.60)] systems appeared to be much lower compared to variations of total metal removals from B[Cu(0.15)+Cr(0.45)] combination. The higher total metal removals from B[Cu(0.15)+Cr(0.45)] combination might be due to removal of Cu(II) and Cr(III) metal ions by precipitation at pH>5.00.

The variations in total metal uptakes at equilibrium (Tq_e) data points with total residual metal concentration at equilibrium (TC_e) obtained under controlled pH conditions from the four selected binary-metal ion combinations namely B[Cu(0.15)+Cr(0.45)], B[Cu(0.30)+Cr(0.30)], B[Cu(0.45)+Cr(0.15)] and B[Cu(0.60)+Cr(0.60)] are presented in Fig. 5.88(b). The variations in Tq_e data points for B[Cu(0.15)+Cr(0.45)], B[Cu(0.30)+Cr(0.30)] and B[Cu(0.45)+Cr(0.15)] combinations with TC_e appeared to vary in a small band (but might not be overlapping at 95% confidence intervals). However, the variations in Tq_e data points for B[Cu(0.60)+Cr(0.60)] combination with TC_e appeared to be outside the band without overlapping at 95% confidence intervals with other binary combinations having total initial metal concentration of approximately 0.60 meq/L. The equilibrium data of total metal uptakes were fitted to Langmuir and Freundlich isotherm models and estimated model parameters are presented in Table 5.46. The higher R^2 values obtained for Freundlich

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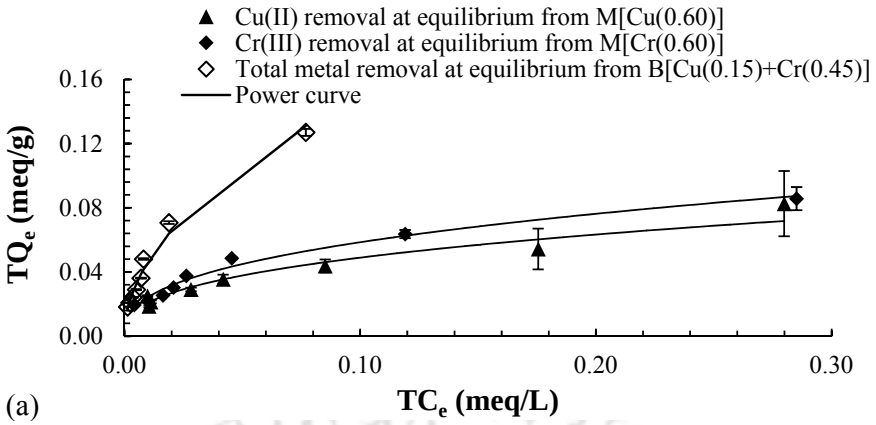
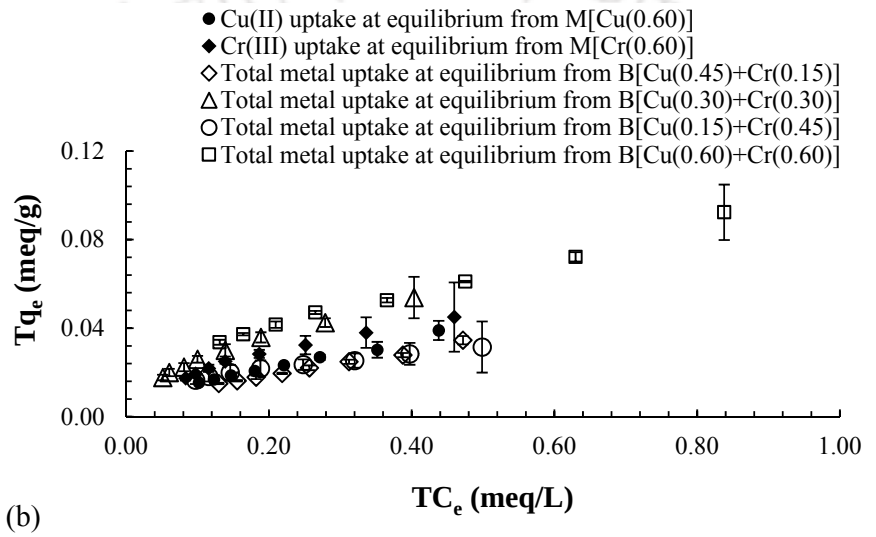


(a)



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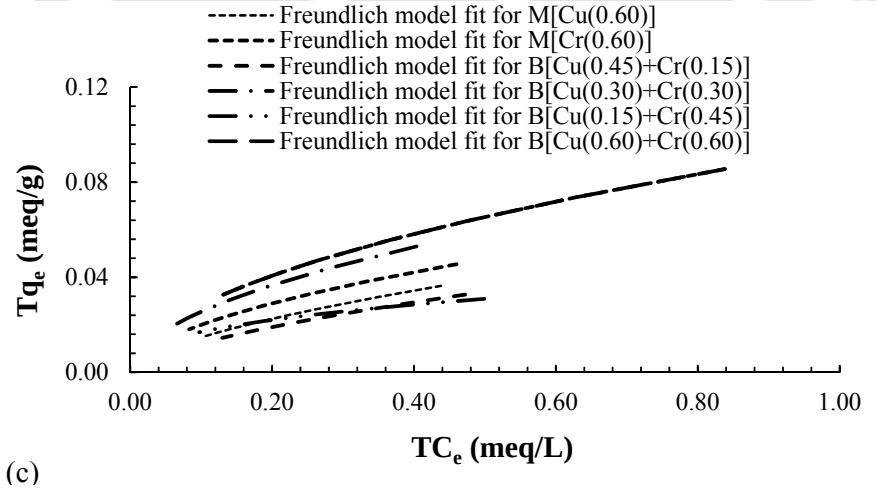

(c)

Fig. 5.88: Variations in (a) total metal removals under uncontrolled pH conditions with fitted power curves, (b) total metal uptakes and (c) fitted Freundlich model to total metal uptakes under controlled pH conditions from mono- and binary-metal ion systems comprising of Cu(II) and Cr(III) ions.

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Table 5.46: Summary of established mathematical relationships for total metal removal at equilibrium under uncontrolled pH conditions and estimated overall adsorption isotherm model parameters for total metal uptake at equilibrium under controlled pH conditions for binary-metal ion systems comprising of Cu(II) and Cr(III) ions.

Uncontrolled pH conditions	Binary-metal ion combination	Fitted Curve					
		Power			Polynomial		
		Equation		R^2	Equation		R^2
	B[Cu(0.15)+Cr(0.45)]	$TQ_e = 0.485(TC_e)^{0.510}$		0.972	$TQ_e = -28.79(TC_e)^2+3.694(TC_e)+0.013$		0.993
Controlled pH conditions	Binary-metal ion combinations	Langmuir isotherm model*			Freundlich isotherm model*		
		q_m (meq/g)	b (L/meq)	R^2	k [(meq/g)/(meq/L)$^{1/n}$]	$1/n$	R^2
	B[Cu(0.45)+Cr(0.15)]	0.0659	2.0511	0.908	0.0525	0.629	0.987
	B[Cu(0.30)+Cr(0.30)]	0.0749	5.3612	0.970	0.0853	0.524	0.997
	B[Cu(0.15)+Cr(0.45)]	0.0390	6.9150	0.985	0.0401	0.371	0.991
	B[Cu(0.60)+Cr(0.60)]	0.1309	2.1850	0.919	0.0938	0.518	0.985

* Model parameters estimated using Tq_e and TC_e values of combination of binary-metal ion systems.

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isotherm model indicated its better suitability to represent the experimental equilibrium total metal uptake data. Since the equilibrium studies with mono-metal ion systems namely M[Cu(0.60)] and M[Cr(0.60)] were also carried out with initial metal ion concentration of approximately 0.60 meq/L, therefore, the variations in experimental metal uptakes under controlled pH conditions have also been plotted in Fig. 5.88(b). The variations in metal uptakes from M[Cu(0.60)] and M[Cr(0.60)] systems appeared to overlap at 95% confidence intervals with variations in total metal uptakes from the combination of binary-metal ion systems having total initial metal ion concentrations of approximately 0.60 meq/L. The best fit curves for metal uptakes under controlled pH conditions from mono- and binary-metal ion systems have been separately plotted in Fig. 5.88(c). The variation in all the curves appeared to be within a small band. These results clearly suggested that the total metal uptakes at equilibrium appeared to depend on the total initial metal ion concentration of Cu(II) and Cr(III) even though ionic radius, valence and atomic weight of metals were different from each other.

5.6.5 Equilibrium studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions

Equilibrium studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) metal ions have been carried out for two selected combinations: T[Cu(0.20)+Pb(0.20)+Cr(0.20)] and T[Cu(0.60)+Pb(0.60)+Cr(0.60)]. Since the precipitation of Cu(II) and Cr(III) metal ions in T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combination was observed at pH>5.00, the equilibrium study under uncontrolled pH conditions was restricted to T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination only. However, equilibrium studies under controlled pH conditions have been carried out for both the selected combinations.

The results of equilibrium studies with T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination under uncontrolled pH conditions have been shown in Fig. 5.89 as variation in target metal removals at equilibrium (Q_e) with residual metal concentrations at equilibrium (C_e). This figure also shows the variation in equilibrium solution pH (pH_e). The average equilibrium pH of the solution was in the range of 6.15-6.20 at higher C_e values which further increased to average equilibrium pH values of 6.87-6.99 at lower C_e values. The increase in average

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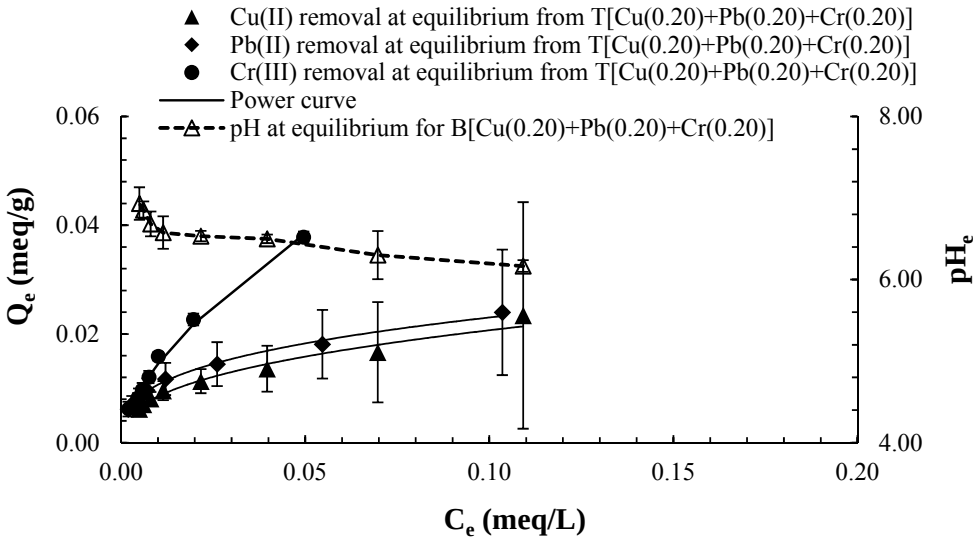

Fig. 5.89: Variations in metal removals and solution pH at equilibrium from ternary-metal ion combination T[Cu(0.20)+Pb(0.20)+Cr(0.20)] under uncontrolled pH conditions {Initial metal conc. in combination T[Cu(0.20)+Pb(0.20)+Cr(0.20)] = 0.20±0.03 meq/L of Cu(II) + 0.20±0.04 meq/L of Pb(II) + 0.20±0.00 meq/L of Cr(III), Initial adjusted pH = 5.00±0.02, Shaking speed = 66 rpm, Reaction volume = 50 mL, GAA dose = 4 to 32 g/L, Mixing time = 180 min., Temp. = 30±2 °C} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

equilibrium pH values at lower C_e values was attributed to use of higher amounts of GAA. Since the average equilibrium pH values of solution were well above precipitation pH values for all the three metal ions, the metal removals from the solutions was mainly due to precipitation as well as adsorption taking place simultaneously. The variations in Q_e values for Cu(II) and Pb(II) metal ions with C_e appeared to follow similar trends with overlap at 95% confidence intervals while Q_e values for Cr(III) metal ion appeared to follow a different trend without any overlap at 95% confidence intervals. The removal of Cr(III) metal ion was observed to be higher compared to Cu(II) and Pb(II) metal ions due to rise in solution pH above metal precipitation pH values. The established mathematical relationships between Q_e and C_e (in terms of power and polynomial curves) for the removal of each of the metal ions from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination are tabulated in Table 5.47 while the power curves have also been drawn and shown in Fig. 5.89. The R^2 values for power and polynomial curves were close to each other indicating either of the two mathematical relationships could be used to predict Q_e value for any of the C_e values within the range.

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Table 5.47: Summary of established mathematical relationship for metal removal at equilibrium under uncontrolled pH conditions and adsorption isotherm model parameters for metal uptake at equilibrium under controlled pH conditions for ternary-metal ion system comprising of Cu(II), Pb(II) and Cr(III) ions.

			Fitted Curve					
			Power			Polynomial		
Uncontrolled pH conditions	Ternary-metal ion combination	Target metal with initial conc. (meq/L)	Equation		R^2	Equation		R^2
	T[Cu(0.20)+Pb(0.20)+Cr(0.20)]	Cu(II) = 0.20±0.03	$Q_e = 0.151C_e^{0.006}$		0.973	$Q_e = -0.267C_e^2+0.180C_e+0.006$		0.960
		Pb(II) = 0.20±0.04	$Q_e = 0.049C_e^{0.334}$		0.997	$Q_e = -1.307C_e^2+0.298C_e+0.006$		0.974
		Cr(III) = 0.20±0.00	$Q_e = 0.238C_e^{0.608}$		0.983	$Q_e = -10.58C_e^2+1.218C_e+0.003$		0.996
			Langmuir isotherm model			Freundlich isotherm model		
Controlled pH conditions	Ternary-metal ion combinations	Target metal with initial conc. (meq/L)	q_m (meq/g)	b (L/meq)	R^2	k [(meq/g)/(meq/L)$^{1/n}$]	$1/n$	R^2
	T[Cu(0.20)+Pb(0.20)+Cr(0.20)]	Cu(II) = 0.19±0.00	0.0195	4.0701	0.693	0.0267	0.679	0.946
		Pb(II) = 0.20±0.01	0.0205	14.3636	0.950	0.0378	0.507	0.992
		Cr(III) = 0.22±0.02	0.0162	9.0974	0.975	0.0250	0.519	0.992
	T[Cu(0.60)+Pb(0.60)+Cr(0.60)]	Cu(II) = 0.61±0.02	0.0796	0.5866	0.522	0.0314	0.801	0.963
		Pb(II) = 0.58±0.00	0.0370	4.3433	0.946	0.0373	0.490	0.916
		Cr(III) = 0.60±0.01	0.0379	2.0722	0.885	0.0285	0.564	0.959

Data presented in xx±yy format represents an average value as xx and standard deviation as yy estimated with three independent data points.

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The results of equilibrium studies obtained under controlled pH conditions have been shown in Fig. 5.90 as variation in metal uptakes at equilibrium (q_e) with residual metal concentrations at equilibrium (C_e). The variations in q_e values for Cu(II) and Cr(III) metal ion uptakes with C_e from both the ternary-metal ion system combinations appeared to follow similar trends and most of the data points appeared not to overlap at 95% confidence intervals. The variations in q_e values for Pb(II) metal ion uptakes with C_e from both the ternary-metal ion combinations appeared to be higher and didn't overlap at 95% confidence intervals. The equilibrium data of metal uptakes were fitted to Langmuir and Freundlich isotherm models without considering the impact of non-target metal ions on the uptakes and estimated model parameters are presented in Table 5.47. The higher R^2 values obtained for Freundlich isotherm model indicated its better suitability to represent the experimental equilibrium metal uptake data and the fitted curves have also been included in Fig. 5.90.

A careful examination of target metal removals under uncontrolled pH conditions and target metal uptakes under controlled pH conditions at equilibrium as presented in Fig. 5.89 and Fig. 5.90 respectively indicated removals and uptakes of non-target metals as well under uncontrolled and controlled pH conditions. Hence, the experimental metal removals data under uncontrolled pH conditions and experimental metal uptakes data under controlled pH conditions have been used to plot variations in total metal removals at equilibrium (TQ_e) and total metal uptakes at equilibrium (Tq_e) with total residual metal concentration at equilibrium (TC_e) and the plots have been presented in Fig. 5.91.

The variation in total metal removals at equilibrium (TQ_e) data points with total residual metal concentration at equilibrium (TC_e) obtained under uncontrolled pH conditions from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination is presented in Fig. 5.91(a). The established mathematical relationships between TQ_e and TC_e (in terms of power and polynomial curves) for the combination are tabulated in Table 5.48 while the power curve has also been drawn and shown in Fig. 5.91(a). The R^2 values for power and polynomial curves were close to each other indicating either of the two mathematical relationships could be used to predict TQ_e value for any of the TC_e values within the range. Since the equilibrium studies with mono-metal ion systems namely M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] were also carried out with initial metal ion concentration of approximately 0.60 meq/L, therefore, the variations in experimental metal removals from mono-metal ion systems under uncontrolled

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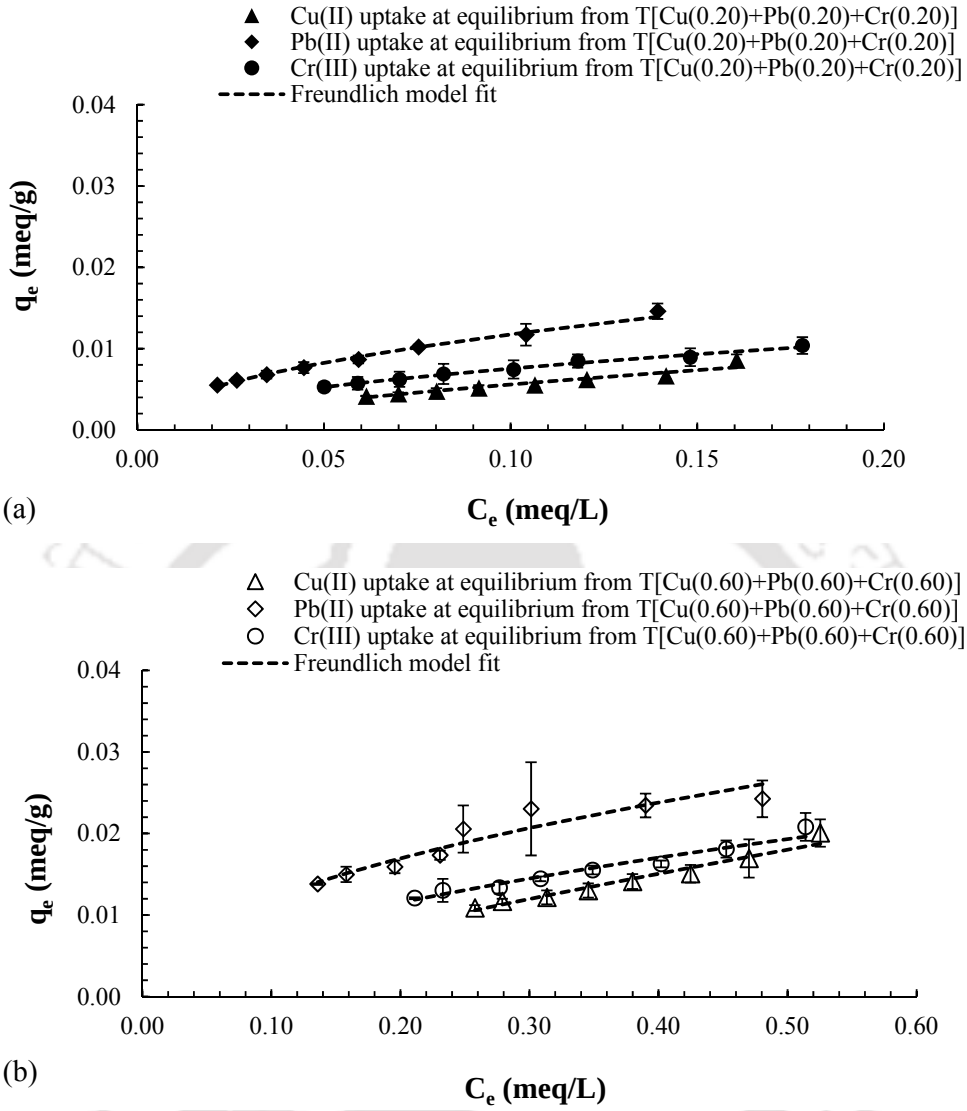

Fig. 5.90: Variations in metal uptakes at equilibrium from ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) under controlled pH conditions for metal ions having initial concentrations: (a) 0.20 meq/L and (b) 0.60 meq/L {Initial metal conc. in combinations T[Cu(0.20)+Pb(0.20)+Cr(0.20)] = 0.19±0.00 meq/L of Cu(II) + 0.20±0.01 meq/L of Pb(II) + 0.22±0.02 meq/L of Cr(III), T[Cu(0.60)+Pb(0.60)+Cr(0.60)] = 0.61±0.02 meq/L of Cu(II) + 0.58±0.00 meq/L of Pb(II) + 0.60±0.01 meq/L of Cr(III), Buffered pH = 5.00±0.02, Shaking speed = 66 rpm, Reaction volume = 50 mL, GAA dose = 4 to 32 g/L, Mixing time = 180 min., Temp. = 30±2 °C} (Each data represents an average of three independent experimental values with vertical bars representing 95% confidence interval).

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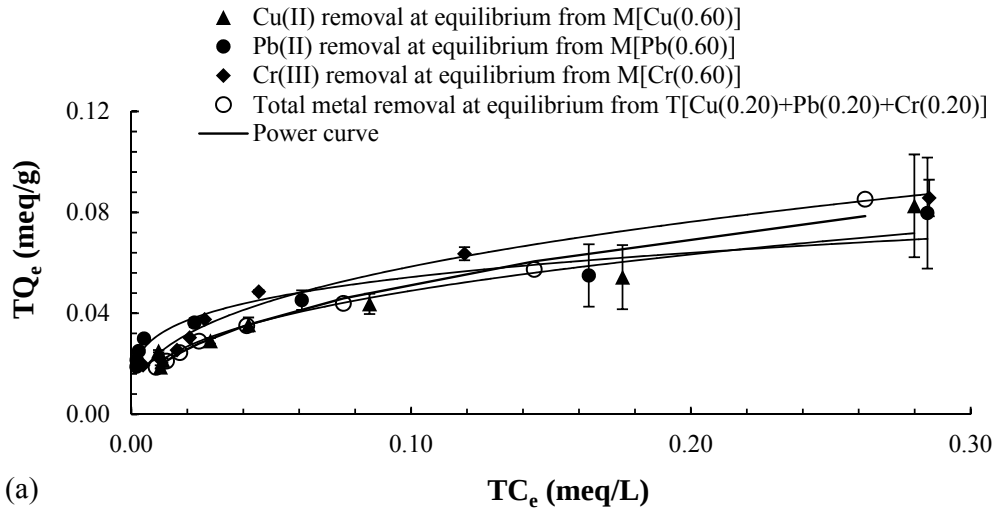
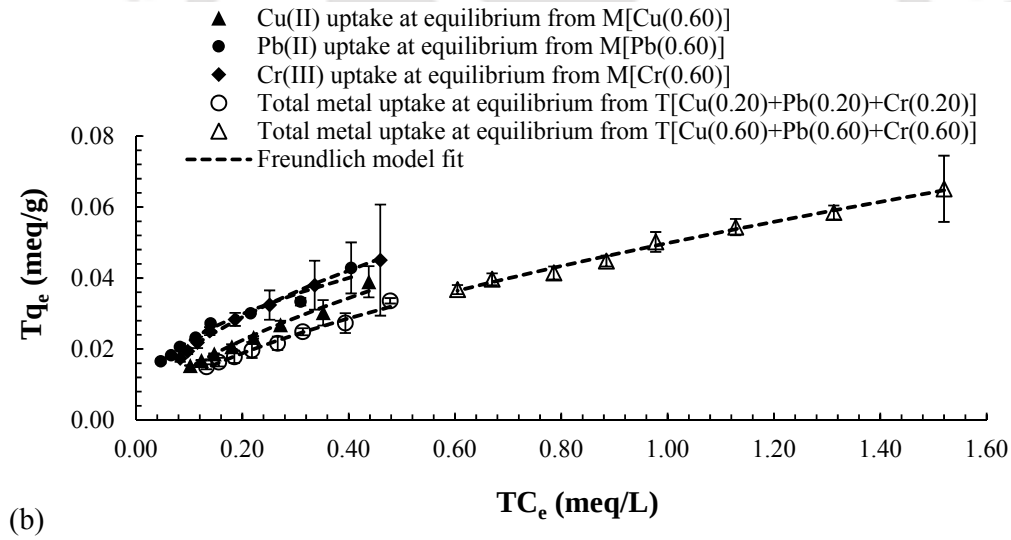


(a)



(b)

Fig. 5.91: Variations in (a) total metal removals under uncontrolled pH conditions with fitted power curves and (b) total metal uptakes under controlled pH conditions with fitted Freundlich model from mono- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions.

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Table 5.48: Summary of established mathematical relationships for total metal removal at equilibrium under uncontrolled pH conditions and estimated overall adsorption isotherm model parameters for total metal uptake at equilibrium under controlled pH conditions for ternary-metal ion system comprising of Cu(II), Pb(II) and Cr(III) ions.

Ternary-metal ion combination under uncontrolled pH conditions	Fitted Curve					
	Power			Polynomial		
	Equation		R^2	Equation		R^2
T[Cu(0.20)+Pb(0.20)+Cr(0.20)]	$TQ_e = 0.140(TC_e)^{0.432}$		0.993	$TQ_e = -0.332(TC_e)^2+0.338(TC_e)+0.018$		0.988
Ternary-metal ion combinations under controlled pH conditions	Langmuir isotherm model*			Freundlich isotherm model*		
	q_m (meq/g)	b (L/meq)	R^2	k [(meq/g)/(meq/L)$^{1/n}$]	$1/n$	R^2
T[Cu(0.20)+Pb(0.20)+Cr(0.20)]	0.0608	2.2600	0.925	0.0500	0.607	0.988
T[Cu(0.60)+Pb(0.60)+Cr(0.60)]	0.1346	0.598	0.955	0.0499	0.623	0.988

* Model parameters estimated using Tq_e and TC_e values of combination of ternary-metal ion systems.

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pH conditions have also been plotted in Fig. 5.91(a). The variations in metal removals from M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] systems appeared to follow similar trends and overlapped at 95% confidence intervals with variations of total metal removals from T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination. These results clearly suggested that the total metal removals at equilibrium appeared to depend on the total initial metal ion concentration of Cu(II), Pb(II) and Cr(III) even though ionic radius, valence and atomic weight of metals were different from each other.

The variation in total metal uptakes at equilibrium (Tq_e) data points with total residual metal concentration at equilibrium (TC_e) obtained under controlled pH conditions from the two ternary-metal ion combinations namely T[Cu(0.20)+Pb(0.20)+Cr(0.20)] and T[Cu(0.60)+Pb(0.60)+Cr(0.60)] are presented in Fig. 5.91(b). The equilibrium data of total metal uptakes were fitted to Langmuir and Freundlich isotherm models and estimated model parameters are presented in Table 5.48. The higher R^2 values obtained for Freundlich isotherm model indicated its better suitability to represent the experimental equilibrium total metal uptake data. Since the equilibrium studies with mono-metal ion systems namely M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] were also carried out with initial metal ion concentration of approximately 0.60 meq/L, therefore, the variations in experimental metal uptakes from mono-metal ion systems under controlled pH conditions have also been plotted in Fig. 5.91(b). The variations in metal uptakes from M[Cu(0.60)], M[Pb(0.60)], M[Cr(0.60)] systems and T[Cu(0.20)+Pb(0.20)+Cr(0.20)] combination appeared to vary within a small band. However, the variations in total metal uptake from T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combination was higher with higher residual TC_e values. The best fit curves for metal uptakes under controlled pH conditions from mono- and ternary-metal ion systems have also been plotted in Fig. 5.91(b). The variations in all the curves appeared to be within the small band for metal ion systems having total initial metal ion concentration of approximately 0.60 meq/L. These results clearly suggested that the metal uptakes at equilibrium appeared to depend on the total initial metal ion concentration of Cu(II), Pb(II) and Cr(III) even though ionic radius, valence and atomic weight of metals were different from each other.

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5.6.6 Comparison of total metal removals at equilibrium under uncontrolled pH conditions and total metal uptakes at equilibrium under controlled pH conditions from mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions

The variations in total metal removals at equilibrium (TQ_e) under uncontrolled pH conditions and total metal uptakes at equilibrium (Tq_e) under controlled pH conditions with total residual metal concentration at equilibrium (TC_e) from binary-metal ion combinations comprising of Cu(II) and Pb(II), Pb(II) and Cr(III), and Cr(III) and Cu(II); and ternary-metal ion combination having total initial metal ion concentration of approximately 0.60 meq/L appeared to vary, in general, within a small band as discussed in previous sections. Even the variation in metal removals at equilibrium and metal uptakes at equilibrium from mono-metal ion systems were also observe to be part of the same small band. It led to believe that the metal removals at equilibrium as well as metal uptakes at equilibrium appeared to depend on the total initial metal ion concentration rather than on the atomic weights, valence, etc. of the participating metal ions. In order to buttress this believe further or otherwise, variations (experimental data points as well as the best fit curves) in TQ_e under uncontrolled pH conditions and Tq_e under controlled pH conditions with TC_e from mono-metal ion systems of Cu(II), Pb(II) and Cr(III); binary-metal ion combinations comprising of Cu(II) and Pb(II), Pb(II) and Cr(III), and Cr(III) and Cu(II); and the ternary-metal ion combination having total initial metal ion concentration approximately 0.60 meq/L have been plotted and shown in Fig. 5.92. The variations (experimental data points as well as the best fit curves) in TQ_e under uncontrolled pH conditions and Tq_e under controlled pH conditions with TC_e from binary-metal ion combinations comprising of Cu(II) and Pb(II), Pb(II) and Cr(III), and Cr(III) and Cu(II) having total initial metal ion concentration approximately 1.20 meq/L have been plotted and shown in Fig. 5.93. It appeared, in general, that the variation in data points of total metal removals {except for B[Cu(0.15)+Cr(0.45)] combination} and total metal uptakes from mono-, binary- and ternary-metal ion systems having total initial metal ion concentration close to 0.60 meq/L followed the similar trends and varied within a small band with overlaps at 95% confidence intervals. In the case of total initial metal ion concentrations in binary-metal ion systems close to 1.20 meq/L, the total metal removals appeared to vary in a narrow band as data points seemed to overlap at 95% confidence intervals while the total metal uptakes appeared to have similar trend in variation within a small band but data points did not overlap at 95% confidence intervals. Hence, this observation support the belief, to some extent, that the total metal removals at equilibrium as well as total metal uptakes at

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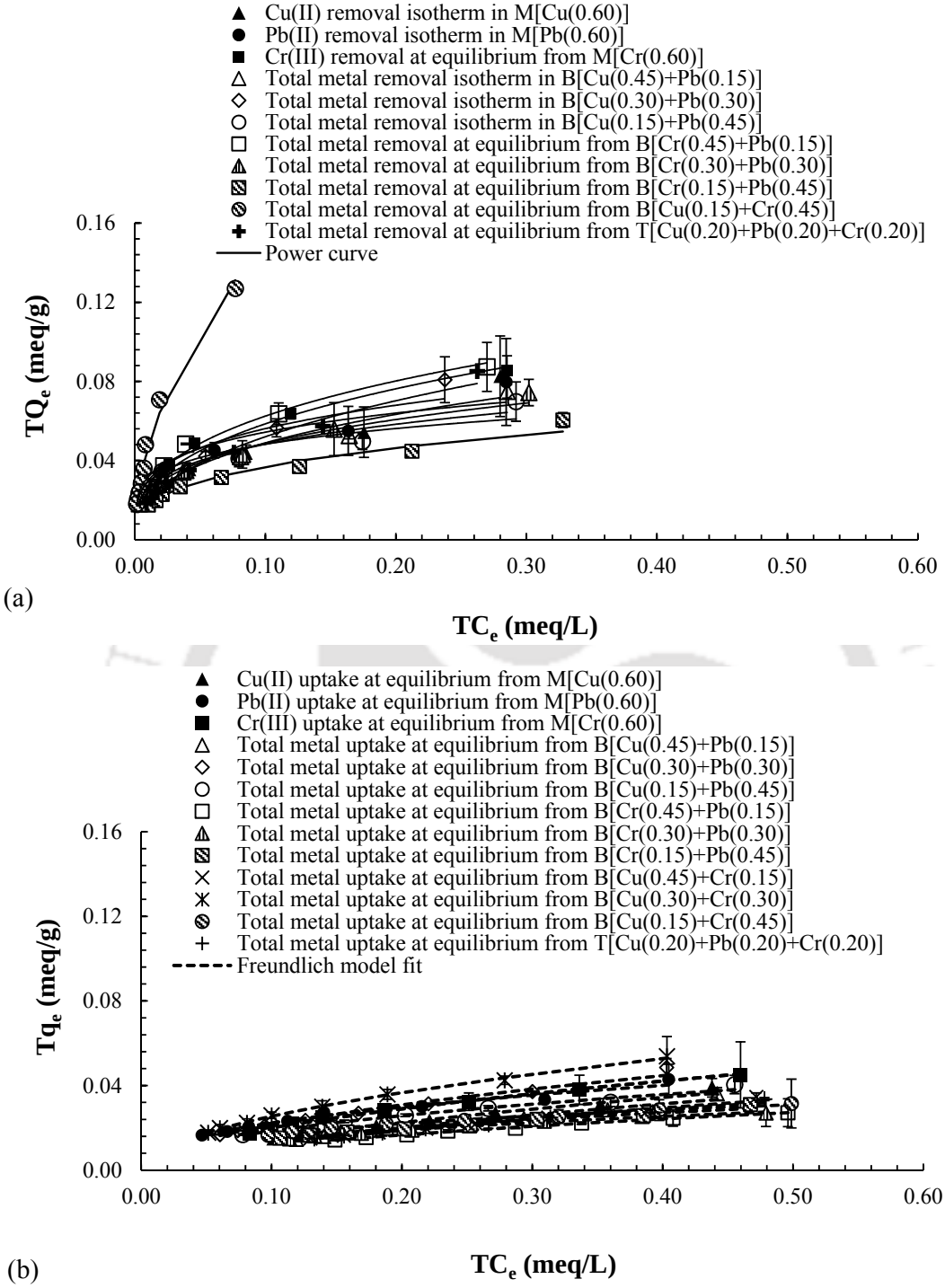

Fig. 5.92: Variations in (a) total metal removals under uncontrolled pH conditions with fitted power curves and (b) total metal uptakes under controlled pH conditions with fitted Freundlich models from mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions having total initial metal ion concentration of approximately 0.60 meq/L.

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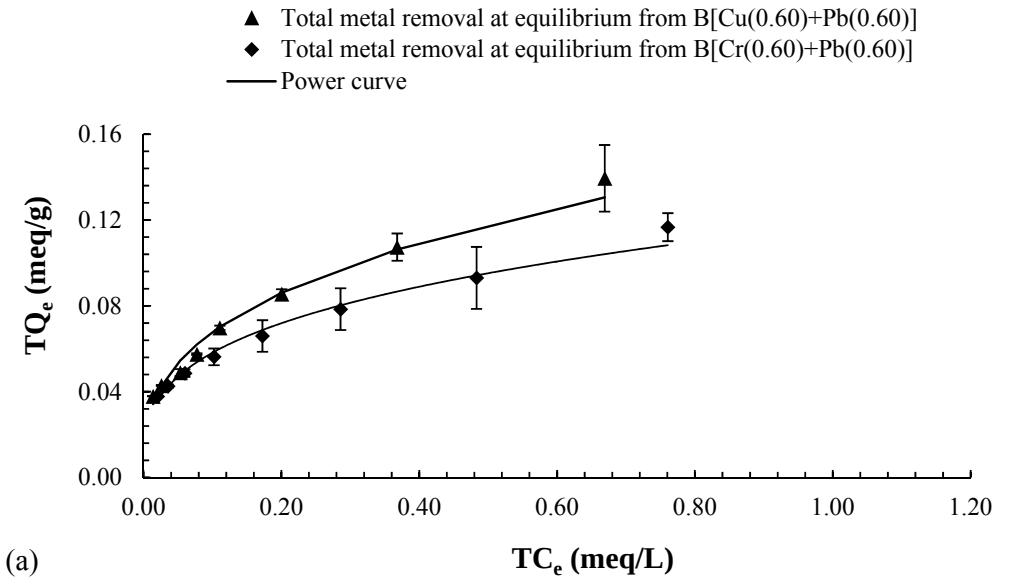
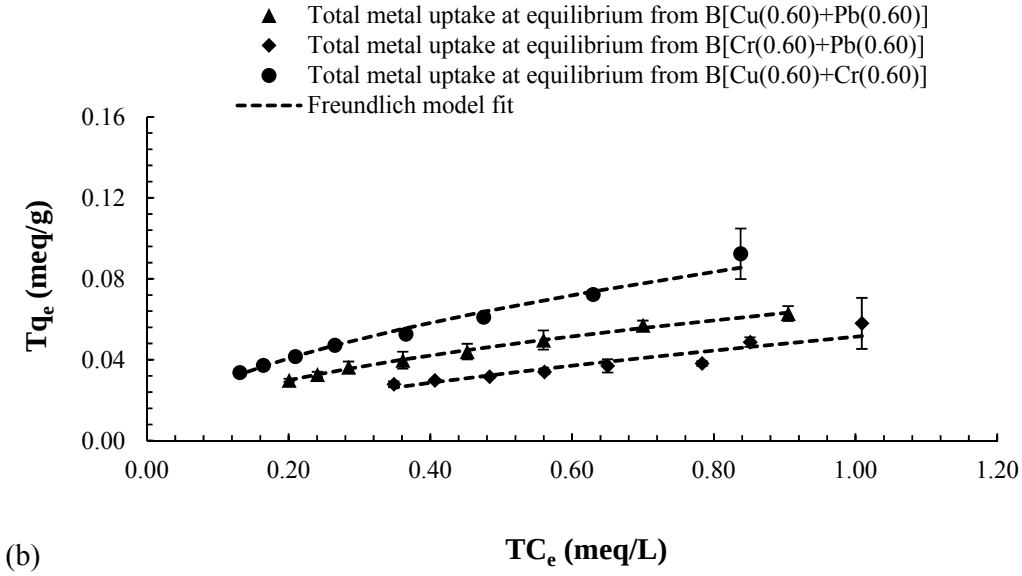


(a)



(b)

Fig. 5.93: Variations in (a) total metal removals under uncontrolled pH conditions with fitted power curves and (b) total metal uptakes under controlled pH conditions with fitted Freundlich model from binary-metal ion systems having total initial metal ion concentration of approximately 1.20 meq/L.

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equilibrium depended on the total initial metal ion concentration rather than on the atomic weights, valence, etc. of the participating metal ions viz. Cu(II), Pb(II) and Cr(III).

5.6.7 Application of available models for competitive uptake of target metal ions at equilibrium from binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions

Based upon literature review and the experimental equilibrium data available, the following four models have been identified for modeling competitive uptake of target metal ions: (a) Modified Competitive Langmuir Model (Bellot & Condoret, 1993) (b) Extended Langmuir Isotherm Model (Yang, 1987), (c) Extended Freundlich Isotherm Model (Fritz & Schluender, 1974) and (d) Sheindorf-Rebuhn-Sheintuch (SRS) Model (Sheindorf et al., 1981). However, all these models needed inputs from single or mono-metal ion systems (except for Extended Langmuir Isotherm Model) obtained under non-competitive environment (i.e. absence of the competing metal ion other than the metal ion being adsorbed). The available literature appeared to be silent on the level or amount of initial metal ion concentration in the single or mono-metal ion systems compared to levels or amounts of the initial metal ion concentrations of competing and non-competing metal ions in the system of interests. In the present work, the available experimental equilibrium data for single or mono-metal ion systems obtained under non-competitive environment are for M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] systems only. Therefore, efforts were made to apply the identified competitive metal uptake models to experimental equilibrium data obtained under competitive environment for three combination of binary-metal ion systems viz. B[Cu(0.60)+Pb(0.60)], B[Cr(0.60)+Pb(0.60)] and B[Cu(0.60)+Cr(0.60)] and one combination of ternary-metal ion system viz. T[Cu(0.60)+Pb(0.60)+Cr(0.60)] only. The identified competitive metal uptake models could not be applied to the other combinations of binary- and ternary-metal ion systems due to non-availability of non-competitive experimental equilibrium data for single or mono-metal ion systems having initial metal ion concentrations of 0.15 meq/L, 0.20 meq/L, 0.30 meq/L and 0.45 meq/L.

In the present work, the identified competitive metal uptake models have been used to describe metal uptakes under controlled pH conditions from B[Cu(0.60)+Pb(0.60)], B[Cr(0.60)+Pb(0.60)], B[Cu(0.60)+Cr(0.60)] and T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combinations utilizing adsorption isotherm parameters estimated for M[Cu(0.60)],

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M[Pb(0.60)] and M[Cr(0.60)] systems. The isotherm parameters of identified competitive metal uptake models were estimated using MS Excel 2007 (solver function) by minimizing Marquardt's percent standard deviation (MPSD) (Srivastava et al., 2006). MPSD is represented as

$$\text{MPSD} = 100\sqrt{\frac{1}{n_m - n_p}\sum_{i=1}^{n}\left(\frac{q_{e,i,\text{exp}} - q_{e,i,cal}}{q_{e,i,\text{exp}}}\right)^2} \tag{5.8}$$

where n_m is the number of experimental data points, n_p is the number of parameters in the isotherm equation, n is number of data points, $q_{e,i,exp}$ is the experimental uptake of 'ith' metal and $q_{e,i,cal}$ is the calculated uptake of 'ith' metal. MPSD had been used to test the adequacy and accuracy of the fit of identified competitive metal uptake models with the experimental equilibrium data. It is similar to the geometric mean error distribution, but modified by incorporating the number of degrees of freedom. Lower the value of MPSD, better shall be the fit. The parametric values of all the identified competitive metal uptake models are presented in Table 5.49. The estimated MPSD values between the experimental and predicted q_e values for metal uptake data of selected combinations are also presented in Table 5.49. The comparisons of the experimental metal uptake values with the predicted metal uptakes obtained by applying identified competitive metal uptake models are presented in Fig. 5.94 for B[Cu(0.60)+Pb(0.60)], Fig. 5.95 for B[Cr(0.60)+Pb(0.60)], Fig. 5.96 for B[Cu(0.60)+Cr(0.60)] and Fig. 5.97 for T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combinations. The identified models – namely Modified Competitive Langmuir model and Extended Langmuir Isotherm model showed poor fit {except good fit to B[Cu(0.60)+Cr(0.60)] combination by Extended Langmuir Isotherm model} to the experimental data from binary-metal ion systems compared to Extended Freundlich Isotherm model and SRS model. Further SRS model also showed good fit to experimental data from T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combination compared to Modified Competitive Langmuir model and Extended Langmuir Isotherm model. This was expected as the adsorbent (GAA) had heterogeneous surface and the adsorption of Cu(II) from M[Cu(0.60)] system, Pb(II) from M[Pb(0.60)] system and Cr(III) from M[Cr(0.60)] system had also been well represented by the Freundlich isotherm. Since all the identified competitive metal uptake models (except the Extended Langmuir Isotherm model) had been developed to estimate the individual metal ion uptakes from a mixture of

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Table 5.49: Estimated parameters for competitive metal uptake models for metal uptakes under controlled pH conditions from selected combinations of binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions.

Metal ion combinations	Metal ions	Modified Competitive Langmuir Model		Extended Langmuir Isotherm Model		Extended Freundlich Isotherm Model			SRS Model		
		Parameter	Values	Parameter	Values	x_i	y_i	z_i	a_{ij}	a_{ij}	a_{ij}
B[Cu(0.60)+Pb(0.60)]	Cu(II)	η_1	0.68	b_1	1.94	0.00049	0.43168	0.11752	1	1.87668	-
	Pb(II)	η_2	0.77	b_2	3.89	0.01991	0.18940	0.21143	0.14906	1	-
		MPSD = 25.28		q_{max}	0.0838	MPSD = 4.41			MPSD = 6.47		
				MPSD = 19.46							
B[Cr(0.60)+Pb(0.60)]	Cr(III)	η_1	0.99	b_1	0.86	0.52591	1.32764	0.29764	1	9.39713	-
	Pb(II)	η_2	0.99	b_2	1.65	0.33494	0.34994	0	0.78895	1	-
		MPSD = 71.65		q_{max}	0.0898	MPSD = 22.57			MPSD = 15.54		
				MPSD = 17.29							
B[Cu(0.60)+Cr(0.60)]	Cu(II)	η_1	0.34	b_1	2.65	0	0	3.2563	1	0	-
	Cr(III)	η_2	0.42	b_2	3.29	0.13114	0	0.1893	0	1	-
		MPSD = 26.73		q_{max}	0.1107	MPSD = 41.09			MPSD = 23.72		
				MPSD = 16.30							
T[Cu(0.60)+Pb(0.60) +Cr(0.60)]	Cu(II)	η_1	0.82	b_1	0.54	-	-	-	1	0.33095	8.41467
	Pb(II)	η_2	0.92	b_2	1.08	-	-	-	0.00272	1	1.21842
	Cr(III)	η_3	0.99	b_3	0.66	-	-	-	4.43955	1.83399	1
		MPSD = 36.62		q_{max}	0.1185				MPSD = 10.73		
				MPSD = 20.28							

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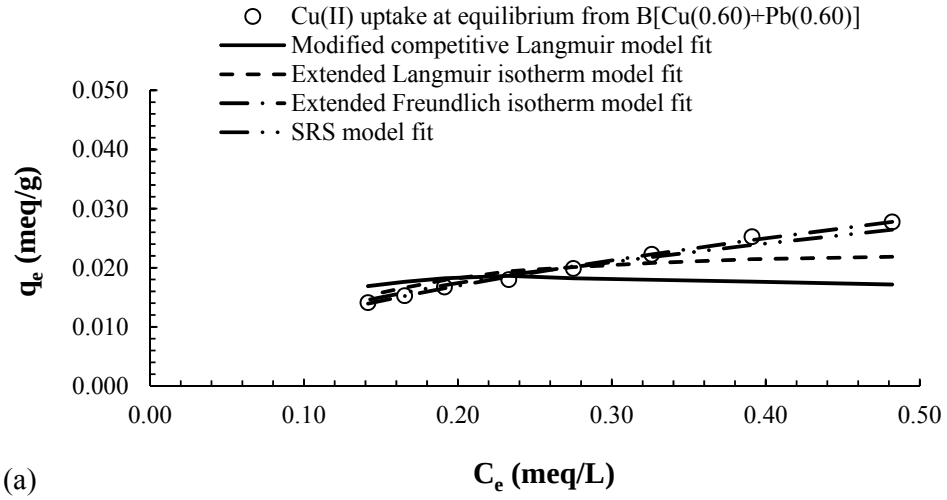
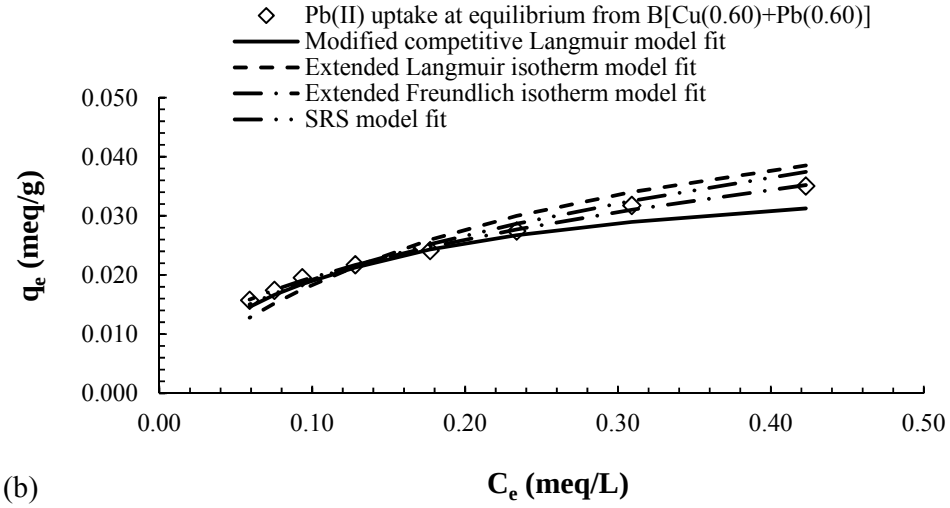


(a)



(b)

Fig. 5.94: Competitive metal uptake models fitted for uptake of (a) Cu(II) and (b) Pb(II) from B[Cu(0.60)+Pb(0.60)] combination under controlled pH conditions.

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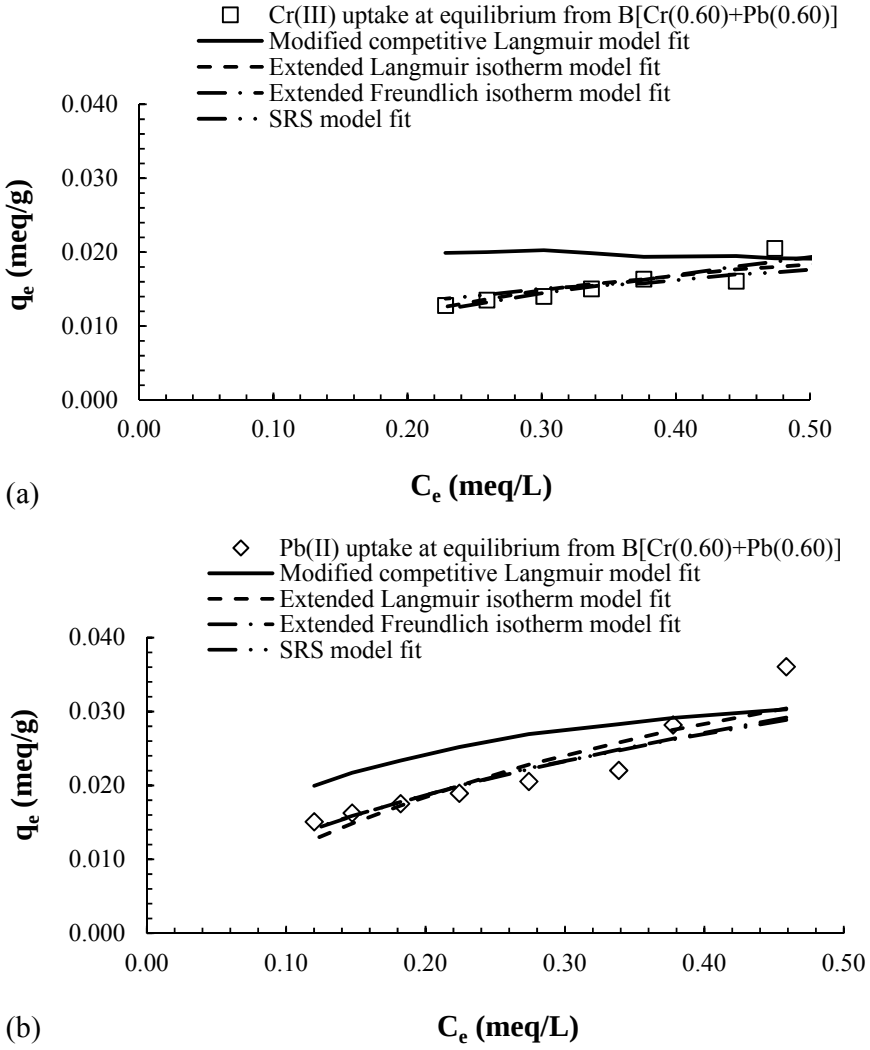

Fig. 5.95: Competitive metal uptake models fitted for uptake of (a) Cr(III) and (b) Pb(II) from B[Cr(0.60)+Pb(0.60)] combination under controlled pH conditions.

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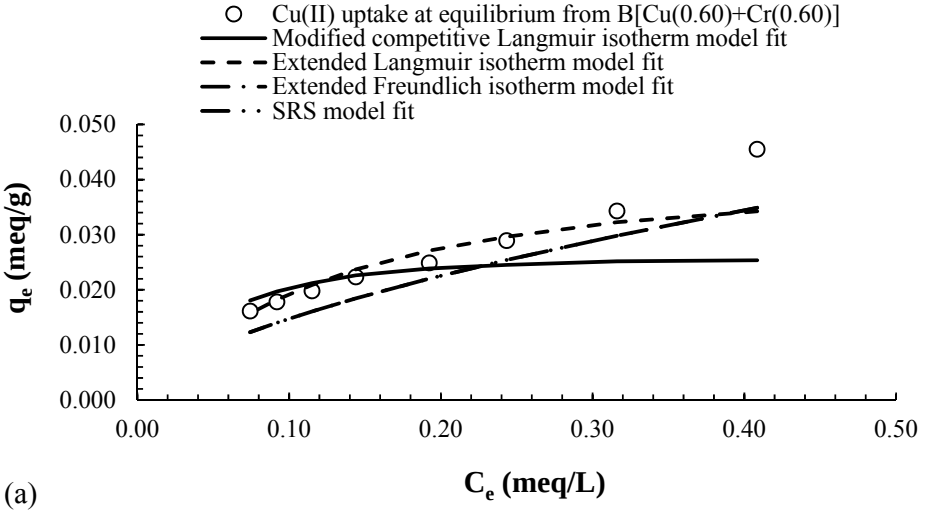
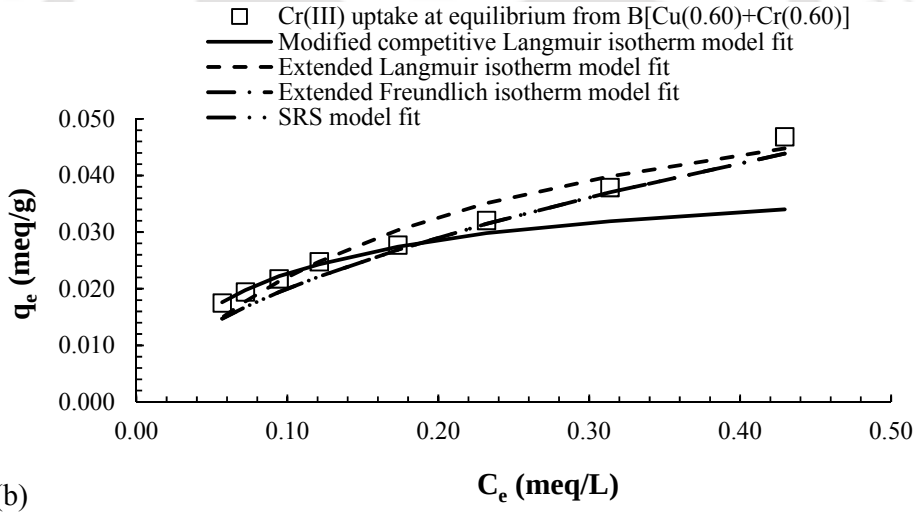


(a)



(b)

Fig. 5.96: Competitive metal uptake models fitted for uptake of (a) Cu(II) and (b) Cr(III) from B[Cu(0.60)+Cr(0.60)] combination under controlled pH conditions.

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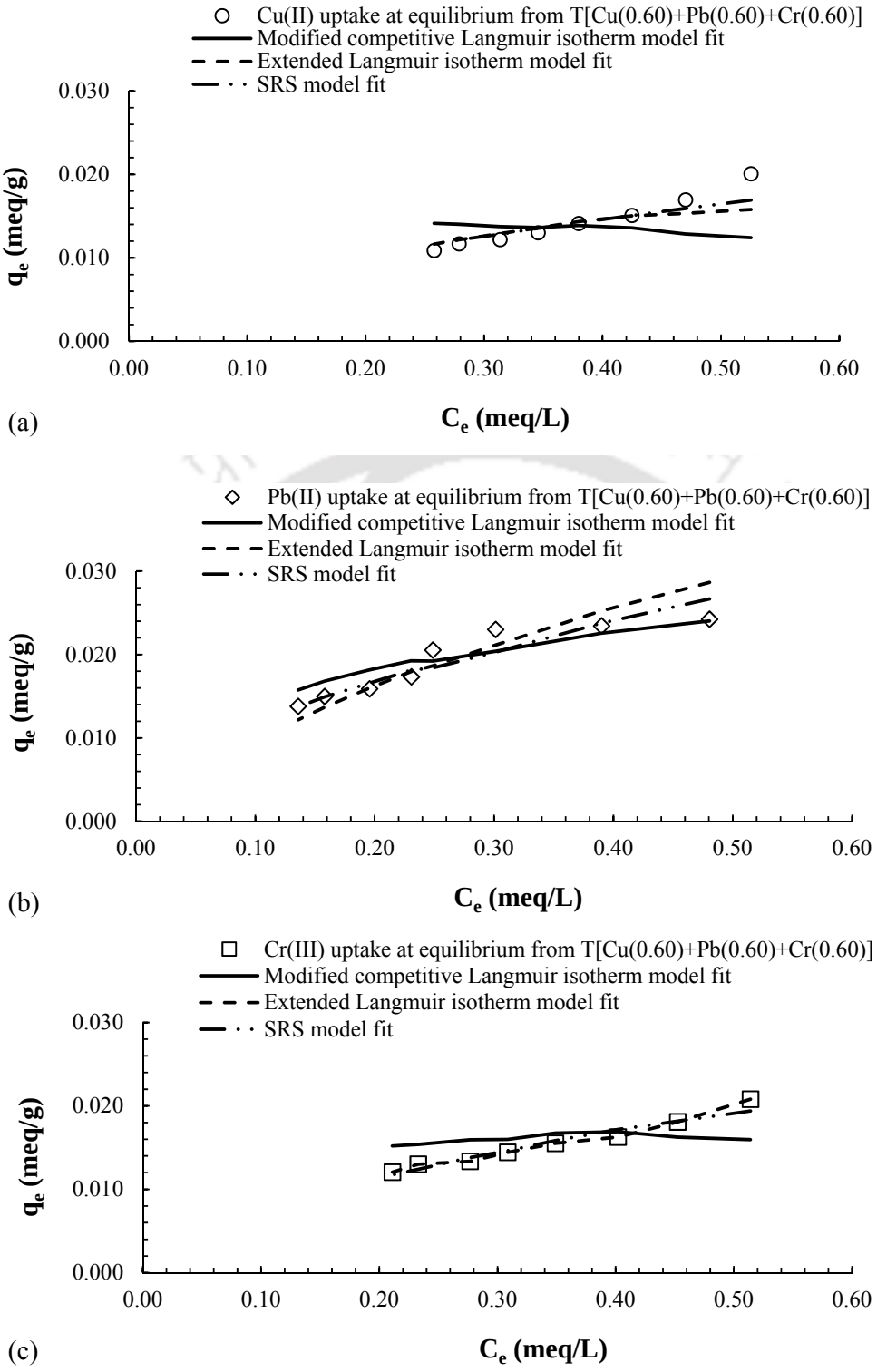

Fig. 5.97: Competitive metal uptake models fitted for uptake of (a) Cu(II) (b) Pb(II) and (c) Cr(III) from T[Cu(0.60)+Pb(0.60)+Cr(0.60)] combination under controlled pH conditions.

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metal ions, these models were not able to predict the total metal uptakes from the combinations under consideration.

5.6.8 Equilibrium studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions when exposed repeatedly with the same metal ion (or same combination) or a different metal ion (or different combination)

Investigations carried out and presented in section 5.4 with repeated exposures of GAA to 6-10 loading cycles to target metal ion concentration of approximately 0.60 meq/L indicated additional metal removal capacity under uncontrolled pH conditions and additional metal uptake capacity under controlled pH conditions in each cycles. The target metal removal and target metal uptake continued even up to 10^{th} loading cycle but with decreasing values. When the GAA exposed to 6-10 loading cycles with the target metal was again exposed to non-target metal ion once, further removal of non-target metal ion under uncontrolled pH conditions and further uptake of non-target metal ion under controlled pH conditions were observed along with displacement of target metal ion into the solution. These interesting results led to undertake further kinetic studies with repeated loadings of GAA with a mono-metal ion system (or a combination of binary-metal ion system) and then followed by loading only once with another mono-metal ion system (or a different combination of binary-metal ion system having the same metals but with different initial metal ion concentrations in the combination).

The experimental kinetics results as presented in section 5.5 obtained for three loading cycles with a mono-metal ion system followed with fourth loading cycle with another mono-metal ion system comprising of Cu(II), Pb(II) and Cr(III) ions indicated the following:

- During the first three loading cycles with mono-metal ion system, additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions was observed in each loading cycle.
- Additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions decreased with increase in number of loading cycles during the first three loading cycles.
- When GAA loaded with a mono-metal ion system during first three loading cycles was exposed to another mono-metal ion system in the fourth loading cycle,

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considerable metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions of other metal ion was observed.

- The migration of adsorbed metal ions during the first three loading cycles from GAA surface to bulk solution was observed during the fourth loading cycle.
- The cumulative metal removal under uncontrolled pH conditions and cumulative metal uptake under controlled pH conditions increased with number of loading cycles.
- These results indicated no definite preference of metal uptake by GAA for the metal ion system when loaded in different orders.

The kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions by GAA with consecutive three loading cycles of a combination of binary-metal ion system followed by fourth loading cycle of another combination of binary-metal ion system comprising of Cu(II), Pb(II) and Cr(III) metals were also investigated and presented in section 5.5. The combination of binary-metal ion system contained the same metal ions but its concentrations were interchanged in the fourth loading cycles compared to the first three loading cycles. These results indicated the following:

- During the first three loading cycles with a combination of binary-metal ion system, metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for the metal ions with higher concentration in the combination decreased with increase in number of loading cycles.
- When GAA loaded with first three loading cycles of a combination of binary-metal ion system was exposed to another combination in the fourth loading cycle, the metal ion having lower concentration in combination had insignificant removal under uncontrolled pH conditions and insignificant uptake under controlled pH conditions while the metal ion having higher concentration in combination had shown higher removal under uncontrolled pH conditions and higher uptake under controlled pH conditions compared to its removal and uptake from previous three loading cycles.
- The variation in total metal removals under uncontrolled pH conditions and total metal uptakes under controlled pH conditions generally decreased with increase in number of loading cycles.

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- The cumulative metal removal under uncontrolled pH conditions and cumulative metal uptake under controlled pH conditions increased with number of loading cycles of binary-metal ion system indicating additional metal removal and additional metal uptake potential of GAA.

These interesting kinetic experimental results strongly made a case to carry out similar equilibrium studies as well. Unfortunately, these equilibrium studies could not be undertaken in this work mainly due to paucity of time and logistic issues related with availability of analytical instruments. However, need to carry out these equilibrium studies shall be highlighted in a separate chapter on scope for further studies towards the end of the thesis.

5.6.9 Summary

The equilibrium studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions were investigated from selected combinations of mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions. Average equilibrium pH of solutions was more than 5.50 at lower C_e values causing metal removals at equilibrium under uncontrolled pH conditions due to combined effects of precipitation as well as adsorption. Two mathematical relationships i.e. power and polynomial curves well predicted individual and total metal ion removals at equilibrium from mono-, binary- and ternary-metal ion systems under uncontrolled pH conditions. However, the metal uptakes at equilibrium from the solutions under controlled pH conditions were mainly due to adsorption. The higher R^2 values obtained for Freundlich isotherm model indicated its better suitability to represent the experimental equilibrium metal uptake data from mono-, binary- and ternary-metal ion systems. The variations in metal removals at equilibrium from mono-metal ion systems generally appeared to overlap at 95% confidence intervals with variations in total metal removals at equilibrium from combinations of binary-metal ion systems and varied in a small band with the ternary-metal ion system having total initial metal ion concentration of 0.60 meq/L. Similarly total metal uptakes at equilibrium from mono-, binary- and ternary-metal ion systems having total initial metal ion concentration of 0.60 meq/L varied within small band. These results suggested that the metal removals at equilibrium and metal uptakes at equilibrium depended on the total initial metal ion concentration present in the solution rather than on atomic weights, valence, etc of

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individual metal ions. Two of the competitive metal uptake models – namely Extended Freundlich Isotherm model and SRS model were able to fit closely the experimental data from binary- and ternary-metal ion combinations having initial metal ion concentration of participating metal ions approximately to 0.60 meq/L. However, these models were not able to predict the total metal uptakes from the combinations considered. The equilibrium studies needed to be conducted for metal removal at equilibrium under uncontrolled pH conditions and metal uptake at equilibrium under controlled pH conditions from mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) metal ions when exposed repeatedly with the same metal ion (or same combination of metal ions) or a different metal ion (or a different combination of same metal ions but with a different initial metal ion concentrations).

5.7 Continuous mode column studies for metal removal under uncontrolled and controlled pH conditions from mono- and binary-metal ion systems

A review of literature indicated that most of the continuous mode column studies have been directed to investigate the effect of bed depths and flow rates on metal removal by adsorbent beds under uncontrolled pH conditions. These studies were mostly carried out at adjusted influent pH but did not monitor pH of the effluents coming out of the adsorbent bed. In the present work while conducting kinetics and equilibrium studies under uncontrolled pH conditions, the solution pH was observed to rise from the initially adjusted pH values to a value higher than the precipitation pH values for the concerned metal ions. However, no such situations were encountered while conducting kinetics and equilibrium studies under controlled pH conditions as the solution was buffered to maintain pH at the desired level throughout the experiments. In addition, the kinetic studies carried out in this work indicated additional metal removal/uptake potential of the adsorbent when re-exposed with other mono-metal ion system or other combination of binary-metal ion systems as well as release of previously removed/adsorbed metal ion to the solution in measurable amounts. Therefore, the continuous mode column studies in this work had been planned to assess the following: (i) monitoring variation in pH of effluents coming out of the column beds, (ii) additional metal removal potential of exhausted/loaded bed if reloaded with another metal ion, and (iii) migration of previously removed metal ion from the bed into the effluent when reloaded with another metal ion, if any. Keeping these broad objectives in mind, the continuous mode column studies for metal removal under uncontrolled and controlled pH conditions have been

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carried out from mono- and binary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) metal ions.

5.7.1 Breakthrough curves for virgin GAA bed loaded with M[Cu(0.60)] system and washed bed reloaded with M[Pb(0.60)] system under uncontrolled and controlled pH conditions

The continuous mode column studies for metal removal under uncontrolled and controlled pH conditions by GAA bed of different depths (3.0, 4.5 and 6.0 cm) at a fixed flow rate of 2.0 mL/min were carried out. The studies were carried out by exposing (or loading) the virgin (or fresh) GAA bed with M[Cu(0.60)] system having initial Cu(II) metal ion concentration of approximately 0.60 meq/L till the bed was exhausted or yielded effluent Cu(II) metal concentration of 80% or more of the initial metal concentration. The exhausted or loaded bed was then washed with 100 bed volumes of de-mineralized water to remove residual or un-adsorbed Cu(II) metal ions from pore volume of the bed. The washed bed was then again exposed (or reloaded) with M[Pb(0.60)] system having initial Pb(II) metal ion concentration of approximately 0.60 meq/L till the bed was exhausted or yielded effluent Pb(II) metal concentration of 70% or more of the initial metal concentration. The typical breakthrough curves in terms of metal ions remaining in effluent (C_t) versus time for virgin bed loaded with M[Cu(0.60)] system followed by reloading of washed bed with M[Pb(0.60)] system for a bed depth of 3.0 cm at a flow rate of 2.0 mL/min along with variation in effluent pH obtained under uncontrolled and controlled pH conditions are presented in Fig. 5.98 and 5.99 respectively.

Under uncontrolled pH conditions (Fig. 5.98), pH of the effluent from the virgin bed of GAA when loaded with M[Cu(0.60)] system increased to 6.30 in the first 10 min. of operation from the initially adjusted pH value of 5.00. After initial 10 min., the effluent pH decreased to around 5.47 within 120 min. of operation. As the operation proceeded beyond 120 min., pH of the effluent further decreased slowly and became constant to a value close to 4.88 in the later phase of the operation. When the washed GAA bed was reloaded with M[Pb(0.60)] system, pH of the effluent increased to a peak value of 5.76 in the first 10 min. After initial 10 min., pH of the effluent decreased to 5.22 at around 150 min. of operation. The pH of the effluent at the end of the operation was observed as 5.46. The variations in effluent pH during column studies was observed to be different than that observed during

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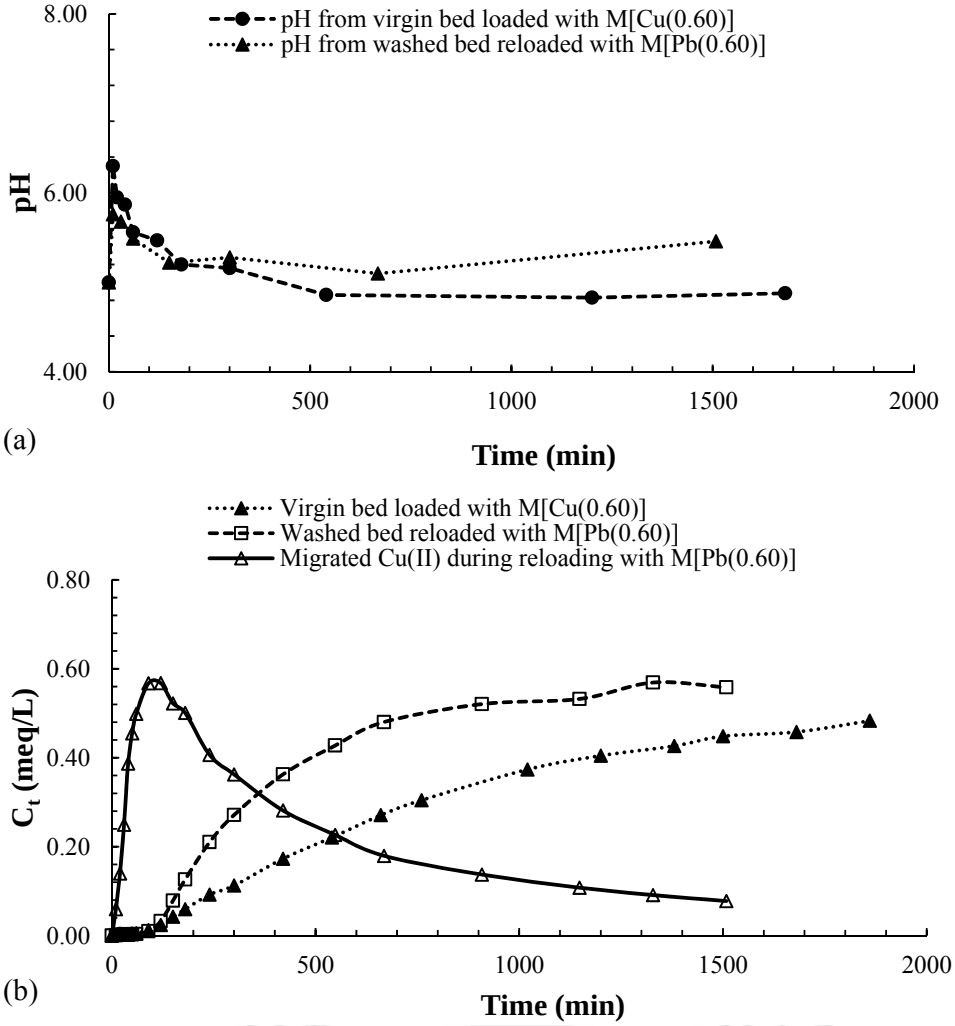

Fig. 5.98: Virgin GAA bed loaded with M[Cu(0.60)] system and washed bed reloaded with M[Pb(0.60)] system under uncontrolled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cu(0.60)] = 0.58±0.02 meq/L, M[Pb(0.60)] = 0.59±0.01 meq/L, Initial adjusted pH = 5.00±0.04, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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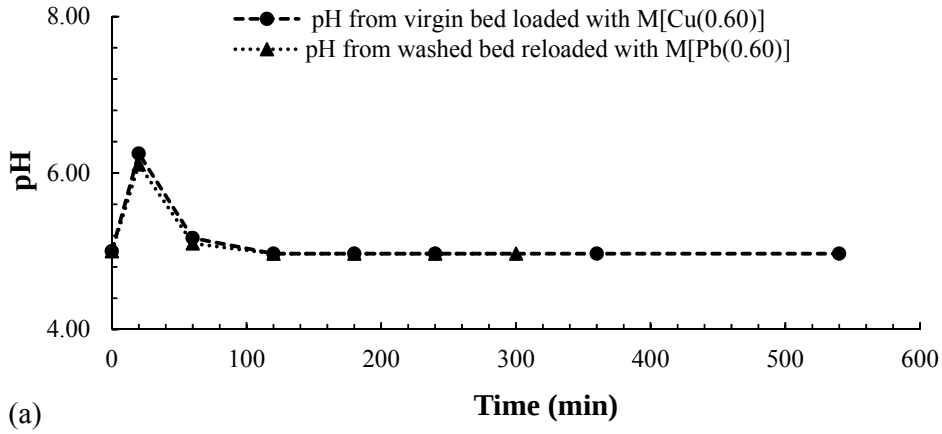
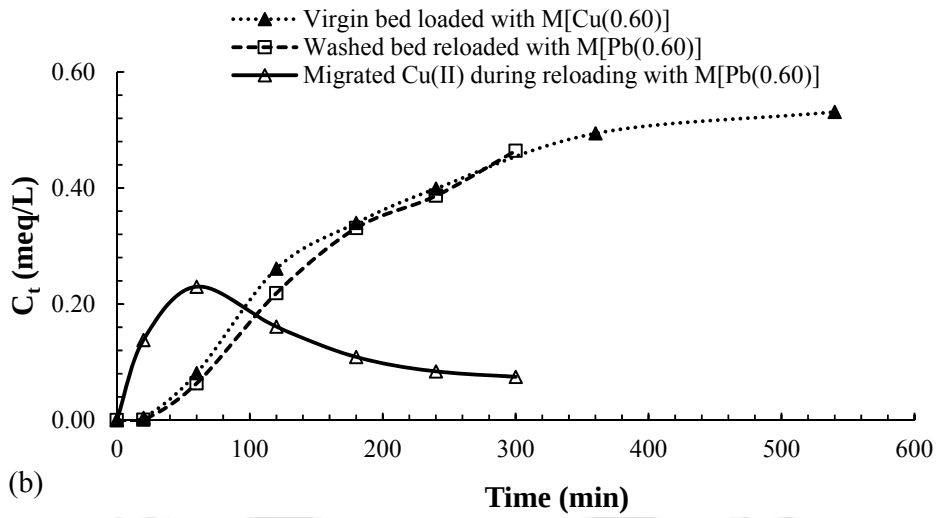


(a)



(b)

Fig. 5.99: Virgin GAA bed loaded with M[Cu(0.60)] system and washed bed reloaded with M[Pb(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cu(0.60)] = 0.60±0.01 meq/L, M[Pb(0.60)] = 0.58±0.00 meq/L, Buffered pH = 5.00±0.05, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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kinetic and equilibrium studies. The pH of the solution increased to higher values from initially adjusted value of around 5.00 during kinetic and equilibrium studies investigated under uncontrolled pH conditions. However, the effluent pH from the column beds observed to initially increase rapidly from the initially adjusted pH level and then decrease close to the initially adjusted pH level. This aspect of variation in effluent pH from column beds appeared to be unusual. One of the possible reasons for such variations in effluent pH might be inadequacy of chemical reagents (in comparison to total amounts of GAA available in the bed) in the solution during initial phase of column operation thereby increasing the effluent pH. As the supply of chemical reagent with adjusted pH close to 5.00 in the solution continued, this inadequacy in supply of chemical reagents might have been compensated and the effluent pH decreased close to adjusted pH range. However, this aspect is needed to be investigated in detail. When the virgin GAA bed was loaded with M[Cu(0.60)] system, effluent pH was observed to be above 5.50 for approximately first 60 min. and then it came down below 5.50 for the rest of the operation. Similarly, when the washed bed was reloaded with M[Pb(0.60)] system, pH of the effluent remained above 5.50 up to approximately first 60 min. Hence, during the first 60 min. of operation of virgin and washed beds, metal ions removal by GAA bed might be due to precipitation as well and thereafter removals might be due to adsorption.

Under uncontrolled pH conditions (Fig. 5.98), no Cu(II) breakthrough was observed from the virgin bed for the initial 60-70 min. of operation. However, Cu(II) breakthrough curve appeared to rise gradually after 90 min. of operation. The Cu(II) concentration in the effluent reached to a value of 0.405 meq/L at 1200 min. of operation and thereafter, increase in effluent Cu(II) concentration was slow [Fig. 5.98(b)]. When the virgin bed loaded with M[Cu(0.60)] system was washed and then reloaded with M[Pb(0.60)] system, it yielded a relatively steeper breakthrough curve for Pb(II) metal. The effluent concentration became constant at around 1100 min. of operation indicating saturation of the washed bed [Fig. 5.98(b)]. When the washed bed was being reloaded with M[Pb(0.60)] system, migration of Cu(II) metal ion from the washed bed into the effluent took place. The migration of Cu(II) metal from washed bed was observed to increase rapidly with a sharp peak around 90-120 min. of operation [Fig. 5.98(b)]. It could also be observed that when the migration of Cu(II) metal ion was taking place during the first 90-120 min. of operation, Pb(II) metal ion was not detected in the effluent. It indicated that Pb(II) metal ions might have been occupying most of

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the spaces vacated by Cu(II) metal ions from the washed bed during the first 90-120 min. of operation. After the first 90-120 min. of operation, migrated Cu(II) metal ion concentration started to decrease and at the same time Pb(II) metal ion concentration in the effluent started to increase. Significant migration of Cu(II) metal from the washed bed was observed up to 1100 min. of operation. As migration of Cu(II) metal reduced after 1100 min. of operation, the effluent Pb(II) metal concentration became constant coinciding with the saturation of the washed bed for Pb(II) metal removal. Similar breakthrough curves for virgin bed loaded with M[Cu(0.60)] system followed by reloading with M[Pb(0.60)] system along with variation in effluent pH for bed depths of 4.5 and 6.0 cm at a flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.1 and B.2). The sharp peaks of migrated Cu(II) metal ions could be observed under uncontrolled pH conditions (Fig. B.1 and B.2) while Pb(II) breakthrough was yet to take place up to the peaks of migrated Cu(II) metal ions.

Under controlled pH conditions (Fig. 5.99), pH of the effluent from the virgin bed of GAA when loaded with M[Cu(0.60)] system increased to 6.25 in the first 20 min. of operation from the initially buffered pH value of 5.00. After initial 20 min., the effluent pH decreased to around 5.17 within 60 min. of operation. As the operation proceeded beyond 60 min., pH of the effluent further decreased slowly and became constant to value of 4.97 in the later phase of the operation. When the washed GAA bed was reloaded with M[Pb(0.60)] system, pH of the effluent increased to 6.11 in the first 20 min. After initial 20 min., pH of the effluent decreased to 5.10 at around 60 min. of the operation. The pH of the effluent at the end of the operation was observed as 4.97. The variations in effluent pH during column studies were observed to be different than that observed during kinetic and equilibrium studies carried out under controlled pH conditions. The pH of the solution remained unchanged to buffered pH values during kinetic and equilibrium studies whereas the effluent pH was observed to initially increase rapidly from the buffered pH level and then decrease to the buffered pH level in the column studies. One of the possible reasons for such variations in effluent pH might be inadequacy of buffering reagents (in comparison to total amounts of GAA available in the bed) in the solution during initial phase of column operation thereby increasing the effluent pH. As the supply of buffered solution continued, this inadequacy in supply of buffering reagents might have been compensated and the effluent pH decreased close to buffered pH level. However, this aspect is needed to be investigated in detail. When the virgin GAA bed was loaded with M[Cu(0.60)] system, pH of the effluent went above 6.00

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and then came down to 5.50 or lower during the first 60 min. of operation. Similarly, when the washed bed was reloaded with M[Pb(0.60)] system, pH of the effluent went above 6.00 and then came down to 5.50 or lower during the first 60 min. of operation. Hence, metal reduction cannot be ruled out due to precipitation during the first 60 min. of operation.

Under controlled pH conditions [Fig. 5.99(b)], no Cu(II) breakthrough was observed from the virgin bed up to first 20 min. of operation. However, Cu(II) breakthrough curve appeared to rise rapidly after initial 20 min. of operation. The Cu(II) concentration in the effluent reached to a value of 0.494 meq/L at 360 min. of operation. After 360 min. of operation, the breakthrough curve rised slowly indicating that the bed had got exhausted [Fig. 5.99(b)]. When the virgin bed loaded with M[Cu(0.60)] system was washed and then reloaded with M[Pb(0.60)] system, it yielded approximately similar Pb(II) metal breakthrough curve as observed for Cu(II) metal with the virgin bed. When the washed bed was being reloaded with M[Pb(0.60)] system, migration of Cu(II) metal ion from the washed bed took place. Initially the migration of Cu(II) metal from the washed bed increased rapidly and then decreased with a flat peak at around 60 min. of operation [Fig. 5.99(b)]. The migration of Cu(II) metal from the washed bed under controlled pH conditions was lower compared to migration of Cu(II) metal from washed bed observed during uncontrolled pH conditions. Similar breakthrough curves for the virgin bed loaded with M[Cu(0.60)] system followed by reloading with M[Pb(0.60)] system along with variations in effluent pH for bed depths of 4.5 and 6.0 cm at flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.3 and B.4). The flat peaks of migrated Cu(II) metal ions from washed beds could be observed under controlled pH conditions (Fig. B.3 and B.4) while Pb(II) breakthrough took place after passage of the peak of migrated Cu(II) metal ions in the case of column bed depths of 4.5 and 6.0 cm.

A mass balance was carried out to estimate the total metal removal by column beds under uncontrolled and controlled pH conditions when virgin bed was loaded with M[Cu(0.60)] system followed by washing and then again reloading with M[Pb(0.60)] system. The amounts of metal removed by the virgin and washed beds were estimated by calculating the area above the breakthrough curves using the trapezoidal rule (Cardoso et al., 2011). The amounts of metal ions which came out of the loaded beds during washings were also estimated. The amount of metal migrated from the washed bed during reloading into the

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effluent was estimated by calculating the area below the curve using the trapezoidal rule. Mass balance for metal removal under uncontrolled and controlled pH conditions by the column beds when loaded and reloaded with mono-metal ion systems was carried out for a time period when effluent metal concentration was equal to or greater than 60% of the influent metal ion concentration for virgin bed loading and washed bed reloading. Under uncontrolled pH conditions, mass balance for metal removal by the column with bed depth of 4.5 cm and operated at a flow rate of 2.0 mL/min were carried out for a time period when the effluent metal concentration was equal to or greater than 50% of the influent metal concentration, as in this case the breakthrough curve hardly yielded 50% of initial metal concentration in the effluent during the course of operation. Mass balance for metal removal under uncontrolled and controlled pH conditions by virgin GAA bed loaded with M[Cu(0.60)] system, washed and then reloaded with M[Pb(0.60)] system is presented in Table 5.50.

Under uncontrolled pH conditions, when the column bed of depth 3.0 cm was loaded with M[Cu(0.60)] system at a flow rate of 2.0 mL/min, exhaustion time (t_E) was estimated as 967 min. for virgin GAA bed and 420 min. for washed bed. The Cu(II) metal removal by virgin GAA bed up to 967 min. was estimated as 0.7601 meq. The loaded bed was washed with 100 bed volumes of de-mineralized water to remove residual metal ions from pore volumes of the bed. Total amount of residual metal ion in the washing was estimated as 0.0539 meq. The washed bed was reloaded with M[Pb(0.60)] system and the removal of Pb(II) metal on the washed bed after 420 min. of operation time was estimated as 0.3620 meq while 0.3380 meq of Cu(II) migrated from the washed bed. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 0.7302 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.0777 meq/g. Under controlled pH conditions, when the column bed of depth 3.0 cm was loaded with M[Cu(0.60)] system at a flow rate of 2.0 mL/min, exhaustion time (t_E) was estimated as 197 min. for virgin GAA bed and 198 min. for washed bed. The Cu(II) metal removal by virgin GAA bed up to 197 min. was estimated as 0.1620 meq. When washed bed reloaded with M[Pb(0.60)] system, the removal of Pb(II) metal up to 198 min. of operation was estimated as 0.1642 meq while 0.0606 meq of Cu(II) metal migrated from the bed. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 0.2156 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.0229

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Table 5.50: Summary of mass balance of metal removed by column beds when virgin GAA bed loaded with M[Cu(0.60)] system followed by reloading with M[Pb(0.60)] system under uncontrolled and controlled pH conditions.

pH conditions	Flow rate (mL/min)	Bed depth (cm)	Virgin bed loaded with M[Cu(0.60)] system			Bed washings	Washed bed reloaded with M[Pb(0.60)] system				Total metal removed by bed (meq)	Total metal removed per unit weight of bed (meq/g)
			Cu(II) initial conc. (meq/L)	t_E (min)	Cu(II) removed by bed (meq)	Amount of washed out Cu(II) (meq)	Pb(II) initial conc. (meq/L)	t_E (min)	Pb(II) removed by bed (meq)	Cu(II) migrated from bed (meq)		
Uncontrolled	2.0	3.0	0.58±0.02	967	0.7601	0.0539	0.59±0.01	420	0.3620	0.3380	0.7302	0.0777
		4.5	0.60±0.03	955*	0.8955	0.0521	0.59±0.01	478*	0.4534	0.3112	0.9856	0.0747
		6.0	0.62±0.00	1680	1.4560	0.0571	0.59±0.00	720	0.6590	0.5180	1.5399	0.0917
Controlled	2.0	3.0	0.60±0.01	197	0.1620	0.0500	0.58±0.00	198	0.1642	0.0606	0.2156	0.0229
		4.5	0.60±0.02	286	0.2400	0.0530	0.58±0.01	297	0.2616	0.1451	0.3035	0.0230
		6.0	0.60±0.02	342	0.2880	0.0570	0.58±0.01	467	0.4157	0.1152	0.5315	0.0316

t_E = exhaustion time (effluent metal concentration equal to 60% of influent concentration from virgin and washed beds respectively, if not specified); * = effluent conc. equal to 50% of influent metal concentration; Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA respectively.

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meq/g.

In order to investigate the effect of GAA bed depths on metal removal when the virgin GAA bed was loaded with M[Cu(0.60)] system and washed bed was again reloaded with M[Pb(0.60)] system, the breakthrough curves for a linear flow rate of 2.0 mL/min with three different bed depths of 3.0, 4.5 and 6.0 cm of GAA operated under uncontrolled and controlled pH conditions are re-plotted and presented in Fig. 5.100 and 5.101 respectively. It could be observed from these figures that breakthrough curves appear to shift towards right with increase in bed depths. The service times (t_B) for virgin and washed beds were estimated from the breakthrough curves when the effluent metal ions concentration was 5% of influent metal ion concentration (i.e. 0.03 meq/L). The corresponding breakthrough throughput volumes (V_B) were also estimated. All the estimated service times and breakthrough throughput volumes under uncontrolled and controlled pH conditions have been tabulated in Table 5.51. The breakthrough throughput volumes increased with increase in bed depths at a fixed flow rate as could be seen from Table 5.51. An increase in the service time was observed when the bed depth increased from 3.0 to 6.0 cm. The increase in the metal removal from the bulk metal ion solution with increase in bed depths was possibly due to increase in the amount of adsorbent mass in the larger beds which provided greater opportunities for metal removal.

Table 5.51: Summary of breakthrough results at a fixed flow rate but varying depths of virgin GAA bed loaded with M[Cu(0.60)] system and washed bed reloaded with M[Pb(0.60)] system under uncontrolled and controlled pH conditions.

pH conditions	Bed depth (cm)	Virgin bed loaded with M[Cu(0.60)] system			Washed bed reloaded with M[Pb(0.60)] system			
		t_B (min)	V_B (mL)	Cu(II) removed (meq)	t_B (min)	V_B (mL)	Pb(II) removed (meq)	Cu(II) migrated (meq)
Uncontrolled	3.0	130	260	0.149	120	240	0.141	0.097
	4.5	260	520	0.305	175	350	0.203	0.101
	6.0	390	780	0.437	255	510	0.300	0.129
Controlled	3.0	33	66	0.039	38	76	0.044	0.009
	4.5	68	136	0.079	81	162	0.092	0.029
	6.0	74	148	0.086	145	290	0.166	0.040

V_B = Breakthrough throughput volumes at effluent metal concentration equal to 0.03 meq/L; t_B = service time at breakthrough; Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA.

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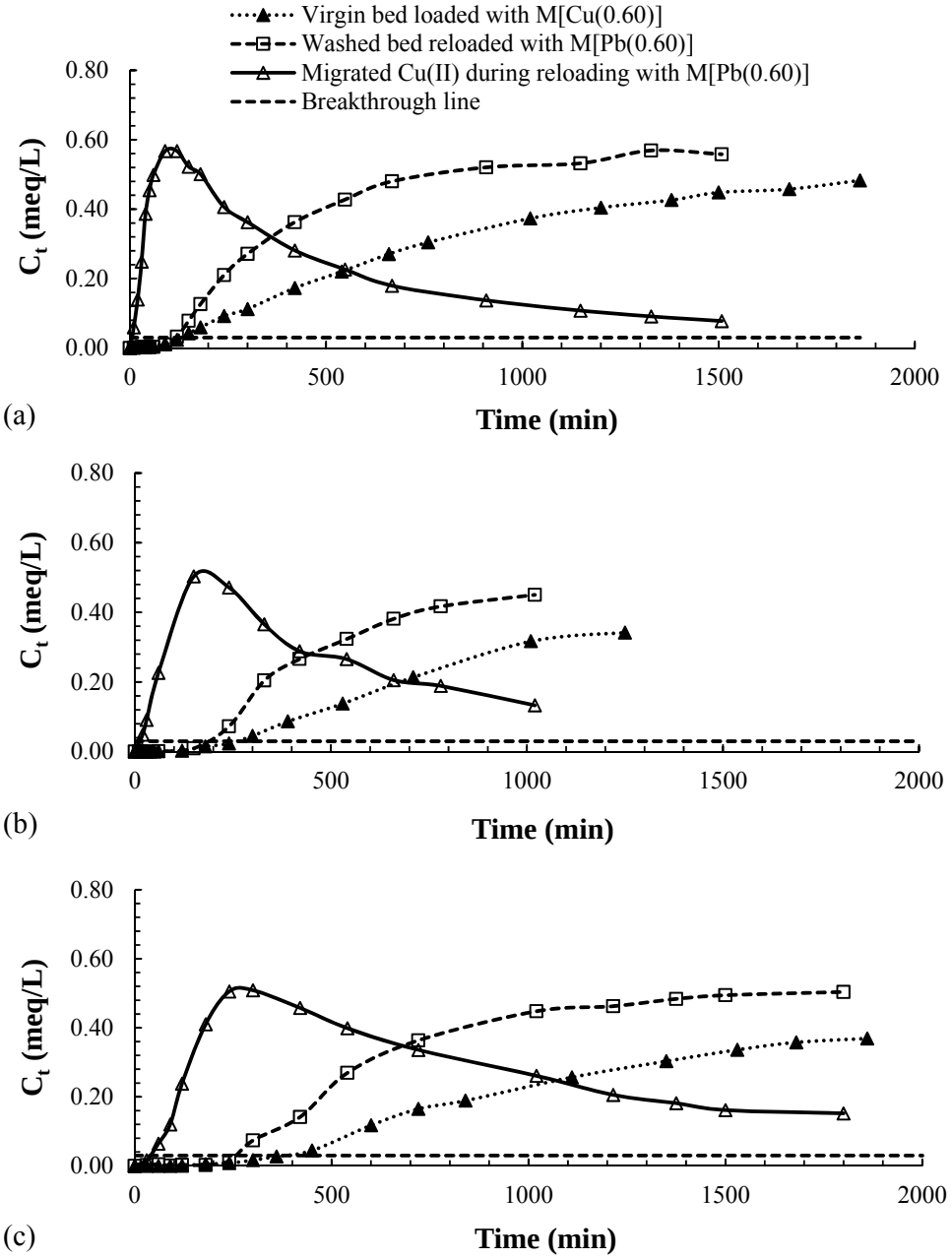

Fig. 5.100: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with M[Cu(0.60)] system and washed bed reloaded with M[Pb(0.60)] system at a flow rate of 2.0 mL/min under uncontrolled pH conditions {Initial metal conc. in M[Cu(0.60)] = 0.60±0.01 meq/L, M[Pb(0.60)] = 0.59±0.01 meq/L, Initial adjusted pH = 5.00±0.04, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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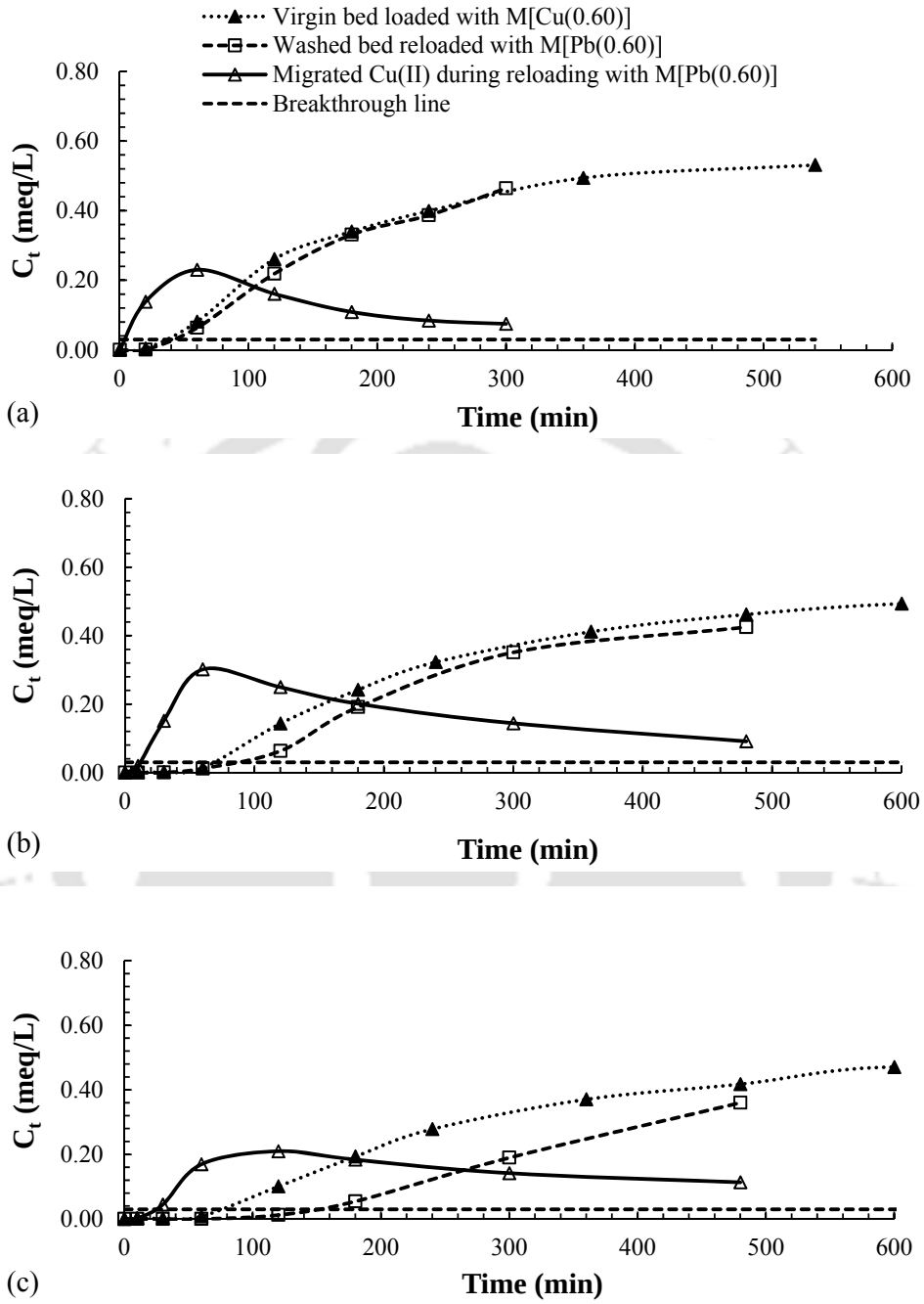

Fig. 5.101: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with M[Cu(0.60)] system and washed bed reloaded with M[Pb(0.60)] system at a flow rate of 2.0 mL/min under controlled pH conditions {Initial metal conc. in M[Cu(0.60)] = 0.60±0.01 meq/L, M[Pb(0.60)] = 0.58±0.01 meq/L, Buffered pH = 5.00±0.05, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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5.7.2 Breakthrough curves for virgin GAA bed loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cu(0.60)] system under uncontrolled and controlled pH conditions

The studies were carried out by exposing (or loading) the virgin (or fresh) GAA bed with M[Pb(0.60)] system having initial Pb(II) metal ion concentration of approximately 0.60 meq/L till the bed was exhausted or yielded effluent Pb(II) metal concentration more than 60% of initial metal concentration. The loaded bed was then washed with 100 bed volumes of de-mineralized water to remove residual or un-adsorbed Pb(II) metal ions from pore volume of the loaded bed. The washed bed was then again exposed (or reloaded) with M[Cu(0.60)] system having initial Cu(II) metal ion concentration of approximately 0.60 meq/L till the bed was exhausted or yielded effluent Cu(II) metal concentration of 60% or more of the initial metal concentration. The washed beds were operated for shorter duration (but at least up to exhaustion times obtained with virgin beds) to save on operation time as time to exhaust the washed bed shall have taken a longer operation period. The typical breakthrough curves in terms of metal ions remaining in effluent (C_t) versus time for virgin bed loaded with M[Pb(0.60)] system followed by reloading of washed bed with M[Cu(0.60)] system for a bed depth of 3.0 cm at a flow rate of 2.0 mL/min along with variation in effluent pH obtained under uncontrolled and controlled pH conditions are presented in Fig. 5.102 and 5.103 respectively.

Under uncontrolled pH conditions (Fig. 5.102), pH of the effluent from the virgin bed of GAA when loaded with M[Pb(0.60)] system increased to 6.30 during the first 10 min. of operation from the initially adjusted pH value of 5.00. After initial 10 min., the effluent pH decreased to around 5.69 within 60 min. of operation. As the operation proceeded beyond 60 min., pH of the effluent further decreased slowly and reached to value of 4.73 at the end of operation. When the washed GAA bed was reloaded with M[Cu(0.60)] system, pH of the effluent solution increased to a peak value of 5.89 in the first 10 min. of operation. After initial 10 min., pH of the effluent decreased to 5.66 at around 120 min. of operation. The pH of the effluent at the end of the operation was observed as 5.12. The variations in effluent pH during column studies was observed to be different than that observed during kinetic and equilibrium studies. The pH of the solution increased from initially adjusted value of around 5.00 during kinetic and equilibrium studies investigated under uncontrolled pH conditions but did not return back near the initially adjusted pH level. However, the effluent pH from the

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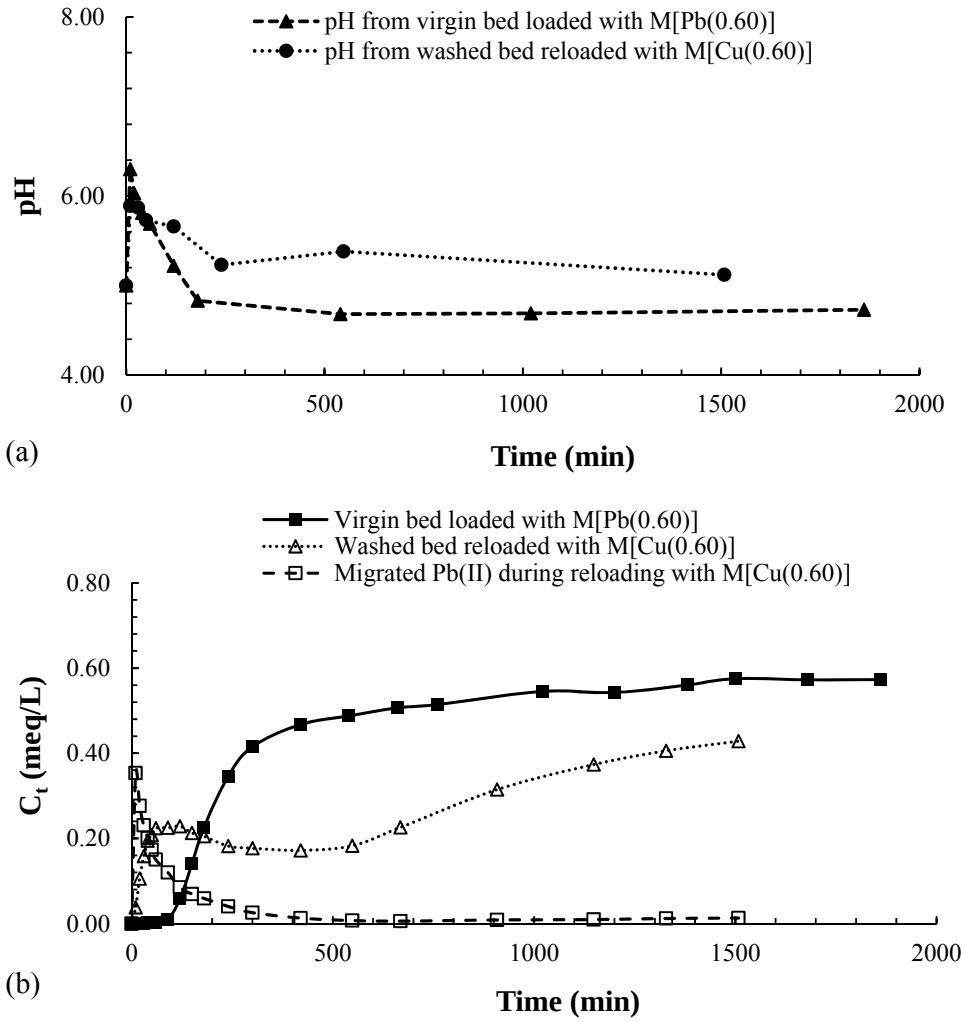

Fig. 5.102: Virgin GAA bed loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cu(0.60)] system under uncontrolled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Pb(0.60)] = 0.58±0.02 meq/L, M[Cu(0.60)] = 0.60±0.02 meq/L, Initial adjusted pH = 5.00±0.03, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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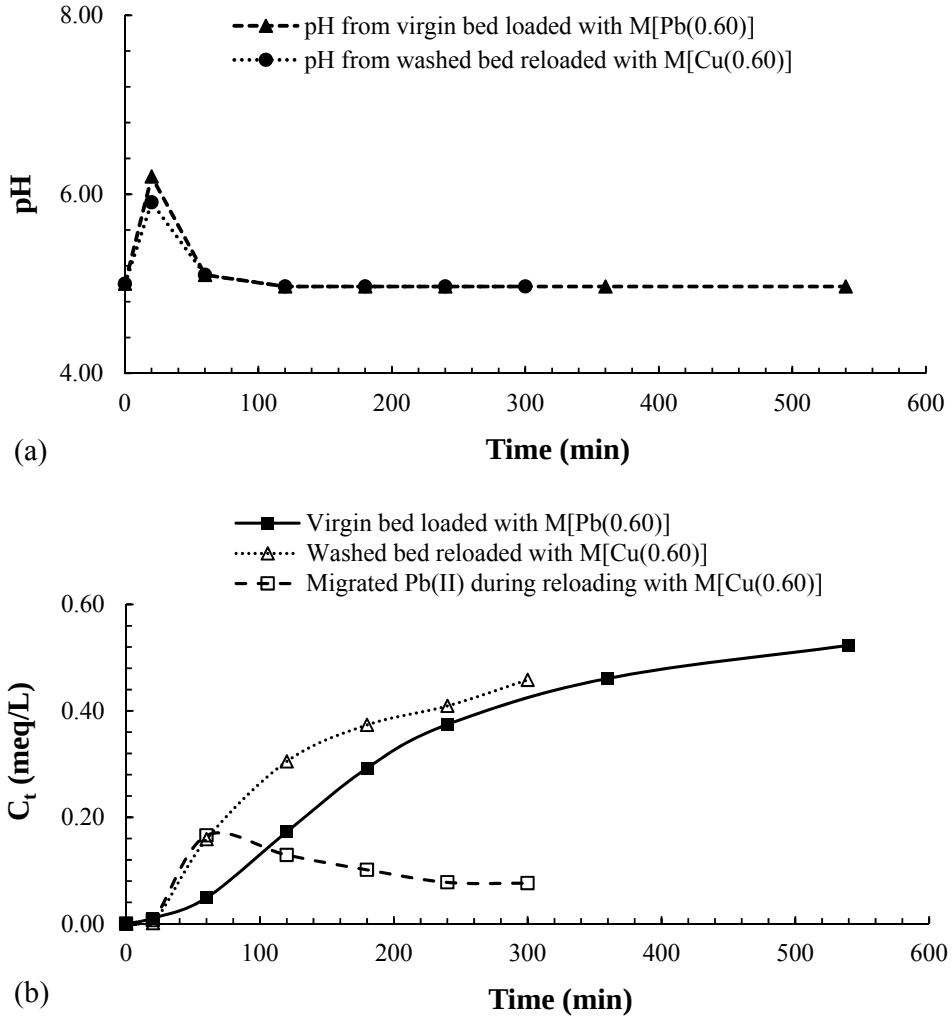

Fig. 5.103: Virgin GAA bed loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cu(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Pb(0.60)] = 0.58±0.02 meq/L, M[Cu(0.60)] = 0.60±0.02 meq/L, Buffered pH = 5.00±0.02, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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column beds observed to initially increase rapidly from the initially adjusted pH values and then decreased back close to the initially adjusted pH level. This aspect of variation in effluent pH from column beds appeared to be unusual which is needed to be investigated in detail. When virgin GAA bed loaded with M[Pb(0.60)] system, effluent pH was observed to be above 5.50 for approximately first 60 min. and then it came down below 5.50 for rest of the operation time. Similarly, when the washed bed reloaded with M[Cu(0.60)] system, pH of the effluent remained above 5.50 up to approximately first 120 min. Hence, during the first 60 min. and 120 min. of operation of virgin and washed beds respectively, metal ions removal by GAA bed might be due to precipitation as well.

Under uncontrolled pH conditions [Fig. 5.102(b)], no Pb(II) breakthrough was observed for the first 60-70 min. of operation. After 60-70 min., Pb(II) concentration in the effluent started to increase rapidly and reached to a value of 0.415 meq/L at 300 min. of operation and thereafter, the increase in effluent Pb(II) concentration was very slow indicating saturation of the bed [Fig. 5.102(b)]. When the virgin bed loaded with M[Pb(0.60)] system was washed and then reloaded with M[Cu(0.60)] system, it yielded a steeper breakthrough curve for Cu(II) metal during first 60 min. of operation reaching a concentration level of 0.224 meq/L. After initial 60 min. of operation, breakthrough curve started to decrease slowly and reached to a minimum concentration level of 0.172 meq/L around 420 min. of operation. After 420 min., it started to rise again and reached a value of 0.429 meq/L at 1508 min. of operation. When the washed bed was being reloaded with M[Cu(0.60)] system, migration of Pb(II) metal from washed bed into the effluent took place [Fig. 5.102(b)]. The concentration of migrated Pb(II) from washed bed was observed to be 0.353 meq/L for the initial 10 min. of operation. Further, it decreased to a value of 0.026 meq/L at around 300 min. of operation and thereafter migration of Pb(II) was almost negligible. The removal of Cu(II) by the washed bed and migration of Pb(II) from the washed bed were taking place simultaneously. However, when migration of Pb(II) from the washed bed was taking place rapidly, the removal of Cu(II) by the washed bed was apparently lower as the concentration of Cu(II) in the effluent was increasing rapidly during initial 40-50 min. of operation. Similar breakthrough curves for virgin bed loaded with M[Pb(0.60)] system followed by reloading with M[Cu(0.60)] system along with variation in effluent pH for bed depths of 4.5 and 6.0 cm at a flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.5 and B.6). It is worth noting that the trends of Cu(II) metal removal by

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the washed beds of depths of 4.5 and 6.0 cm were similar to the bed depth of 3.0 cm. However, the concentration of migrated Pb(II) metal appeared to increase to a flat peak level before decreasing with increase in operation time which was at variance compared to the 3.0 cm bed depth.

Under controlled pH conditions (Fig. 5.103), pH of the effluent from the virgin bed of GAA when loaded with M[Pb(0.60)] system increased to 6.20 in the first 20 min. of operation from the initially buffered pH value of 5.00. After initial 20 min., the effluent pH decreased to around 5.10 within 60 min. of operation. As the operation proceeded beyond 60 min., pH of the effluent further decreased slowly and stabilized at pH value of 4.97. When the washed GAA bed was reloaded with M[Cu(0.60)] system, pH of the effluent increased to 5.91 in the first 20 min of operation. After initial 20 min., pH of the effluent decreased to 5.10 at around 60 min. of operation which further stabilized at 4.97 towards the end of the operation. The variations in effluent pH during column studies were observed to be different than that observed during kinetic and equilibrium studies carried out under controlled pH conditions. The effluent pH was observed to initially increase rapidly from the buffered pH level and then decreased back to the buffered pH level in the column studies which requires investigation in detail. When virgin GAA bed was loaded with M[Pb(0.60)] system, pH of the effluent went above 6.00 and then came down to 5.50 or lower between 20-60 min. of operation. Similarly, when the washed bed was reloaded with M[Cu(0.60)] system, pH of the effluent went above 5.50 and then came down to 5.50 or lower between 20-60 min. of operation. Hence, metal removal might also be possible due to precipitation during the first 20-60 min. of operation.

Under controlled pH conditions [Fig. 5.103(b)], no Pb(II) metal ion was detected in the effluent from the virgin bed for the initial 20 min. of operation. However, Pb(II) breakthrough curve appeared to increase gradually after initial 20 min. of operation with Pb(II) concentration in the effluent reaching to a value of 0.374 meq/L at 240 min. of operation. After 240 min., the breakthrough curve increased slowly indicating that the bed was nearing to get exhausted [Fig. 5.103(b)]. When the virgin bed loaded with M[Pb(0.60)] system was washed and then reloaded with M[Cu(0.60)] system, no Cu(II) metal ion was detected in the effluent for the initial 20 min. of operation. However, Cu(II) breakthrough curve started to rise rapidly after first 20 min. of operation and reached to a concentration

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value of 0.374 meq/L at 180 min. of operation. After 180 min. of operation, the breakthrough curve increased slowly indicating that the bed was nearing to get exhausted [Fig. 5.103(b)]. When the washed bed was reloaded with M[Cu(0.60)] system, migration of Pb(II) metal ion from the washed bed into the effluent took place. Initially up to first 20 min. of operation, migration of Pb(II) metal from washed bed appeared to be negligible, but it increased with a flat peak having a value of 0.166 meq/L around 60 min. and then decreased to a value of 0.076 meq/L around 300 min. of operation [Fig. 5.103(b)]. Similar breakthrough curves for the virgin bed loaded with M[Pb(0.60)] system followed by reloading with M[Cu(0.60)] system along with variations in effluent pH for bed depths of 4.5 and 6.0 cm at flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.7 and B.8). The flat peaks of migrated Pb(II) metal ions from washed beds could be observed under controlled pH conditions (Fig. B.7 and B.8) while Cu(II) breakthrough took place approximately below the peaks of migrated Pb(II) metal ions in the case of column bed depths of 4.5 and 6.0 cm.

A mass balance was carried out to estimate the total metal removal by column beds under uncontrolled and controlled pH conditions when virgin bed was loaded with M[Pb(0.60)] system followed by washing and then again reloaded with M[Cu(0.60)] system. Mass balance for metal removal under uncontrolled and controlled pH conditions by the column beds when loaded with mono-metal ion systems was carried out for a time period when effluent metal concentration was equal to 60% of the influent metal ion concentration for virgin bed loading. Under uncontrolled pH conditions, Cu(II) breakthrough curve during reloading of washed beds did not yield 60% or more of influent concentration. Hence, the breakthrough curve for Cu(II) from washed bed was considered up to the exhaustion time for Pb(II) metal from the virgin GAA bed for the purpose of carrying out mass balance for Cu(II) metal removal. Mass balance for metal removed under uncontrolled and controlled pH conditions by virgin GAA bed loaded with M[Pb(0.60)] system, washed and then reloaded with M[Cu(0.60)] system is presented in Table 5.52.

Under uncontrolled pH conditions, when the virgin column bed of depth 3.0 cm was loaded with M[Pb(0.60)] system at a flow rate of 2.0 mL/min, exhaustion time (t_E) was estimated to be 251 min. However, Cu(II) metal breakthrough curve from washed beds during reloading did not yield 60% or more of influent metal concentration from all the three column bed depths (i.e. 3.0, 4.5 and 6.0 cm) with 2 mL/min of flow rate, the breakthrough

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Table 5.52: Summary of mass balance of metal removed by column beds when virgin GAA bed loaded with M[Pb(0.60)] system followed by reloading with M[Cu(0.60)] system under uncontrolled and controlled pH conditions.

pH conditions	Flow rate (mL/min)	Bed depth (cm)	Virgin bed loaded with M[Pb(0.60)] system			Bed washings	Washed bed reloaded with M[Cu(0.60)] system				Total metal removed by bed (meq)	Total metal removed per unit weight of bed (meq/g)
			Pb(II) initial conc. (meq/L)	t_E (min)	Pb(II) removed by bed (meq)	Amount of washed out Pb(II) (meq)	Cu(II) initial conc. (meq/L)	t_E (min)	Cu(II) removed by bed (meq)	Pb(II) migrated from bed (meq)		
Uncontrolled	2.0	3.0	0.60±0.01	251	0.2379	0.0155	0.59±0.01	251*	0.1964	0.0557	0.3631	0.0386
		4.5	0.60±0.01	443	0.4169	0.0129	0.59±0.01	443*	0.4067	0.0430	0.7678	0.0581
		6.0	0.59±0.01	626	0.5763	0.0215	0.59±0.00	626*	0.5085	0.1424	0.9210	0.0548
Controlled	2.0	3.0	0.60±0.01	221	0.1855	0.0120	0.60±0.01	221*	0.1561	0.0459	0.2837	0.0302
		4.5	0.60±0.02	358	0.3354	0.0170	0.60±0.02	358*	0.2743	0.0856	0.5072	0.0384
		6.0	0.60±0.02	459	0.4037	0.0180	0.60±0.02	459*	0.3193	0.1087	0.5962	0.0355

t_E = exhaustion time (effluent metal concentration equal to 60% of influent concentration from virgin beds, if not specified); * = adopted t_E values from virgin GAA bed with 60% of influent Pb(II) concentration; Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA respectively.

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curve for Cu(II) metal was considered only up to exhaustion time for respective Pb(II) metal from virgin beds for the purpose of carrying out mass balance for metal removal. The Pb(II) metal removal by virgin GAA bed of 3.0 cm depth up to 251 min. of operation was estimated as 0.2379 meq. When the washed bed was reloaded with M[Cu(0.60)] system, the removal of Cu(II) metal on the washed bed up to 251 min. of operation time was estimated as 0.1964 meq while 0.0557 meq of Pb(II) metal migrated from the washed bed. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 0.3631 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.0386 meq/g (Table 5.52). Under controlled pH conditions, when the virgin column bed of depth 3.0 cm was loaded with M[Pb(0.60)] system at a flow rate of 2.0 mL/min, exhaustion time (t_E) was estimated to be 221 min. However, Cu(II) metal breakthrough curve from washed beds did not yield 60% or more of influent metal concentration for all the three column bed depths (i.e. 3.0, 4.5 and 6.0 cm), the breakthrough curve for Cu(II) metal from washed bed was considered only up to exhaustion time for respective Pb(II) metal from virgin beds for the purpose of carrying out mass balance for metal removal. The Pb(II) metal removal by virgin GAA bed of 3.0 cm depth up to 221 min. was estimated as 0.1855 meq. When the washed bed was reloaded with M[Cu(0.60)] system, the removal of Cu(II) metal on the washed bed up to 221 min. of operation time was estimated as 0.1561 meq while 0.0459 meq of Pb(II) metal migrated from the washed bed. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 0.2837 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.0302 meq/g.

In order to investigate the effect of GAA bed depths on metal removal when the virgin GAA bed was loaded with M[Pb(0.60)] system and washed bed was again reloaded with M[Cu(0.60)] system, the breakthrough curves for a linear flow rate of 2.0 mL/min with three different bed depths of 3.0, 4.5 and 6.0 cm of GAA operated under uncontrolled and controlled pH conditions are re-plotted and presented in Fig. 5.104 and 5.105 respectively. It could be observed from these figures that breakthrough curves appear to shift towards right with increase in bed depths. The service times (t_B) for virgin and washed beds were estimated from the breakthrough curves when the effluent metal ions concentration was 5% of influent metal ion concentration (i.e. 0.03 meq/L). The corresponding breakthrough throughput volumes (V_B) were also estimated. All the estimated service times and breakthrough throughput volumes for uncontrolled and controlled pH conditions have been tabulated in

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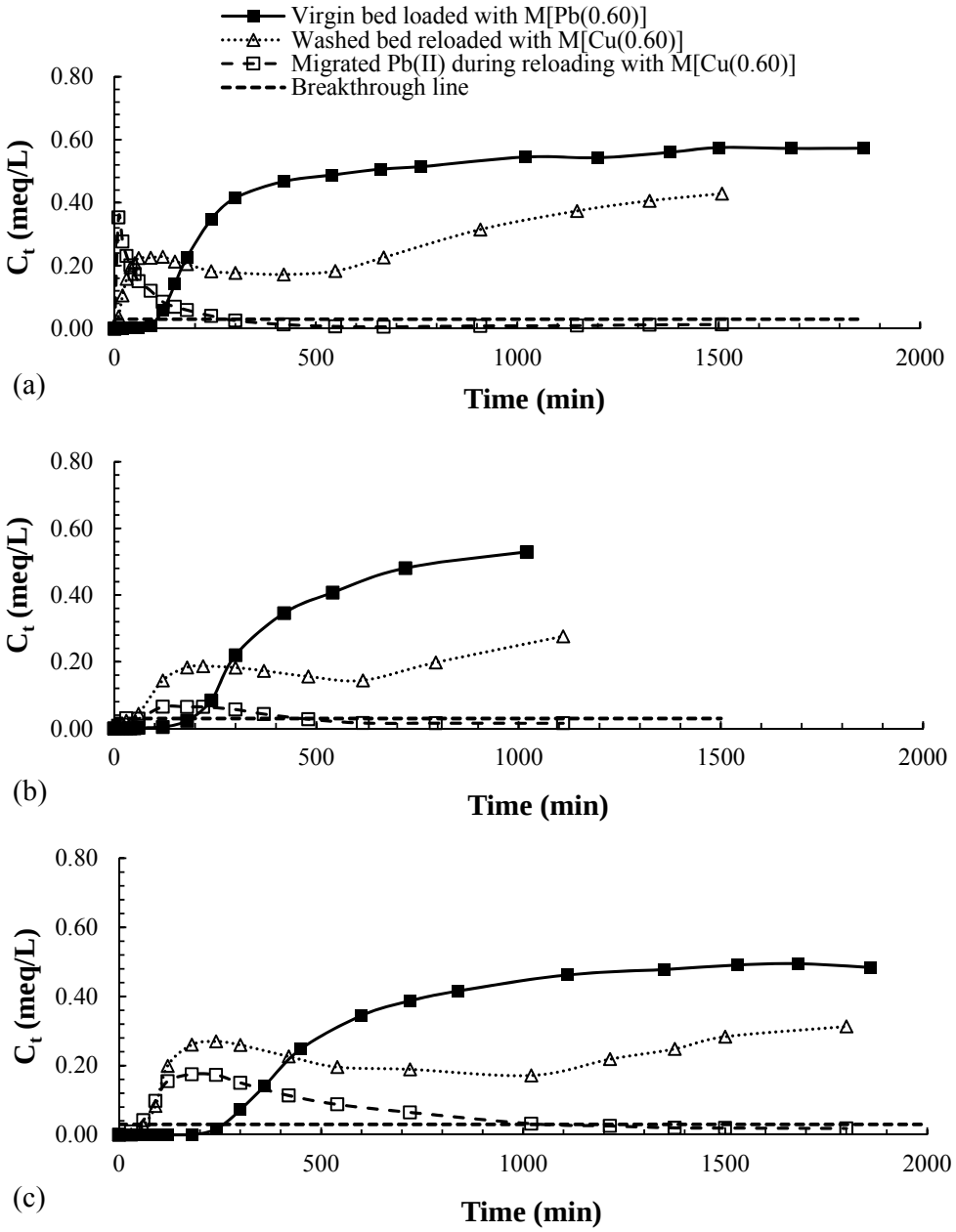

Fig. 5.104: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cu(0.60)] system at a flow rate of 2.0 mL/min under uncontrolled pH conditions {Initial metal conc. in M[Cu(0.60)] = 0.59±0.01 meq/L, M[Pb(0.60)] = 0.60±0.01 meq/L, Initial adjusted pH = 5.00±0.03, Temp. = 30±1°C] (Each data represents an average of two independent experimental values).

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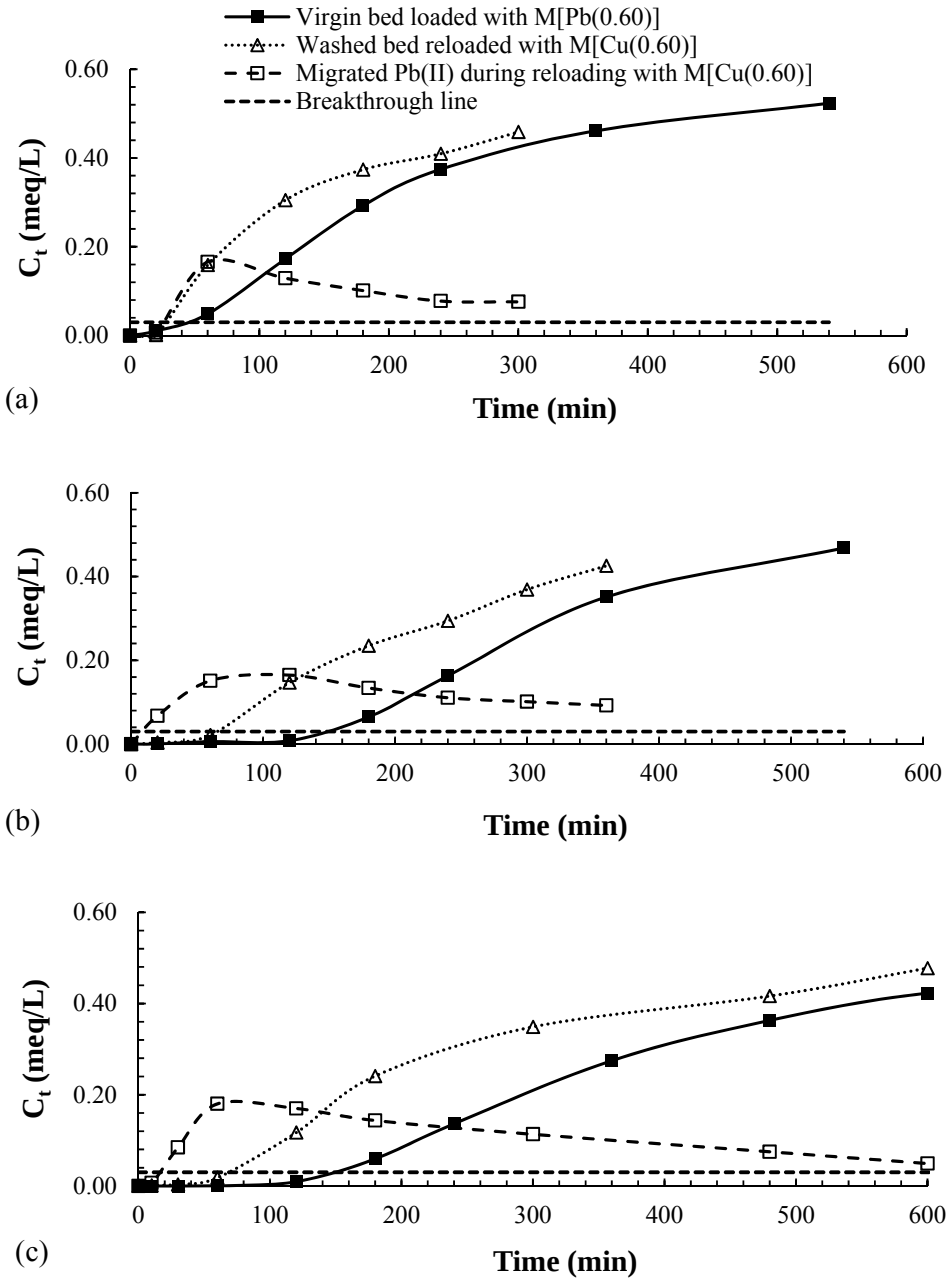

Fig. 5.105: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cu(0.60)] system at a flow rate of 2.0 mL/min under controlled pH conditions {Initial metal conc. in M[Cu(0.60)] = 0.60±0.01 meq/L, M[Pb(0.60)] = 0.58±0.01 meq/L, Buffered pH = 5.00±0.02, Temp. = 30±1°C] (Each data represents an average of two independent experimental values).

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Table 5.53. The breakthrough throughput volumes increased with increase in bed depths at the fixed flow rate as could be seen from Table 5.53. An increase in the service time was observed when the bed depth increased from 3.0 to 6.0 cm. The increase in the metal removal from the bulk metal ion solution with increase in bed depths was possibly due to increase in the amount of adsorbent mass in the larger beds which provided greater opportunities for metal removal.

Table 5.53: Summary of breakthrough results at a fixed flow rate but varying depths of virgin GAA bed loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cu(0.60)] system under uncontrolled and controlled pH conditions.

pH conditions	Bed depth (cm)	Virgin bed loaded with M[Pb(0.60)] system			Washed bed reloaded with M[Cu(0.60)] system			
		t_B (min)	V_B (mL)	Pb(II) removed (meq)	t_B (min)	V_B (mL)	Cu(II) removed (meq)	Pb(II) migrated (meq)
Uncontrolled	3.0	105	210	0.124	8	16	0.013	0.009
	4.5	180	360	0.213	40	80	0.047	0.001
	6.0	260	520	0.304	65	130	0.076	0.003
Controlled	3.0	40	80	0.046	27	54	0.032	0.001
	4.5	143	286	0.163	64	128	0.074	0.011
	6.0	144	288	0.166	67	134	0.078	0.012

V_B = Breakthrough throughput volumes at effluent metal concentration equal to 0.03 meq/L; t_B = service time at breakthrough; Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA.

5.7.3 Breakthrough curves for virgin GAA bed loaded with M[Cr(0.60)] system and washed bed reloaded with M[Pb(0.60)] system under uncontrolled and controlled pH conditions

The studies were carried out by exposing (or loading) the virgin (or fresh) GAA bed with M[Cr(0.60)] system having initial Cr(III) metal ion concentration of approximately 0.60 meq/L. The effluent Cr(III) concentration was observed to increase very slowly during the course of column operation and therefore, column operations were terminated when the bed yielded effluents with more than 40% of initial Cr(III) metal ion concentration [except for 6.0 cm depth for which column operation was terminated at Cr(III) effluent concentration of 0.014 meq/L (i.e. 2.3% of initial concentration)]. The loaded bed was then washed with 100 bed volumes of de-mineralized water to remove residual or un-adsorbed Cr(III) metal ions from pore volume of the bed. The washed bed was then again exposed (or reloaded) with M[Pb(0.60)] system having initial Pb(II) metal ion concentration of approximately 0.60 meq/L till the bed was exhausted or yielded effluent Pb(II) metal concentration of 80% or

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more of the initial concentration. The typical breakthrough curves in terms of metal ions remaining in effluent (C_t) versus time for virgin bed loaded with M[Cr(0.60)] system followed by reloading of washed bed with M[Pb(0.60)] system for a bed depth of 3.0 cm at a flow rate of 2.0 mL/min along with variation in effluent pH obtained under uncontrolled and controlled pH conditions are presented in Fig. 5.106 and 5.107 respectively.

Under uncontrolled pH conditions (Fig. 5.106), pH of the effluent from the virgin bed of GAA when loaded with M[Cr(0.60)] system increased to 6.73 in the first 15 min. of operation from the initially adjusted pH value of 5.00. After initial 15 min., the effluent pH decreased to around 6.06 within 120 min. of operation. As the operation proceeded beyond 120 min., pH of the effluent further decreased to 5.49 at around 300 min. of operation and reduced drastically to 4.30 at around 600 min. of operation and remained at the same level thereafter. When the washed GAA bed was reloaded with M[Pb(0.60)] system, pH of the effluent solution increased to a peak value of 5.38 in the first 10 min. of operation. After 10 min., pH of the effluent started to decrease and reached a value of 4.50 at the end of 660 min. of operation. Hence the major fraction of Cr(III) metal removal by GAA bed might have taken place due to precipitation as pH of the effluent remained above 5.50 for initial 300 min. of operation. However, when washed Cr(III) metal loaded bed was reloaded with M[Pb(0.60)] system, the effluent pH never increased above 5.50. Hence, the removal of Pb(II) metal might be mainly due to adsorption. The effluent pH from the column beds was observed to initially increase rapidly and then decrease. This aspect of variation in effluent pH from column beds appeared to be unusual which is needed to be investigated in detail.

Under uncontrolled pH conditions [Fig. 5.106(b)], no Cr(III) concentration was observed in the effluent from virgin bed for the initial 180 min. of operation. However, Cr(III) breakthrough curve appeared to increase fast after initial 180 min. of operation. The Cr(III) concentration in the effluent reached to a value of 0.220 meq/L at 480 min. of operation. At the end of 1080 min. of operation, Cr(III) metal concentration in the effluent was around 0.362 meq/L. Since the removal of Cr(III) metal was taking place slowly, the column operation was terminated when the effluent Cr(III) metal concentration was approximately 60% of initial Cr(III) metal ion concentration. The virgin bed loaded with M[Cr(0.60)] system was washed and then reloaded with M[Pb(0.60)] system. It yielded a relatively steeper breakthrough curve for Pb(II) metal [Fig. 5.106(b)]. The washed bed loaded

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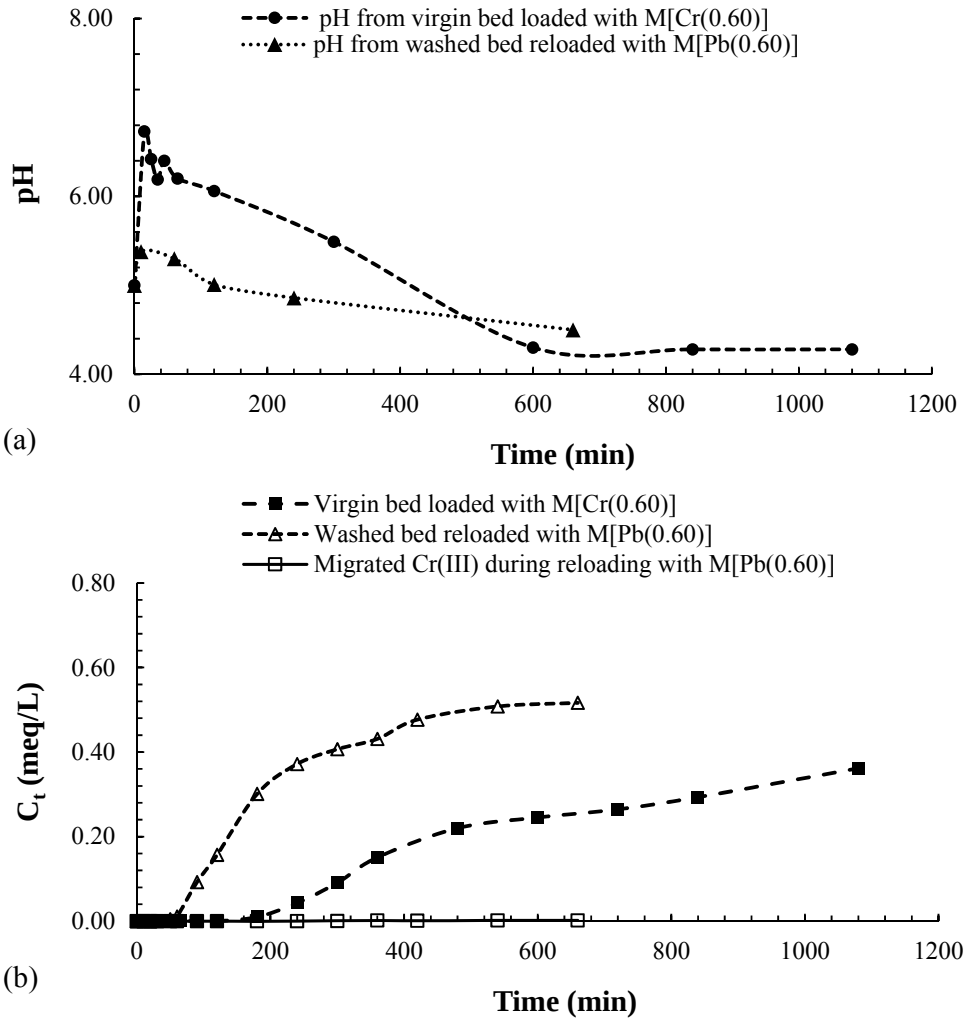

Fig. 5.106: Virgin GAA bed loaded with M[Cr(0.60)] system and washed bed reloaded with M[Pb(0.60)] system under uncontrolled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cr(0.60)] = 0.61±0.01 meq/L, M[Pb(0.60)] = 0.59±0.00 meq/L, Initial adjusted pH = 5.00±0.02, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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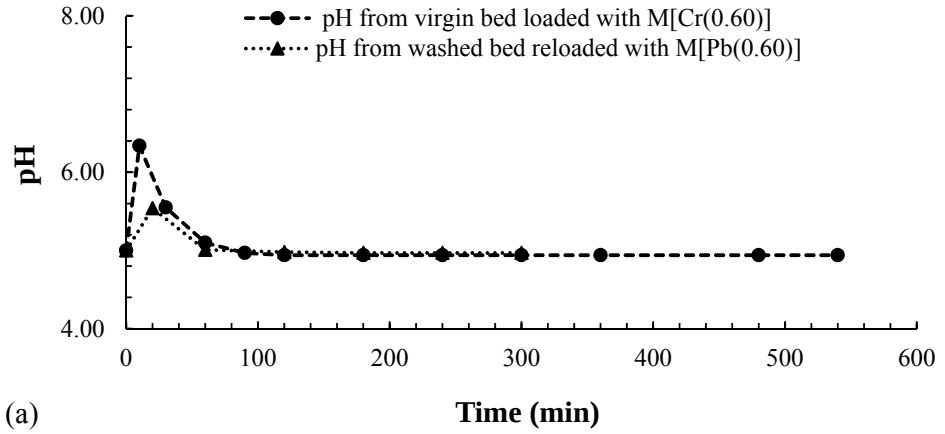
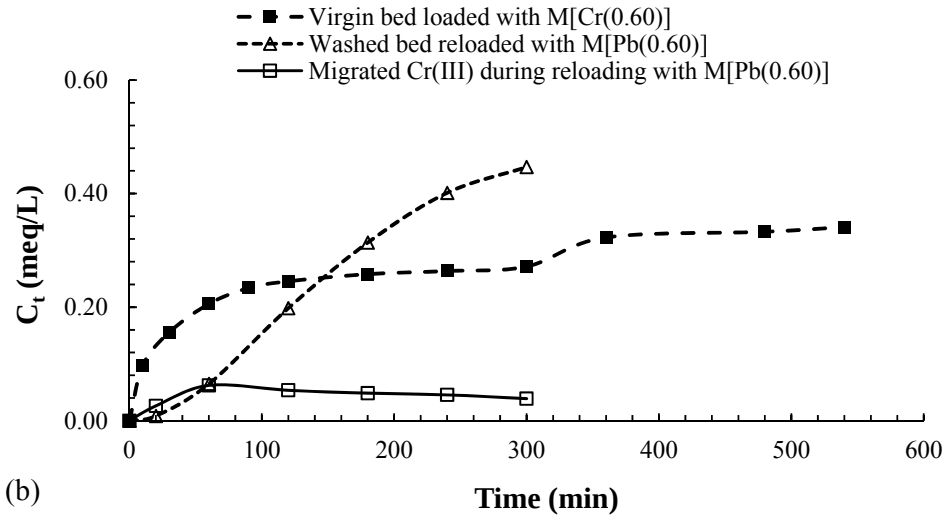


(a)



(b)

Fig. 5.107: Virgin GAA bed loaded with M[Cr(0.60)] system and washed bed reloaded with M[Pb(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cr(0.60)] = 0.61±0.01 meq/L, M[Pb(0.60)] = 0.58±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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with Cr(III) metal was exhausted with Pb(II) metal in approximately 660 min. of operation. During reloading of the washed bed with M[Pb(0.60)] system, migration of Cr(III) metal from the washed bed into the effluent was observed to be negligible. It indicated that the washed Cr(III) loaded bed could remove Pb(II) metal without any migration of Cr(III) metal from the washed bed. The removal of Pb(II) metal was mainly due to adsorption as effluent pH remained below 5.50. Similar breakthrough curves for virgin bed loaded with M[Cr(0.60)] system followed by reloading with M[Pb(0.60)] system along with variation in effluent pH for bed depths of 4.5 and 6.0 cm at a flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.9 and B.10). It is worth mentioning that no migration of Cr(III) metal took place from the washed beds when reloaded with Pb(II) metal ions. Even, no Cr(III) concentration was detected from virgin bed depth of 6.0 cm when the column was operated for more than 1000 min.

Under controlled pH conditions (Fig. 5.107), pH of the effluent from the virgin bed of GAA when loaded with M[Cr(0.60)] system increased to 6.34 in the first 10 min. of operation from initially buffered pH value of 5.00. After initial 10 min., the effluent pH decreased to around 5.55 within 30 min. of operation. As the operation proceeded beyond 30 min., pH of the effluent further decreased slowly and became constant to a value of 4.94 in the later phase of the operation. When the washed GAA bed was reloaded with M[Pb(0.60)] system, pH of the effluent solution increased to 5.54 in the first 20 min. After initial 20 min., pH of the effluent decreased to 5.01 at around 60 min. of the operation. The pH of the effluent at the end of the operation was observed as 4.97. The effluent pH was observed to initially increase rapidly and then decrease in the column studies which is needed to be investigated in detail. When virgin GAA bed loaded with M[Cr(0.60)] system, pH of the effluent increased above 6.00 and then came down to 5.50 or lower within 60-80 min. of operation time. Similarly, when the washed bed was reloaded with M[Pb(0.60)] system, pH of the effluent increased above 5.50 and then came down to 5.50 or lower between 20-60 min. of operation time. Hence, metal removals cannot be ruled out due to precipitation in the initial phases of operation.

Under controlled pH conditions [Fig. 5.107(b)], Cr(III) breakthrough curve for virgin GAA bed appeared to rise fast right from the beginning of the operation. After 60 min. of operation, the rise in breakthrough curve slowed down indicating that the bed was nearing to

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get exhausted [Fig. 5.107(b)]. When the virgin bed loaded with M[Cr(0.60)] system was washed and then reloaded with M[Pb(0.60)] system, Pb(II) metal breakthrough curve rised gradually up to first 20 min. of operation. After 20 min. of operation, it increased rapidly and reached to a value of 0.447 meq/L at around 300 min. of operation. The breakthrough curve of Cr(III) metal was observed to be steeper than the breakthrough curve of Pb(II) metal indicating relatively higher removal of Pb(II) metal by Cr(III) metal loaded washed GAA bed. When Cr(III) metal loaded washed bed was being reloaded with M[Pb(0.60)] system, migration of Cr(III) metal from the washed bed into the effluent took place. Initially the migration of Cr(III) metal from washed bed increased and then decreased with a flat peak at around 60 min. of operation [Fig. 5.107(b)]. Similar breakthrough curves for the virgin bed loaded with M[Cr(0.60)] system followed by reloading with M[Pb(0.60)] system along with variations in effluent pH for bed depths of 4.5 and 6.0 cm at a flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.11 and B.12). The flat peaks of migrated Cr(III) metal ions from washed beds could be observed under controlled pH conditions while Pb(II) breakthrough took place after passage of flat peaks of migrated Cr(III) metal ions in the case of column bed depths of 4.5 and 6.0 cm.

A mass balance was carried out to estimate the total metal removal by column beds under uncontrolled and controlled pH conditions when virgin bed was loaded with M[Cr(0.60)] system followed by washing and then again reloading with M[Pb(0.60)] system which is presented in Table 5.54. Mass balance for 6.0 cm bed depth was not carried out as breakthrough curves for Cr(III) metal hardly yielded 2% of initial concentration under uncontrolled pH conditions and 34% of initial concentration under controlled pH conditions.

Under uncontrolled pH conditions, when the virgin column bed of depth 3.0 cm was loaded with M[Cr(0.60)] system at a flow rate of 2.0 mL/min, exhaustion time (t_E) was estimated as 1067 min. The Cr(III) metal removal by virgin GAA bed up to 1067 min. was estimated as 0.8710 meq. When the washed bed was reloaded with M[Pb(0.60)] system, the removal of Pb(II) metal on the washed bed up to 219 min. of operation time was estimated as 0.1968 meq with no migration of Cr(III) metal from the washed bed. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 1.0588 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.1126 meq/g (Table 5.54). Under controlled pH conditions, when the virgin column bed of depth 3.0 cm

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Table 5.54: Summary of mass balance of metal removed by column beds when virgin GAA bed loaded with M[Cr(0.60)] system followed by reloading with M[Pb(0.60)] system under uncontrolled and controlled pH conditions.

pH conditions	Flow rate (mL/min)	Bed depth (cm)	Virgin bed loaded with M[Cr(0.60)] system			Bed washings	Washed bed reloaded with M[Pb(0.60)] system				Total metal removed by bed (meq)	Total metal removed per unit weight of bed (meq/g)
			Cr(III) initial conc. (meq/L)	t_E (min)	Cr(III) removed by bed (meq)	Amount of washed out Cr(III) (meq)	Pb(II) initial conc. (meq/L)	t_E (min)	Pb(II) removed by bed (meq)	Cr(III) migrated from bed (meq)		
Uncontrolled	2.0	3.0	0.61±0.01	1067	0.8710	0.009	0.59±0.00	219	0.1968	0.0000	1.0588	0.1126
		4.5	0.61±0.01	1104*	1.0556	0.010	0.59±0.01	234*	0.2448	0.0002	1.2902	0.0977
		6.0	0.61±0.02	-	-	-	0.60±0.02	-	-	-	-	-
Controlled	2.0	3.0	0.61±0.01	503^+	0.3430	0.008	0.58±0.01	183^+	0.1608	0.0175	0.4783	0.0509
		4.5	0.61±0.01	540*	0.4470	0.009	0.58±0.01	226*	0.2289	0.0181	0.6488	0.0492
		6.0	0.61±0.01	-	-	-	0.58±0.01	-	-	-	-	-

t_E = exhaustion time (effluent metal concentration equal to 60% of influent concentration from virgin and washed beds, if not specified); * = effluent concentration equal to 40% of influent concentration; $^+$ = effluent concentration equal to 55% of influent concentration; Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA respectively.

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was loaded with M[Cr(0.60)] system at a flow rate of 2.0 mL/min, exhaustion time (t_E) was estimated as 503 min. The Cr(III) metal removal by virgin GAA bed up to 503 min. was estimated as 0.3430 meq. When the washed bed was reloaded with M[Pb(0.60)] system, the removal of Pb(II) metal on the washed bed up to 183 min. of operation time was estimated as 0.1608 meq while 0.0175 meq of Cr(III) metal migrated from the washed bed. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 0.4783 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.0509 meq/g.

In order to investigate the effect of GAA bed depths on metal removal when the virgin GAA bed was loaded with M[Cr(0.60)] system and washed bed was again reloaded with M[Pb(0.60)] system, the breakthrough curves for a linear flow rate of 2.0 mL/min with three different bed depths of 3.0, 4.5 and 6.0 cm of GAA operated under uncontrolled and controlled pH conditions are re-plotted and presented in Fig. 5.108 and 5.109 respectively. It could be observed from these figures that breakthrough curves appear to shift towards right with increase in bed depths. The service times (t_B) for virgin and washed beds were estimated from the breakthrough curves when the effluent metal ions concentration was 5% of influent metal ion concentration (i.e. 0.03 meq/L). The corresponding breakthrough throughput volumes (V_B) were also estimated. All the estimated service times and breakthrough throughput volumes for uncontrolled and controlled pH conditions have been tabulated in Table 5.55. The breakthrough throughput volumes increased with increase in bed depths at the fixed flow rate as could be seen from Table 5.55. An increase in the service time was observed when the bed depth increased from 3.0 to 6.0 cm. The increase in the metal removal from the bulk metal ion solution with increase in bed depths was possibly due to increase in the amount of adsorbent mass in the larger beds which provided greater opportunities for metal removal.

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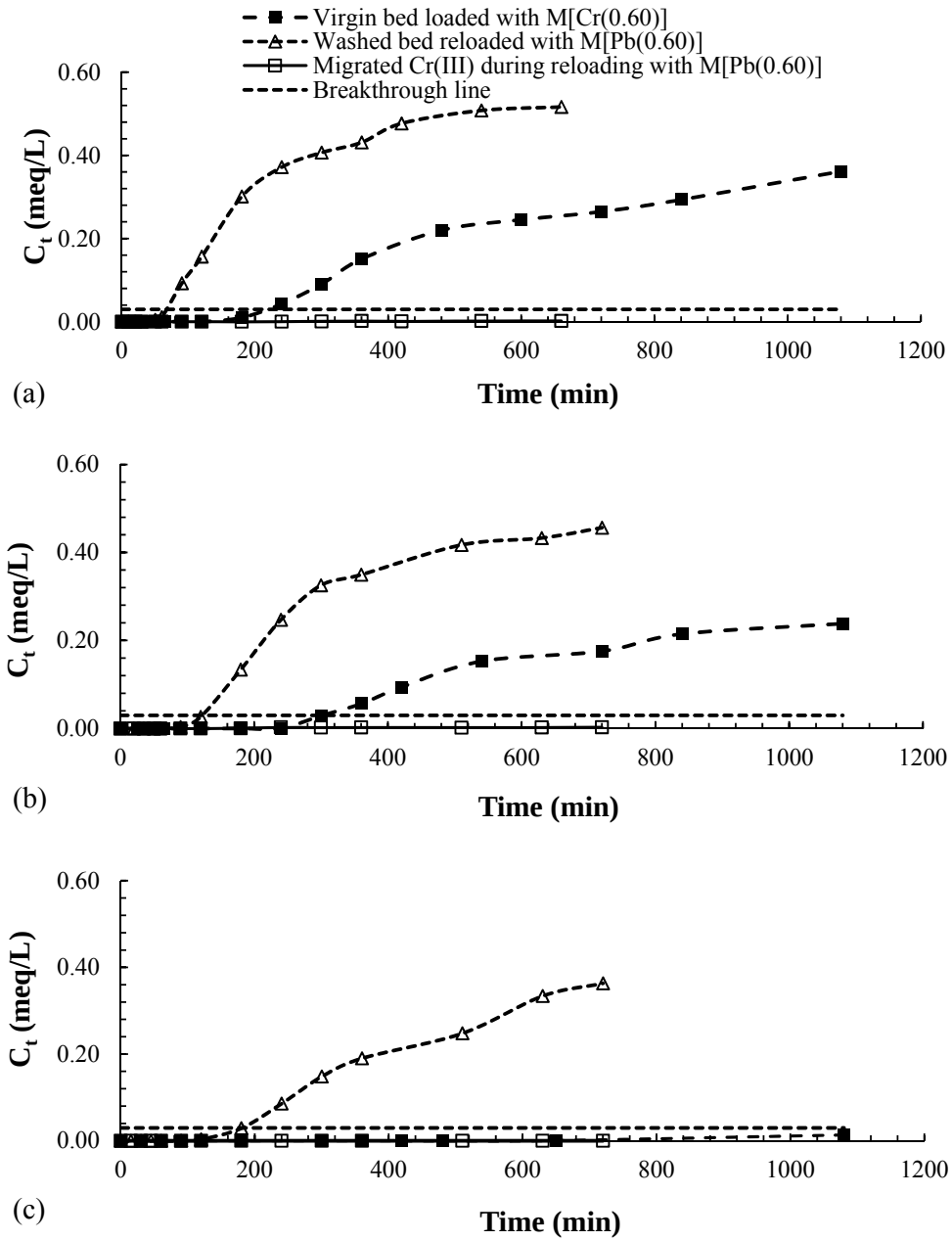

Fig. 5.108: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with M[Cr(0.60)] system and washed bed reloaded with M[Pb(0.60)] system at a flow rate of 2.0 mL/min under uncontrolled pH conditions {Initial metal conc. in M[Cr(0.60)] = 0.59±0.01 meq/L, M[Pb(0.60)] = 0.60±0.01 meq/L, Initial adjusted pH = 5.00±0.02, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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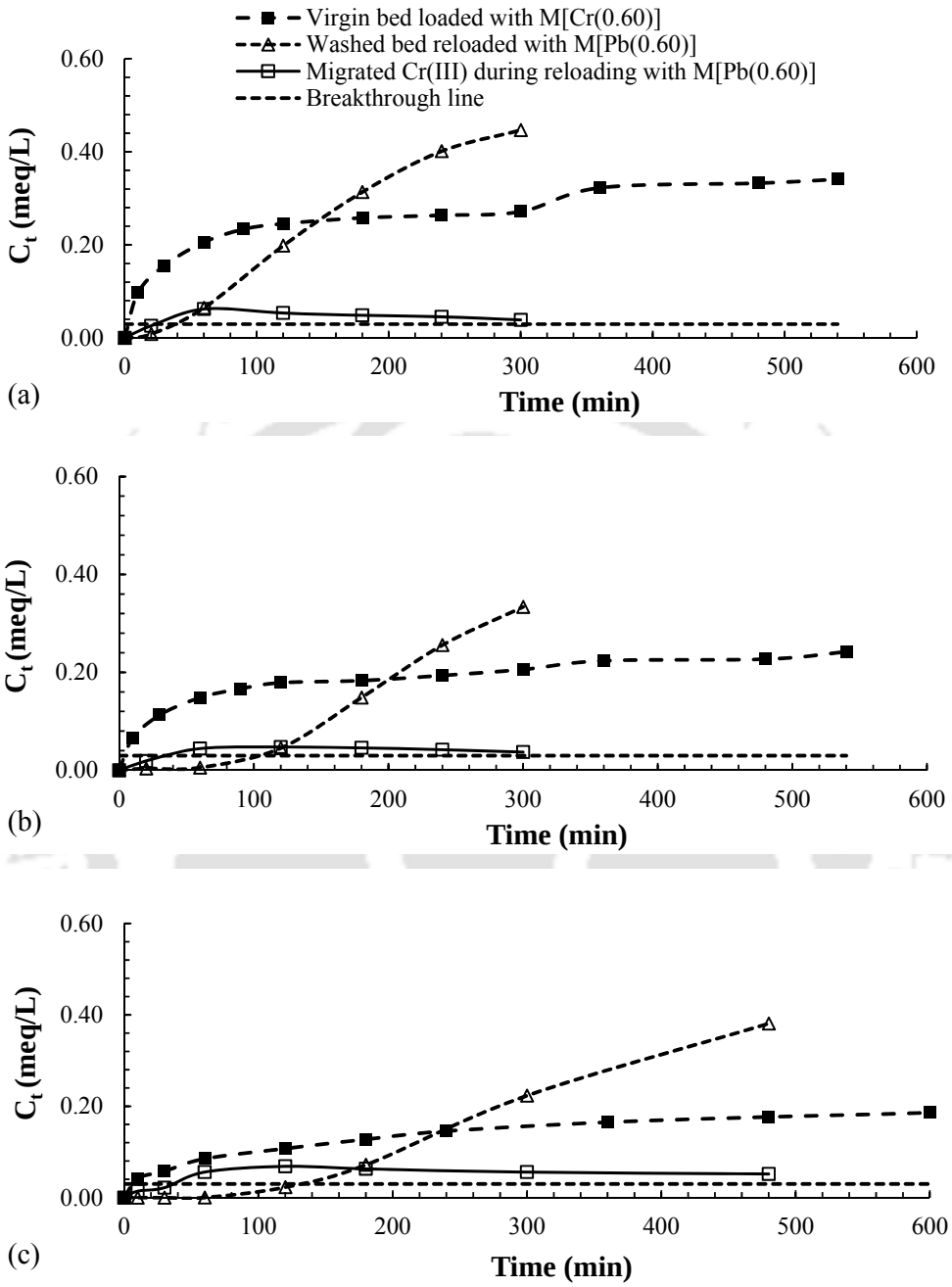

Fig. 5.109: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with M[Cr(0.60)] system and washed bed reloaded with M[Pb(0.60)] system at a flow rate of 2.0 mL/min under controlled pH conditions {Initial metal conc. in M[Cr(0.60)] = 0.59±0.01 meq/L, M[Pb(0.60)] = 0.60±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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Table 5.55: Summary of breakthrough results at a fixed flow rate but varying depths of virgin GAA bed loaded with M[Cr(0.60)] system and washed bed reloaded with M[Pb(0.60)] system under uncontrolled and controlled pH conditions.

pH conditions	Bed depth (cm)	Virgin bed loaded with M[Cr(0.60)] system			Washed bed reloaded with M[Pb(0.60)] system			
		t_B (min)	V_B (mL)	Cr(III) removed (meq)	t_B (min)	V_B (mL)	Pb(II) removed (meq)	Cr(III) migrated (meq)
Uncontrolled	3.0	216	432	0.256	67	134	0.079	0.000
	4.5	302	604	0.361	122	244	0.143	0.000
	6.0	-	-	-	181	362	0.214	0.000
Controlled	3.0	3	6	0.003	35	70	0.034	0.002
	4.5	4	8	0.005	97	194	0.110	0.006
	6.0	7	14	0.009	128	256	0.147	0.012

V_B = Breakthrough throughput volumes at effluent metal concentration equal to 0.03 meq/L; t_B = service time at breakthrough; Bed depths of 3.0 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA.

5.7.4 Breakthrough curves for virgin GAA bed loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cr(0.60)] system under uncontrolled and controlled pH conditions

The studies were carried out by exposing (or loading) the virgin (or fresh) GAA bed with M[Pb(0.60)] system having initial Pb(II) metal ion concentration of approximately 0.60 meq/L till the bed was exhausted or yielded effluent Pb(II) metal concentration more than 60% of initial metal concentration. The loaded bed was then washed with 100 bed volumes of de-mineralized water to remove residual or un-adsorbed Pb(II) metal ions from pore volume of the bed. The washed bed was then again exposed (or reloaded) with M[Cr(0.60)] system till the bed was again exhausted or yielded effluents with more than 30% of initial Cr(III) metal ion concentration. The washed column beds were operated for shorter duration to save on operation time as time to exhaust the bed shall have taken a long operation period. The typical breakthrough curves in terms of metal ions remaining in effluent (C_t) versus time for virgin bed loaded with M[Pb(0.60)] system followed by reloading of washed bed with M[Cr(0.60)] system for a bed depth of 3.0 cm at a flow rate of 2.0 mL/min along with variation in effluent pH obtained under uncontrolled and controlled pH conditions are presented in Fig. 5.110 and 5.111 respectively.

Under uncontrolled pH conditions (Fig. 5.110), pH of the effluent from the virgin bed of GAA when loaded with M[Pb(0.60)] system increased to 6.62 in the first 15 min. of operation from the initially adjusted pH value of 5.00. After initial 15 min., the effluent pH started to decrease and came down to around 6.31 within 45 min. of operation. As the

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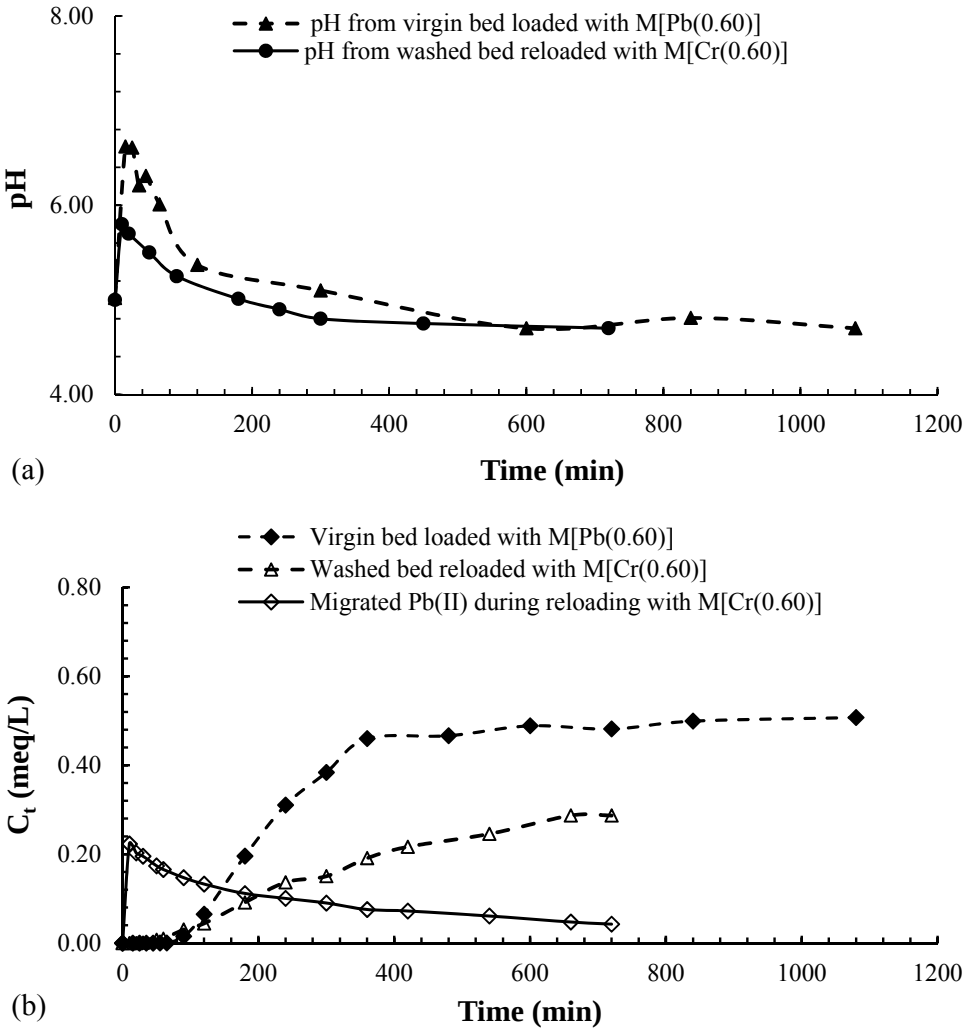

Fig. 5.110: Virgin GAA bed loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cr(0.60)] system under uncontrolled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Pb(0.60)] = 0.62±0.01 meq/L, M[Cr(0.60)] = 0.58±0.01 meq/L, Initial adjusted pH = 5.00±0.01, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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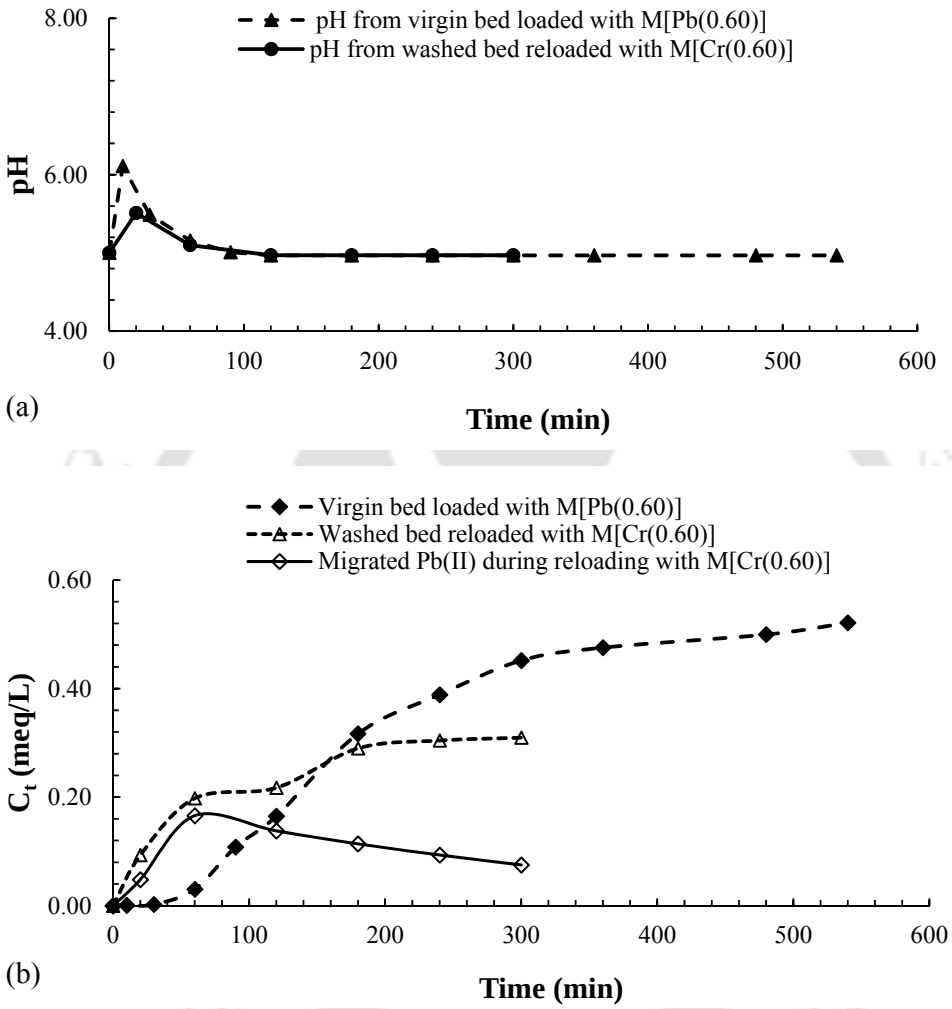

Fig. 5.111: Virgin GAA bed loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cr(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Pb(0.60)] = 0.58±0.01 meq/L, M[Cr(0.60)] = 0.61±0.01 meq/L, Buffered pH = 5.00±0.01, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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operation proceeded beyond 45 min., pH of the effluent further decreased to 5.37 at around 120 min. of operation and finally reached to a value of 4.70 at around 1080 min. of operation. When the washed GAA bed was reloaded with M[Cr(0.60)] system, pH of the effluent solution increased to a peak value of 5.80 in the first 10 min. of operation. After 10 min., pH of the effluent started to decrease and came down to 5.50 at around 50 min. of operation. The pH of the effluent at the end of 720 min. of operation was observed as 4.70. Hence Pb(II) metal removal by virgin GAA bed and Cr(III) metal removal by washed bed might have been due to combined effects of precipitation and adsorption as pH of the effluent remained above 5.50 for initial 120 and 50 min. of operations respectively. The effluent pH from the column beds was observed to initially increase rapidly and then decrease. This aspect of variation in effluent pH from column beds appeared to be unusual which is needed to be investigated in detail.

Under uncontrolled pH conditions, no Pb(II) concentration was observed in the effluent from the virgin bed for the initial 60-70 min. of operation. However, Pb(II) breakthrough curve appeared to increase faster after initial 60-70 min. of operation [Fig. 5.110(b)]. The Pb(II) concentration in the effluent reached to a value of 0.460 meq/L at around 360 min. of operation. Thereafter, the breakthrough curve proceeded gently and Pb(II) concentration reached to a value of 0.508 meq/L towards the end of operation. When the virgin bed loaded with M[Pb(0.60)] system was washed and then reloaded with M[Cr(0.60)] system, it yielded relatively gentle rising breakthrough curve for Cr(III) metal. During reloading of washed bed with M[Cr(0.60)] system, migration of Pb(II) metal from the washed bed was observed right from the beginning of the operation. The migration of Pb(II) metal in the solution was observed as 0.223 meq/L at the beginning of operation and it gradually decreased to a value of 0.043 meq/L at around 720 min. of operation. Similar breakthrough curves for virgin bed loaded with M[Pb(0.60)] system followed by reloading with M[Cr(0.60)] system along with variation in effluent pH for bed depths of 4.5 and 6.0 cm at a flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.13 and B.14). The flat peaks of migrated Pb(II) metal ions from washed beds could be observed under uncontrolled pH conditions in the case of column bed depths of 4.5 and 6.0 cm.

Under controlled pH conditions (Fig. 5.111), pH of the effluent from the virgin bed of GAA when loaded with M[Pb(0.60)] system increased to 6.11 in the first 10 min. of

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operation from initially buffered pH value of 5.00. After initial 10 min., the effluent pH decreased to around 5.49 within 30 min. of operation. As the operation proceeded beyond 30 min., pH of the effluent further decreased slowly and became constant to a value of 4.97 in the later phase of the operation. When the washed GAA bed was reloaded with M[Cr(0.60)] system, pH of the effluent solution increased to 5.51 in the first 20 min. of operation. After initial 20 min., pH of the effluent decreased to 5.10 at around 60 min. of operation. The pH of the effluent at the end of the operation was observed as 4.97. The effluent pH was observed to initially increase rapidly and then decrease in the column studies. This aspect is needed to be investigated in detail. When virgin GAA bed was loaded with M[Pb(0.60)] system, pH of the effluent increased above 6.00 and then came down to 5.50 or lower at around 30 min. of operation. Further, when the washed bed was reloaded with M[Cr(0.60)] system, pH of the effluent increased above 5.50 within first 20 min. and then came down to 5.50 or below. Hence, metal reduction cannot be ruled out due to precipitation during the first 20-30 min. of operation.

Under controlled pH conditions, no Pb(II) concentration was observed in the effluent from virgin bed for initial 60 min. of operation. However, Pb(II) breakthrough curve appeared to increase fast after initial 60 min. of operation [Fig. 5.111(b)]. The Pb(II) concentration in the effluent reached to a value of 0.452 meq/L at 300 min. of operation. After 300 min., the breakthrough curve increased slowly and the bed appeared to get exhausted [Fig. 5.111(b)]. When the virgin bed loaded with M[Pb(0.60)] system was washed and then reloaded with M[Cr(0.60)] system, Cr(III) metal breakthrough curve increased rapidly and reached to a value of 0.290 meq/L at around 180 min. of operation. The breakthrough curve for Cr(III) metal was observed to be steeper than the breakthrough curve for Pb(II) metal which indicated relatively lower removal of Cr(III) metal by Pb(II) metal loaded washed GAA bed. When Pb(II) metal loaded washed bed was being reloaded with M[Cr(0.60)] system, migration of Pb(II) metal from the washed column bed into the effluent took place. Initially the migration of Pb(II) metal from washed column bed increased rapidly and then decreased after peaking at 60 min. of operation [Fig. 5.111(b)]. Similar breakthrough curves for the virgin bed loaded with M[Pb(0.60)] system followed by reloading with M[Cr(0.60)] system along with variations in effluent pH for bed depths of 4.5 and 6.0 cm at flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.15 and B.16). A flat peak of migrated Pb(II) metal ions from washed beds could be

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observed under controlled pH conditions in the case of column bed depth of 4.5 cm while no peak was observed for 6.0 cm bed depth up to the operation time of the column.

A mass balance was carried out to estimate the total metal removal by column beds under uncontrolled and controlled pH conditions when virgin bed was loaded with M[Pb(0.60)] system followed by washing and then again reloading with M[Cr(0.60)] system which is presented in Table 5.56. Mass balance for metal removal under uncontrolled and controlled pH conditions by the virgin column beds when loaded with mono-metal ion systems was carried out for a time period when effluent metal concentration was equal to or more than 60% of the influent metal ion concentration. Under uncontrolled and controlled pH conditions, Cr(III) breakthrough curve during reloading of washed beds did not yield 60% or more of influent concentration. Hence, the breakthrough curve for Cr(III) from washed bed was considered up to the exhaustion time for Pb(II) metal from the virgin GAA bed for the purpose of carrying out mass balance for Cr(III) metal removal.

Under uncontrolled pH conditions, when the virgin column bed of depth 3.0 cm was loaded with M[Pb(0.60)] system at a flow rate of 2.0 mL/min, exhaustion time (t_E) was estimated as 278 min. However, Cr(III) metal breakthrough curve did not yield 60% concentration of the influent for all three column bed depths (i.e. 3.0, 4.5 and 6.0 cm) with 2.0 mL/min of flow rate; therefore, the breakthrough curve for Cr(III) metal was considered up to exhaustion time for Pb(II) metal from the respective virgin GAA beds for the purpose of carrying out mass balance for metal removed. The Pb(II) metal removal by virgin GAA bed up to 278 min. was estimated as 0.2554 meq. When the washed bed was reloaded with M[Cr(0.60)] system, the removal of Cr(III) metal on the washed bed up to 278 min. of operation time was estimated as 0.2954 meq while 0.0734 meq of Pb(II) metal migrated from the washed bed. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 0.4601 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.0490 meq/g (Table 5.56). Under controlled pH conditions, when the virgin column bed of depth 3.0 cm was loaded with M[Pb(0.60)] system at a flow rate of 2.0 mL/min, exhaustion time (t_E) was estimated as 206 min. However, Cr(III) metal breakthrough curve from the washed bed did not yield 60% concentration of the influent; therefore, the breakthrough curve for Cr(III) metal from the washed bed was considered up to the exhaustion time for Pb(II) metal from the respective virgin GAA beds for the purpose of

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Table 5.56: Summary of mass balance of metal removed by column beds when virgin GAA bed loaded with M[Pb(0.60)] system followed by reloading with M[Cr(0.60)] system under uncontrolled and controlled pH conditions.

pH conditions	Flow rate (mL/min)	Bed depth (cm)	Virgin bed loaded with M[Pb(0.60)] system			Bed washings	Washed bed reloaded with M[Cr(0.60)] system				Total metal removed by bed (meq)	Total metal removed per unit weight of bed (meq/g)
			Pb(II) initial conc. (meq/L)	t_E (min)	Pb(II) removed by bed (meq)	Amount of washed out Pb(II) (meq)	Cr(III) initial conc. (meq/L)	t_E (min)	Cr(III) removed by bed (meq)	Pb(II) migrated from bed (meq)		
Uncontrolled	2.0	3.0	0.62±0.01	278	0.2554	0.017	0.58±0.01	278*	0.2954	0.0734	0.4601	0.0490
		4.5	0.62±0.01	382	0.3397	0.020	0.58±0.01	382*	0.4351	0.0651	0.6896	0.0522
		6.0	0.62±0.02	597	0.5604	0.022	0.62±0.01	597*	0.6418	0.2316	0.9485	0.0565
Controlled	2.0	3.0	0.58±0.01	206	0.1783	0.026	0.61±0.01	206*	0.1657	0.0482	0.2698	0.0287
		4.5	0.58±0.01	350	0.3110	0.030	0.61±0.01	300^	0.2460	0.0530	0.4740	0.0359
		6.0	0.58±0.01	448	0.4092	0.029	0.61±0.01	448*	0.3643	0.0686	0.6759	0.0402

t_E = exhaustion time (effluent metal concentration equal to 60% of influent concentration from virgin bed, if not specified); * = adopted t_E values from virgin GAA bed with 60% of influent Pb(II) concentration; ^ = effluent concentration of Cr(III) equal to 44% of influent concentration; Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.7 g of GAA respectively.

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carrying out mass balance for metal removal. The Pb(II) metal removal by virgin GAA bed up to 206 min. was estimated as 0.1783 meq. When the washed bed was reloaded with M[Cr(0.60)] system, the removal of Cr(III) metal on the washed bed up to 206 min. of operation time was estimated as 0.1657 meq while 0.0482 meq of Pb(II) metal migrated from the washed bed. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 0.2698 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.0287 meq/g.

In order to investigate the effect of GAA bed depths on metal removal when the virgin GAA bed was loaded with M[Pb(0.60)] system and washed bed was again reloaded with M[Cr(0.60)] system, the breakthrough curves for a linear flow rate of 2.0 mL/min with three different bed depths of 3.0, 4.5 and 6.0 cm of GAA operated under uncontrolled and controlled pH conditions are re-plotted and presented in Fig. 5.112 and 5.113 respectively. It could be observed from these figures that breakthrough curves appear to shift towards right with increase in bed depths. The service times (t_B) for virgin and washed beds were estimated from the breakthrough curves when the effluent metal ions concentration was 5% of influent metal ion concentration (i.e. 0.03 meq/L). The corresponding breakthrough throughput volumes (V_B) were also estimated. All the estimated service times and breakthrough throughput volumes for uncontrolled and controlled pH conditions have been tabulated in Table 5.57. The breakthrough throughput volumes increased with increase in bed depths at the fixed flow rate as could be seen from Table 5.57. An increase in the service time was observed when the bed depth increased from 3.0 to 6.0 cm. The increase in the metal removal from the bulk metal ion solution with increase in bed depths was possibly due to increase in the amount of adsorbent mass in the larger beds which provided greater opportunities for metal removal.

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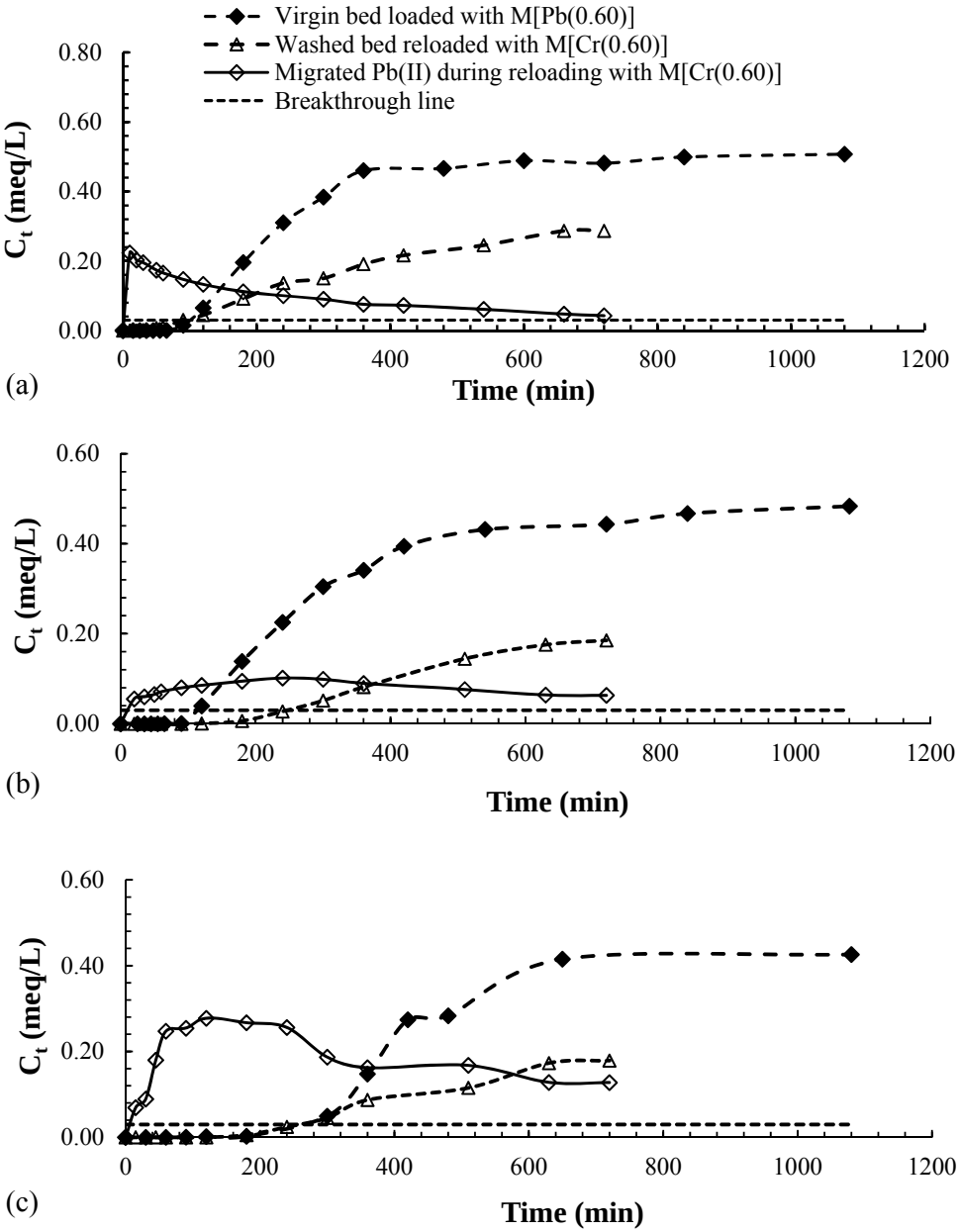

Fig. 5.112: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cr(0.60)] system at a flow rate of 2.0 mL/min under uncontrolled pH conditions {Initial metal conc. in M[Pb(0.60)] = 0.61±0.01 meq/L, M[Cr(0.60)] = 0.58±0.01 meq/L, Initial adjusted pH = 5.00±0.01, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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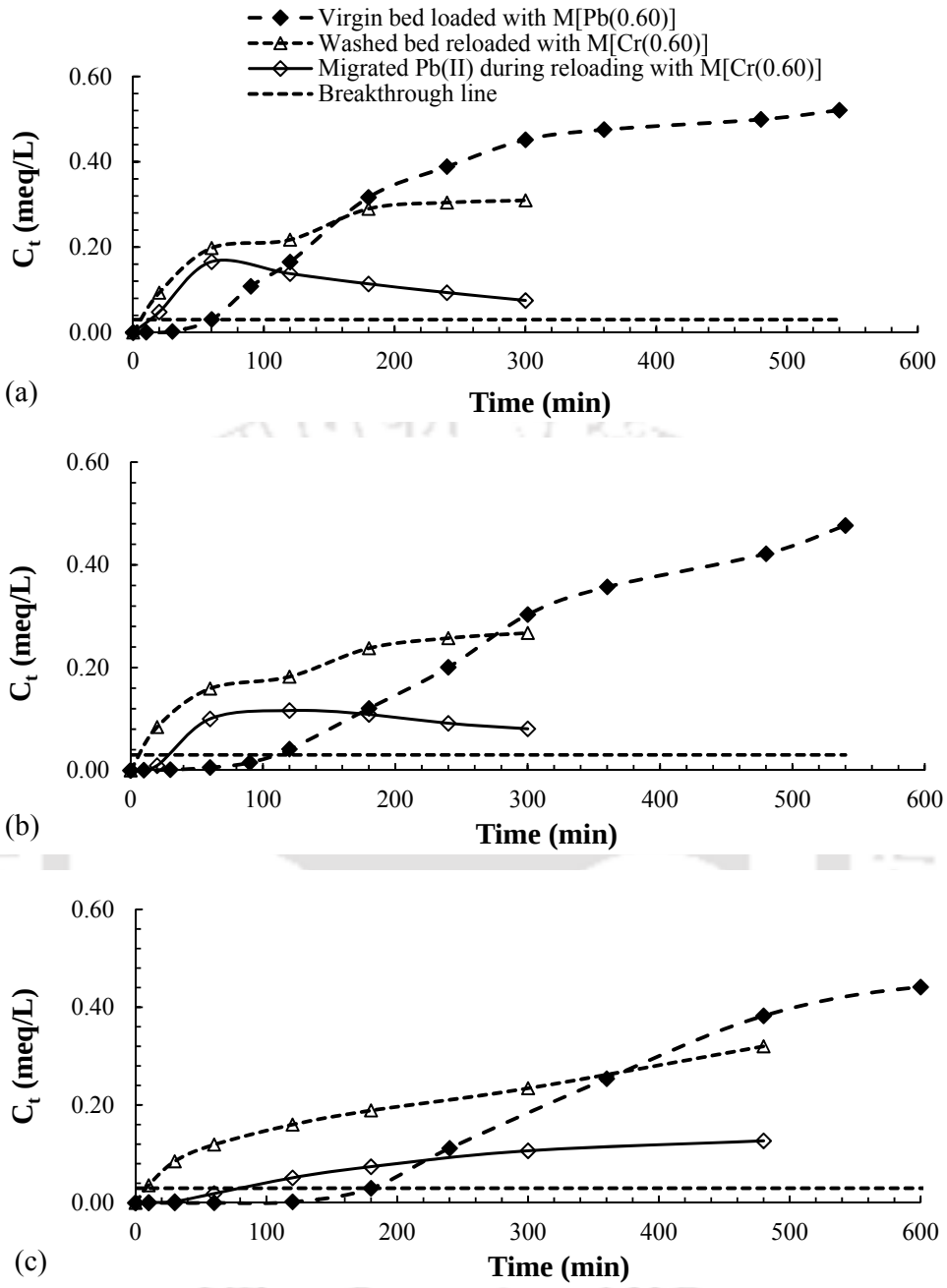

Fig. 5.113: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cr(0.60)] system at a flow rate of 2.0 mL/min under controlled pH conditions {Initial metal conc. in M[Pb(0.60)] = 0.58±0.01 meq/L, M[Cr(0.60)] = 0.61±0.01 meq/L, Buffered pH = 5.00±0.01, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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Table 5.57: Summary of breakthrough results at a fixed flow rate but varying depths of virgin GAA bed loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cr(0.60)] system under uncontrolled and controlled pH conditions.

pH conditions	Bed depth (cm)	Virgin bed loaded with M[Pb(0.60)] system			Washed bed reloaded with M[Cr(0.60)] system			
		t_B (min)	V_B (mL)	Pb(II) removed (meq)	t_B (min)	V_B (mL)	Cr(III) removed (meq)	Pb(II) migrated (meq)
Uncontrolled	3.0	99	198	0.117	89	178	0.104	0.031
	4.5	112	224	0.134	245	490	0.290	0.039
	6.0	252	504	0.299	257	514	0.303	0.117
Controlled	3.0	60	120	0.069	6	12	0.007	0.000
	4.5	107	214	0.123	7	14	0.008	0.000
	6.0	180	360	0.207	8	16	0.010	0.000

V_B = Breakthrough throughput volumes at effluent metal concentration equal to 0.03 meq/L; t_B = service time at breakthrough; Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA.

5.7.5 Breakthrough curves for virgin GAA bed loaded with M[Cu(0.60)] system and washed bed reloaded with M[Cr(0.60)] system under uncontrolled and controlled pH conditions

The studies were carried out by exposing (or loading) the virgin (or fresh) GAA bed with M[Cu(0.60)] system having initial Cu(II) metal ion concentration of approximately 0.60 meq/L till the bed was exhausted or yielded effluent Cu(II) metal concentration of 60% or more of initial metal concentration. The loaded bed was then washed with 100 bed volumes of de-mineralized water to remove residual or un-adsorbed Cu(II) metal ions from pore volume of the bed. The washed bed was then again exposed (or reloaded) with M[Cr(0.60)] system. The typical breakthrough curves in terms of metal ions remaining in effluent (C_t) versus time for virgin bed loaded with M[Cu(0.60)] system followed by reloading of washed bed with M[Cr(0.60)] system for a bed depth of 3.0 cm at a flow rate of 2.0 mL/min along with variation in effluent pH obtained under uncontrolled and controlled pH conditions are presented in Fig. 5.114 and 5.115 respectively.

Under uncontrolled pH conditions (Fig. 5.114), pH of the effluent from the virgin bed of GAA when loaded with M[Cu(0.60)] system increased to 6.76 in the first 10 min. of operation from initially adjusted pH value of 5.00. After initial 10 min., the effluent pH decreased to a value of 6.15 within 60 min. of operation. As the operation proceeded beyond 60 min., pH of the effluent further decreased to 5.66 at around 180 min. of operation and finally reached to a value of 5.06 at around 1800 min. of operation. When the washed GAA

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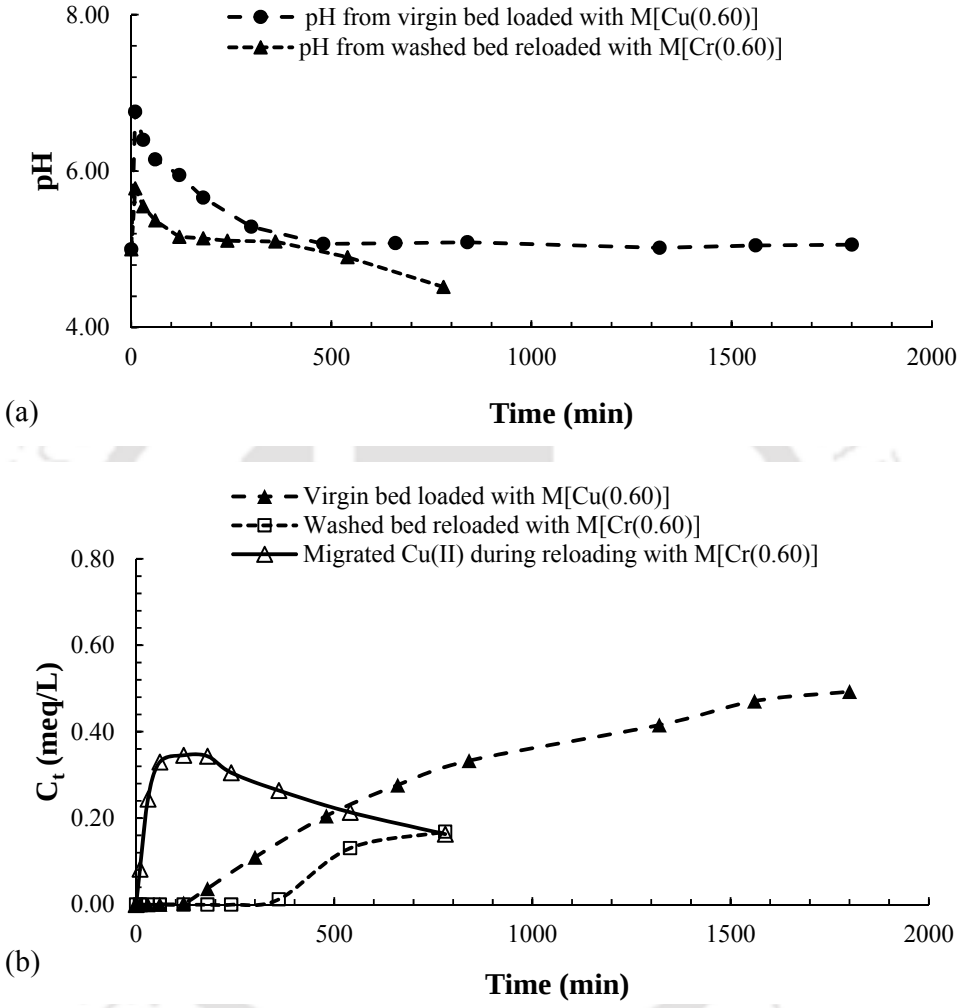

Fig. 5.114: Virgin GAA bed loaded with M[Cu(0.60)] system and washed bed reloaded with M[Cr(0.60)] system under uncontrolled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cu(0.60)] = 0.58±0.01 meq/L, M[Cr(0.60)] = 0.58±0.01 meq/L, Initial adjusted pH = 5.00±0.02, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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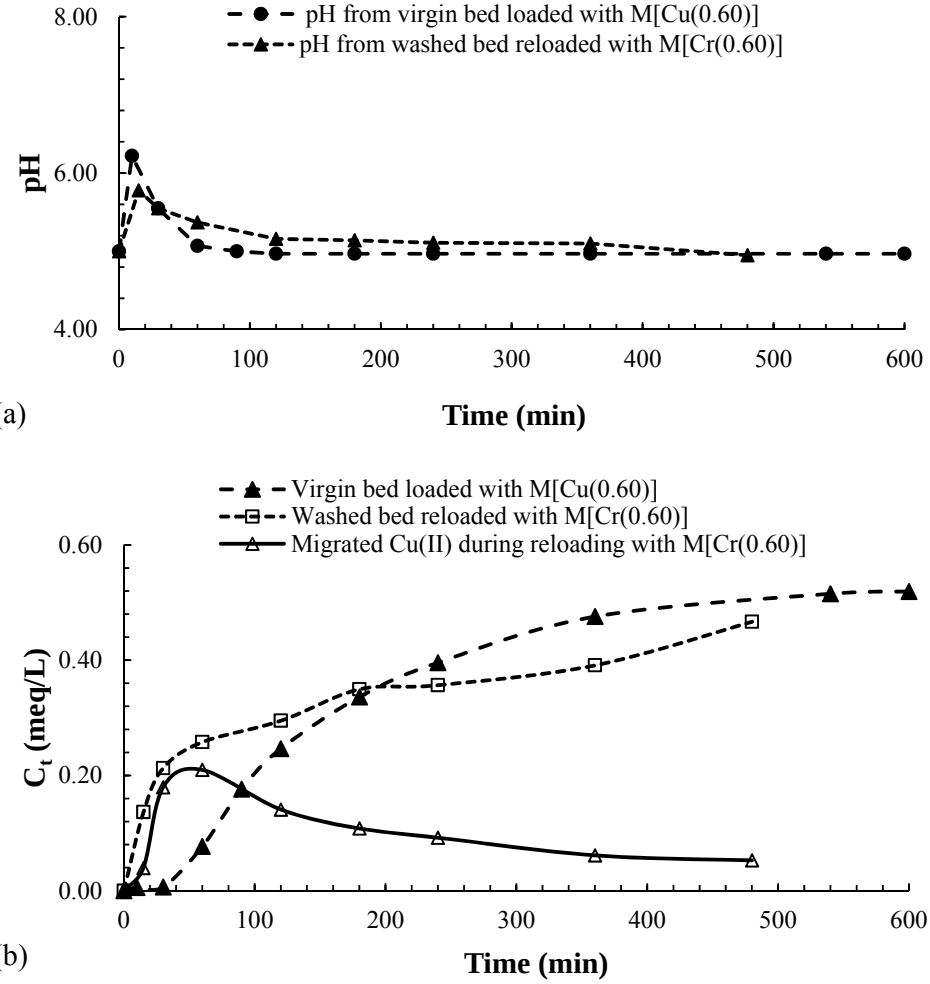

Fig. 5.115: Virgin GAA bed loaded with M[Cu(0.60)] system and washed bed reloaded with M[Cr(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cu(0.60)] = 0.58±0.01 meq/L, M[Cr(0.60)] = 0.58±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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bed was reloaded with M[Cr(0.60)] system, pH of the effluent solution increased to a peak value of 5.78 in the first 10 min. of operation. After 10 min., pH of the effluent decreased to 5.55 at around 30 min. of operation. The pH of the effluent at the end of 780 min. of operation was observed as 4.52. Therefore, Cu(II) metal removal by virgin GAA bed up to 180-300 min. of operation and Cr(III) metal removal by Cu(II) metal loaded washed GAA bed up to 30-60 min. of operation might be due to combined effects of precipitation and adsorption as pH of the effluent remained above 5.50. The effluent pH from the column beds were observed to initially increase rapidly and then decrease. This aspect of variation in effluent pH from column beds appeared to be unusual which is needed to be investigated in detail.

Under uncontrolled pH conditions, Cu(II) metal concentration was not detected in the effluent during initial 120 min. of operation [Fig. 5.114(b)]. However, it increased gradually to 0.333 meq/L at around 840 min. of operation and eventually reached to a value of 0.493 meq/L around 1800 min. of operation. When the virgin bed loaded with M[Cu(0.60)] system was washed and then reloaded with M[Cr(0.60)] system, Cr(III) metal concentration was not detected in the effluent during initial 360 min. of operation. After 360 min., Cr(III) metal concentration in the effluent increased to 0.131 meq/L at 540 min. of operation and eventually reached to 0.169 meq/L around 780 min. of operation. The effluent Cr(III) concentration was observed to increase slowly and hence column operation was terminated when the washed bed yielded effluents with more than 5% of initial Cr(III) metal ion concentration for higher bed depths. When the washed bed was being reloaded with M[Cr(0.60)] system, migration of Cu(II) metal from washed column bed into the effluent took place [Fig. 5.114(b)]. The migration of Cu(II) from washed bed was observed to peak to a value of 0.345 meq/L at around 120 min. of operation and then it gradually decreased to 0.163 meq/L towards the end of operation. Similar breakthrough curves for virgin bed loaded with M[Cu(0.60)] system followed by reloading with M[Cr(0.60)] system along with variation in effluent pH for bed depths of 4.5 and 6.0 cm at a flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.17 and B.18).

Under controlled pH conditions (Fig. 5.115), pH of the effluent from the virgin bed of GAA when loaded with M[Cu(0.60)] system increased to 6.22 in the first 10 min. of

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operation from initially buffered pH value of 5.00. After initial 10 min., the effluent pH decreased to 5.55 within 30 min. of operation. As the operation proceeded beyond 30 min., pH of the effluent further decreased slowly and became constant to a value of 4.97 in the later phase of the operation. When the washed GAA bed was reloaded with M[Cr(0.60)] system, pH of the effluent solution increased to 5.78 in the first 15 min. of operation. After initial 15 min., pH of the effluent decreased to 5.55 at around 30 min. of operation and to 5.16 at around 120 min. of operation. The pH of the effluent at the end of the operation was observed as 4.95. The effluent pH was observed to initially increase rapidly and then decrease in the column studies. This aspect is needed to be investigated in detail. When virgin GAA bed was loaded with M[Cu(0.60)] system, pH of the effluent increased above 6.00 and then came down to 5.55 around 30 min. of operation. Similarly, when the washed bed was reloaded with M[Cr(0.60)] system, pH of the effluent went above 5.50 up to approximately first 30 min. and then came down to 5.50 or lower. Hence, metal reduction might be due to precipitation as well during the first 30 min. of operation.

Under controlled pH conditions (Fig. 5.115), no Cu(II) concentration was observed in the effluent from virgin bed for the initial 30 min. of operation. However, Cu(II) breakthrough curve appeared to increase fast after initial 30 min. of operation. The Cu(II) concentration in the effluent reached to a value of 0.476 meq/L at 360 min. of operation. After 360 min., the breakthrough curve increased slowly indicating that the bed was nearing to get exhausted [Fig. 5.115(b)]. When the virgin bed loaded with M[Cu(0.60)] system was washed and then reloaded with M[Cr(0.60)] system, Cr(III) metal breakthrough curve increased rapidly right from the beginning of the operation and reached to a value of 0.258 meq/L at around 60 min. of operation. The breakthrough curve for Cr(III) metal was observed to be steeper than the breakthrough curve for Cu(II) metal which indicated relatively lower removal of Cr(III) metal by Cu(II) metal loaded washed GAA bed. When the washed bed was being reloaded with M[Cr(0.60)] system, migration of Cu(II) metal from washed column bed into the effluent took place. Initially the migration of Cu(II) metal from washed column bed increased rapidly and then decreased after peaking at around 60 min. of operation [Fig. 5.115(b)]. Similar breakthrough curves for the virgin bed loaded with M[Cu(0.60)] system followed by reloading with M[Cr(0.60)] system along with variations in effluent pH for bed depths of 4.5 and 6.0 cm at a flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.19 and B.20).

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A mass balance was carried out to estimate the total metal removal by column beds under uncontrolled and controlled pH conditions when virgin bed was loaded with M[Cu(0.60)] system followed by washing and then again reloading with M[Cr(0.60)] system. Under uncontrolled pH conditions, Cr(III) breakthrough curve during reloading of washed beds hardly yielded 5% of influent concentration, hence mass balance for metal removal was not carried out. Under controlled pH conditions, metal ion removal by the washed bed was estimated only up to exhaustion time of the respective virgin beds. Mass balance for metal removal under uncontrolled and controlled pH conditions by virgin GAA bed loaded with M[Cu(0.60)] system, washed and then reloaded with M[Cr(0.60)] system is presented in Table 5.58.

Under uncontrolled pH conditions, when the virgin bed of depth 3.0 cm was loaded with M[Cu(0.60)] system at a flow rate of 2.0 mL/min, exhaustion time (t_E) was estimated to be 932 min. However, Cr(III) metal breakthrough curve from the washed beds hardly yielded 5% concentration of influent metal solution for 4.5 and 6.0 cm bed depths with 2.0 mL/min flow rate and therefore, no mass balance for metal removal were carried out for all the washed beds reloaded with M[Cr(0.60)] system. The Cu(II) metal removal by virgin GAA bed up to 932 min. was estimated as 0.7411 meq (Table 5.58). Under controlled pH conditions, when the virgin bed of depth 3.0 cm was loaded with M[Cu(0.60)] system at a flow rate of 2.0 mL/min, exhaustion time (t_E) was estimated to be 193 min. However, Cr(III) metal breakthrough curve from washed beds did not yield 60% concentration of influent metal solution; therefore, the breakthrough curve for Cr(III) metal was considered up to exhaustion time for Cu(II) metal from respective virgin GAA beds for the purpose of carrying out mass balance for metal removal. The Cu(II) metal removal by virgin GAA bed up to 193 min. was estimated as 0.1567 meq. When Cu(II) metal loaded bed was reloaded with M[Cr(0.60)] system, the removal of Cr(III) metal on the washed bed up to 193 min. of operation was estimated as 0.1201 meq while 0.0674 meq of Cu(II) metal migrated from the washed bed. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 0.1614 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.0172 meq/g.

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Table 5.58: Summary of mass balance of metal removed by column beds when virgin GAA bed loaded with M[Cu(0.60)] system followed by reloading with M[Cr(0.60)] system under uncontrolled and controlled pH conditions.

pH conditions	Flow rate (mL/min)	Bed depth (cm)	Virgin bed loaded with M[Cu(0.60)] system			Bed washings	Washed bed reloaded with M[Cr(0.60)] system				Total metal removed by bed (meq)	Total metal removed per unit weight of bed (meq/g)
			Cu(II) initial conc. (meq/L)	t_E (min)	Cu(II) removed by bed (meq)	Amount of washed out Cu(II) (meq)	Cr(III) initial conc. (meq/L)	t_E (min)	Cr(III) removed by bed (meq)	Cu(II) migrated from bed (meq)		
Uncontrolled	2.0	3.0	0.58±0.01	932	0.7411	0.051	0.58±0.01	-	-	-	-	-
		4.5	0.58±0.01	1371	1.1227	0.054	0.58±0.01	-	-	-	-	-
		6.0	0.58±0.01	1906	1.6067	0.059	0.58±0.01	-	-	-	-	-
Controlled	2.0	3.0	0.58±0.01	193	0.1567	0.048	0.58±0.01	193^	0.1201	0.0674	0.1614	0.0172
		4.5	0.58±0.01	236	0.2073	0.040	0.58±0.01	236^	0.2020	0.0821	0.2872	0.0218
		6.0	0.58±0.01	330	0.2809	0.042	0.58±0.01	330^	0.2654	0.1131	0.3912	0.0233

t_E = exhaustion time (effluent metal concentration equal to 60% of influent concentration from virgin beds, if not specified); ^ = adopted t_E value from virgin GAA bed with 60% of influent Cu(II) concentration; Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA respectively.

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In order to investigate the effect of GAA bed depths on metal removal when the virgin GAA bed was loaded with M[Cu(0.60)] system and washed bed was again reloaded with M[Cr(0.60)] system, the breakthrough curves for a linear flow rate of 2.0 mL/min with three different bed depths of 3.0, 4.5 and 6.0 cm of GAA operated under uncontrolled and controlled pH conditions are re-plotted and presented in Fig. 5.116 and 5.117 respectively. It could be observed from these figures that breakthrough curves appear to shift towards right with increase in bed depths. The service times (t_B) for virgin and washed beds were estimated from the breakthrough curves when the effluent metal ions concentration was 5% of influent metal ion concentration (i.e. 0.03 meq/L). The corresponding breakthrough throughput volumes (V_B) were also estimated. All the estimated service times and breakthrough throughput volumes for uncontrolled and controlled pH conditions have been tabulated in Table 5.59. The breakthrough throughput volumes increased with increase in bed depths at the fixed flow rate as could be seen from Table 5.59. An increase in the service time was observed when the bed depth increased from 3.0 to 6.0 cm. The increase in the metal removal from the bulk metal ion solution with increase in bed depths was possibly due to increase in the amount of adsorbent mass in the larger beds which provided greater opportunities for metal removal.

Table 5.59: Summary of breakthrough results at a fixed flow rate but varying depths of virgin GAA bed loaded with M[Cu(0.60)] system and washed bed reloaded with M[Cr(0.60)] system under uncontrolled and controlled pH conditions.

pH conditions	Bed depth (cm)	Virgin bed loaded with M[Cu(0.60)] system			Washed bed reloaded with M[Cr(0.60)] system			
		t_B (min)	V_B (mL)	Cu(II) removed (meq)	t_B (min)	V_B (mL)	Cr(III) removed (meq)	Cu(II) migrated (meq)
Uncontrolled	3.0	167	334	0.193	387	774	0.442	0.227
	4.5	229	458	0.262	780	1560	0.894	0.514
	6.0	354	708	0.406	1203	2407	1.374	0.735
Controlled	3.0	40	80	0.046	3	6	0.003	0.000
	4.5	60	120	0.068	5	10	0.005	0.000
	6.0	85	170	0.097	6	12	0.007	0.000

V_B = Breakthrough throughput volumes at effluent metal concentration equal to 0.03 meq/L; t_B = service time at breakthrough; Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA.

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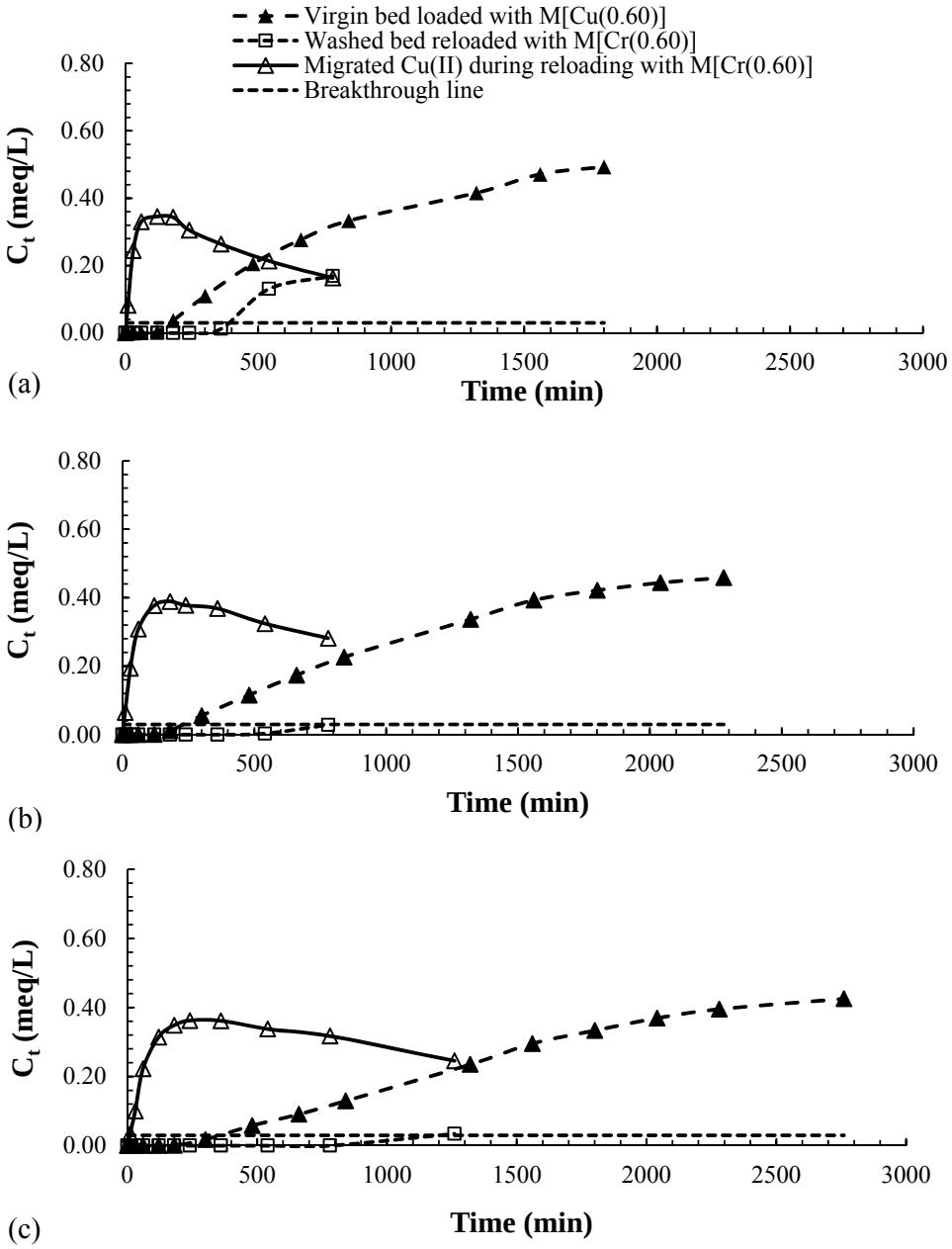

Fig. 5.116: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with M[Cu(0.60)] system and washed bed reloaded with M[Cr(0.60)] system at a flow rate of 2.0 mL/min under uncontrolled pH conditions {Initial metal conc. in M[Cu(0.60)] = 0.58±0.01 meq/L, M[Cr(0.60)] = 0.58±0.01 meq/L, Initial adjusted pH = 5.00±0.02, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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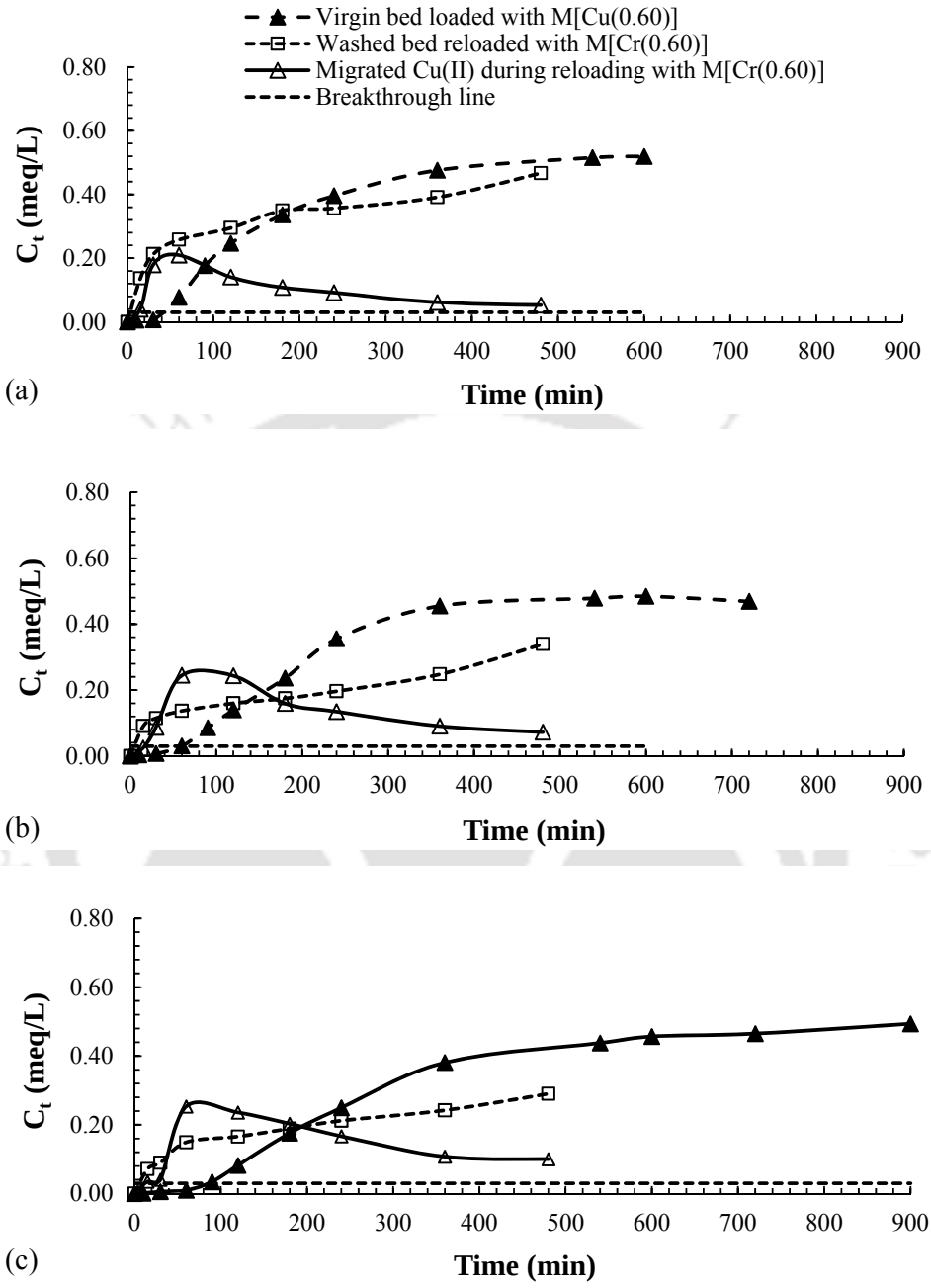

Fig. 5.117: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with M[Cu(0.60)] system and washed bed reloaded with M[Cr(0.60)] system at a flow rate of 2.0 mL/min under controlled pH conditions {Initial metal conc. in M[Cu(0.60)] = 0.58±0.01 meq/L, M[Cr(0.60)] = 0.58±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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5.7.6 Breakthrough curves for virgin GAA bed loaded with M[Cr(0.60)] system and washed bed reloaded with M[Cu(0.60)] system under uncontrolled and controlled pH conditions

The studies were carried out by exposing (or loading) the virgin (or fresh) GAA bed with M[Cr(0.60)] system having initial Cr(III) metal ion concentration of approximately 0.60 meq/L till the bed was exhausted or yielded effluent Cr(III) metal concentration of 50% or more of the initial concentration. The loaded bed was then washed with 100 bed volumes of de-mineralized water to remove residual or un-adsorbed Cr(III) metal ions from pore volume of the bed. The washed bed was then again exposed (or reloaded) with M[Cu(0.60)] system having initial Cu(II) metal ion concentration of approximately 0.60 meq/L. The typical breakthrough curves in terms of metal ions remaining in effluent (C_t) versus time for virgin bed loaded with M[Cr(0.60)] system followed by reloading of washed bed with M[Cu(0.60)] system for a bed depth of 3.0 cm at a flow rate of 2.0 mL/min along with variation in effluent pH obtained under uncontrolled and controlled pH conditions are presented in Fig. 5.118 and 5.119 respectively.

Under uncontrolled pH conditions (Fig. 5.118), pH of the effluent from the virgin bed of GAA when loaded with M[Cr(0.60)] system increased to 6.98 in the first 10 min. of operation from the initially adjusted pH value of 5.00. After initial 10 min., the effluent pH started to decrease and came down to around 6.10 within 120 min. of operation. As the operation proceeded beyond 120 min., pH of the effluent further decreased to 5.20 at around 300 min. of operation and finally reached to a value of 4.50 at around 1800 min. of operation. When the washed GAA bed was reloaded with M[Cu(0.60)] system, pH of the effluent increased to 5.35 in the first 10 min. of operation. After 10 min., pH of the effluent decreased to a value of 4.99 at around 60 min. of operation. The pH of the effluent at the end of 780 min. of operation was observed as 4.70. Therefore, Cr(III) metal removal by virgin GAA bed up to 180-300 min. of operation might be due to combined effects of precipitation and adsorption and Cu(II) removal by Cr(III) metal loaded washed GAA bed might be due to adsorption only. The effluent pH from column beds was observed to initially increase rapidly and then decrease. This aspect of variation in effluent pH from column beds appeared to be unusual which is needed to be investigated in detail.

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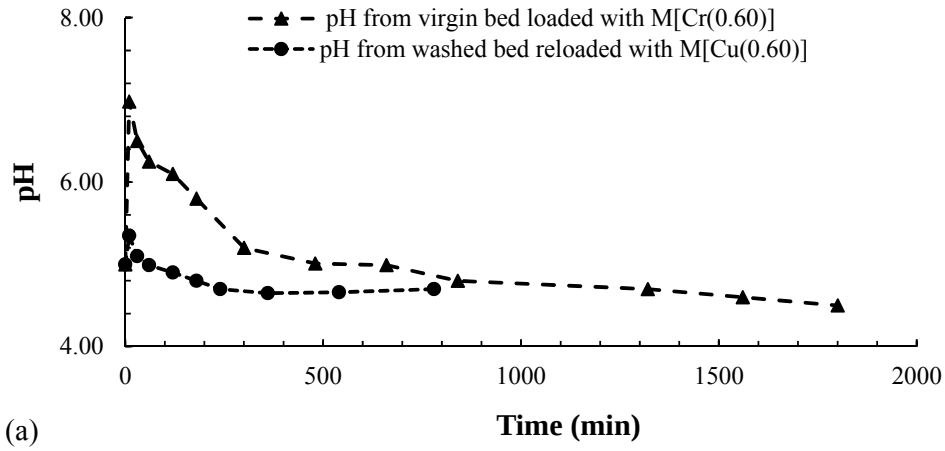
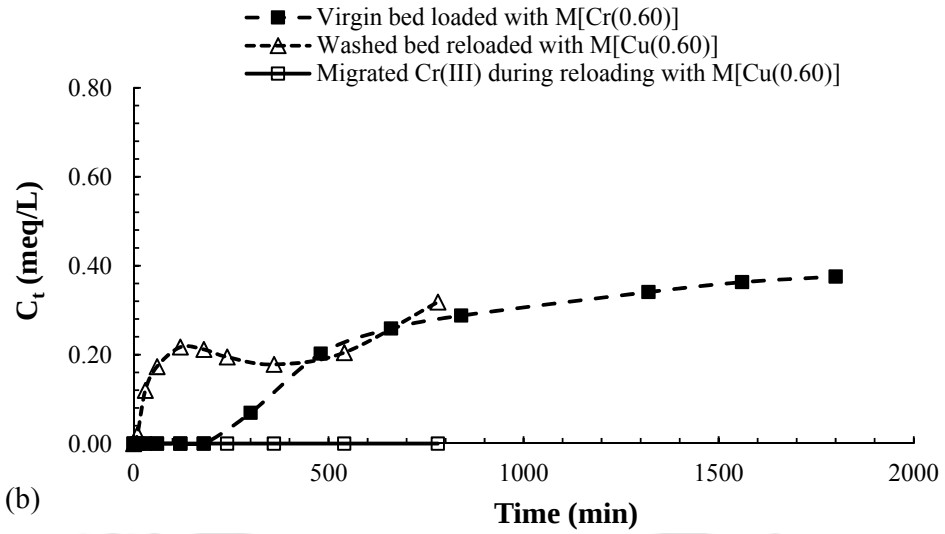


(a)



(b)

Fig. 5.118: Virgin GAA bed loaded with M[Cr(0.60)] system and washed bed reloaded with M[Cu(0.60)] system under uncontrolled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cr(0.60)] = 0.58±0.01 meq/L, M[Cu(0.60)] = 0.58±0.01 meq/L, Initial adjusted pH = 5.00±0.03, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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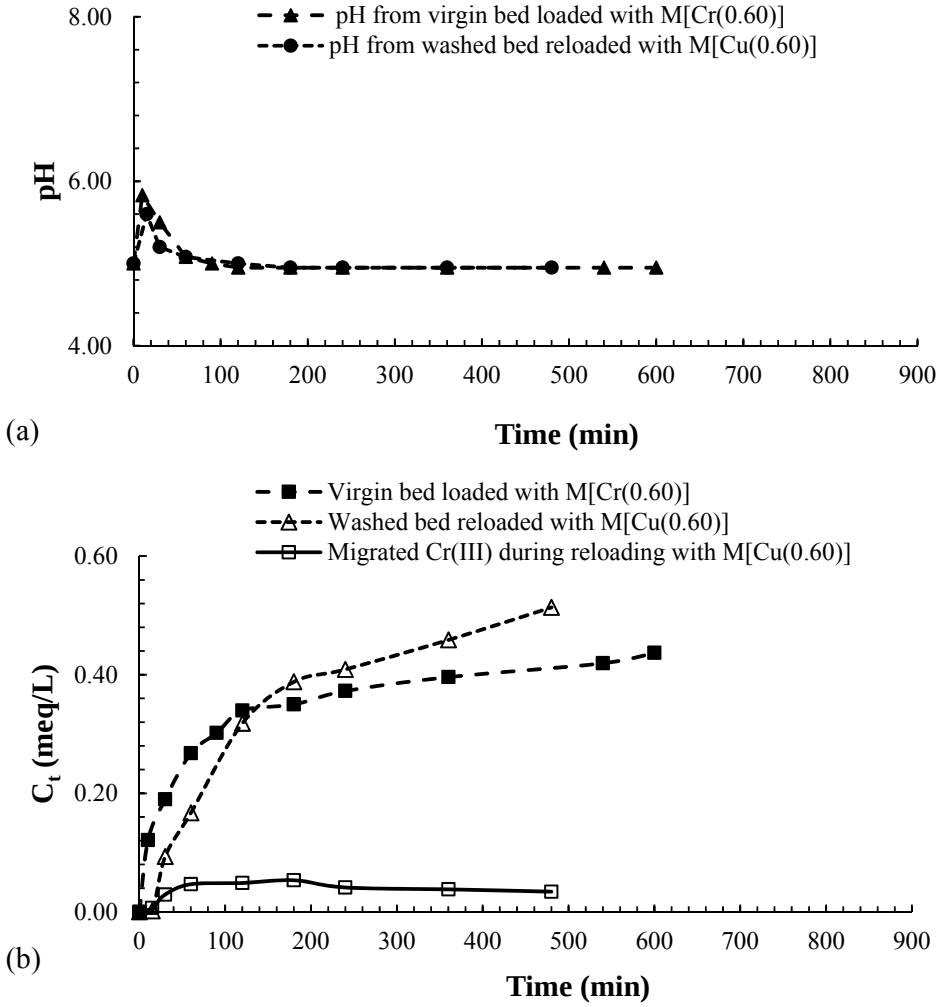

Fig. 5.119: Virgin GAA bed loaded with M[Cr(0.60)] system and washed bed reloaded with M[Cu(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cr(0.60)] = 0.58±0.01 meq/L, M[Cu(0.60)] = 0.58±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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Under uncontrolled pH conditions (Fig. 5.118), no Cr(III) concentration was observed in the effluent from the virgin bed for initial 180 min. of operation. However, Cr(III) breakthrough curve appeared to increase fast after 180 min. of operation. The Cr(III) concentration in the effluent increased to 0.202 meq/L at around 480 min., and eventually reached to a value of 0.376 meq/L around 1800 min. of operation. When the virgin bed loaded with M[Cr(0.60)] system was washed and then reloaded with M[Cu(0.60)] system, Cu(II) metal concentration increased rapidly with the start of operation and reached a concentration value of 0.217 meq/L in the effluent at around 120 min. of operation. After 120 min., Cu(II) metal concentration started to decrease and reached to a lower value of 0.178 meq/L at 360 min. of operation and thereafter it again started to increase and reached to a value of 0.318 meq/L at around 780 min. of operation. When Cr(III) metal loaded washed GAA bed was being reloaded with M[Cu(0.60)] system, Cr(III) metal migration from the washed bed was not observed. Even though migration of Cr(III) metal from the washed bed was not observed, but Cu(II) concentration in the effluent from the washed bed was observed to increase to a peak in the initial phase of operation, then showed either decreasing trend or remained at the level of peak for a duration of operation and therefore again showed increasing trend as the operation proceeded further. Similar breakthrough curves for virgin bed loaded with M[Cr(0.60)] system followed by reloading with M[Cu(0.60)] system along with variation in effluent pH for bed depths of 4.5 and 6.0 cm at a flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.21 and B.22). It is worth noting that the trends of Cu(II) metal removal by the washed beds of depths of 4.5 and 6.0 cm were similar to the bed depth of 3.0 cm.

Under controlled pH conditions (Fig. 5.119), pH of the effluent solution when virgin bed of GAA was loaded with M[Cr(0.60)] system increased to 5.83 in the first 10 min. of operation from initially buffered pH value of 5.00. After initial 10 min., the effluent pH decreased to 5.50 within 30 min. of operation. As the operation proceeded beyond 30 min., pH of the effluent further decreased slowly and became constant to value of 4.95 in the later phase of the operation. When the washed GAA bed was reloaded with M[Cu(0.60)] system, pH of the effluent increased to 5.60 in the first 15 min. of operation. After initial 15 min., pH of the effluent decreased to 5.20 at around 30 min. of operation. The pH of the effluent at the end of operation was observed as 4.95. The effluent pH was observed to initially increase rapidly and then decrease in the column studies. This aspect is needed to be investigated in

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detail. When virgin GAA bed was loaded with M[Cr(0.60)] system, pH of the effluent increased above 5.50 within first 10 min. and then came down to 5.50 or lower. Similarly, when the washed bed was reloaded with M[Cu(0.60)] system, pH of the effluent went above 5.50 within first 15 min. and then it came down below 5.50. Hence, metal reduction cannot be ruled out due to precipitation during the first 15-30 min. of operation.

Under controlled pH conditions (Fig. 5.119), a steep breakthrough curve for Cr(III) metal was observed with the start of virgin column operation. The Cr(III) breakthrough curve increased rapidly and reached to a value of 0.340 meq/L at 120 min. of operation. After 120 min. of operation, the breakthrough curve increased rather slowly indicating that the bed was nearing to get exhausted [Fig. 5.119(b)]. When the virgin bed loaded with M[Cr(0.60)] system was washed and then reloaded with M[Cu(0.60)] system, Cu(II) metal breakthrough curve also increased rapidly after initial 15 min. of operation and reached to a concentration value of 0.388 meq/L at around 180 min. of operation. The breakthrough curve of Cr(III) metal was observed to be steeper than the breakthrough curve of Cu(II) metal which indicated relatively higher removal of Cu(II) metal by Cr(III) metal loaded washed GAA bed. When Cr(III) metal loaded washed bed was being reloaded with M[Cu(0.60)] system, migration of Cr(III) metal from the washed bed took place. Similar breakthrough curves for virgin beds loaded with M[Cr(0.60)] system followed by reloading with M[Cu(0.60)] system along with variations in effluent pH for bed depths of 4.5 and 6.0 cm at a flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.23 and B.24).

A mass balance was carried out to estimate the total metal removal by column beds under uncontrolled and controlled pH conditions when virgin bed was loaded with M[Cr(0.60)] system followed by washing and then again reloaded with M[Cu(0.60)] system which is presented in Table 5.60.

Under uncontrolled pH conditions, when the virgin column bed of depth 3.0 cm was loaded with M[Cr(0.60)] system at a flow rate of 2.0 mL/min, exhaustion time (t_E) was estimated as 840 min. However, Cu(II) metal breakthrough curve from washed beds hardly yielded 30% concentration of the influent, therefore the breakthrough curve for Cu(II) metal was considered only up to Cu(II) effluent concentration of 30% of the influent concentration for the purpose of carrying out mass balance for metal removal. The Cr(III) metal removal by

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Table 5.60: Summary of mass balance of metal removed by column beds when virgin GAA bed loaded with M[Cr(0.60)] system followed by reloading with M[Cu(0.60)] system under uncontrolled and controlled pH conditions.

pH conditions	Flow rate (mL/min)	Bed depth (cm)	Virgin bed loaded with M[Cr(0.60)] system			Bed washings	Washed bed reloaded with M[Cu(0.60)] system				Total metal removed by bed (meq)	Total metal removed per unit weight of bed (meq/g)
			Cr(III) initial conc. (meq/L)	t_E (min)	Cr(III) removed by bed (meq)	Amount of washed out Cr(III) (meq)	Cu(II) initial conc. (meq/L)	t_E (min)	Cu(II) removed by bed (meq)	Cr(III) migrated from bed (meq)		
Uncontrolled	2.0	3.0	0.58±0.01	840	0.7320	0.008	0.58±0.01	360^	0.2880	-	1.0120	0.1077
		4.5	0.58±0.01	1629	1.3780	0.009	0.58±0.01	360^	0.3100	-	1.6790	0.1272
		6.0	0.58±0.01	2727	2.2794	0.010	0.58±0.01	1058^	0.9356	-	3.2050	0.1908
Controlled	2.0	3.0	0.58±0.01	79	0.0592	0.011	0.58±0.01	109	0.0938	0.0076	0.1344	0.0143
		4.5	0.58±0.01	421	0.2842	0.008	0.58±0.01	174	0.1574	0.0134	0.4206	0.0319
		6.0	0.58±0.01	600	0.4130	0.010	0.58±0.01	267	0.2356	0.0224	0.6163	0.0367

t_E = exhaustion time (effluent metal concentration equal to 50% of influent concentration from virgin and washed beds, if not specified); ^ = effluent concentration of Cu(II) equal to 30% of influent concentration; Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA respectively.

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virgin GAA bed up to 840 min. was estimated as 0.7320 meq. When the washed bed was reloaded with M[Cu(0.60)] system, the removal of Cu(II) metal on the washed bed up to 360 min. of operation time was estimated as 0.2880 meq with no migration of Cr(III) metal from the washed bed. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 1.0120 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.1077 meq/g (Table 5.60). Under controlled pH conditions, when the virgin column bed of depth 3.0 cm was loaded with M[Cr(0.60)] system at a flow rate of 2.0 mL/min, exhaustion time (t_E) was estimated as 79 min. The Cr(III) metal removal by virgin GAA bed up to 79 min. was estimated as 0.0592 meq. When the washed bed was reloaded with M[Cu(0.60)] system, the removal of Cu(II) metal on the washed bed up to 109 min. of operation time was estimated as 0.0938 meq while 0.0076 meq of Cr(III) migrated from the washed bed. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 0.1344 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.0143 meq/g.

In order to investigate the effect of GAA bed depths on metal removal when the virgin GAA bed was loaded with M[Cr(0.60)] system and washed bed was again reloaded with M[Cu(0.60)] system, the breakthrough curves for a linear flow rate of 2.0 mL/min with three different bed depths of 3.0, 4.5 and 6.0 cm of GAA operated under uncontrolled and controlled pH conditions are re-plotted and presented in Fig. 5.120 and 5.121 respectively. It could be observed from these figures that breakthrough curves appear to shift towards right with increase in bed depths. The service times (t_B) for virgin and washed beds were estimated from the breakthrough curves when the effluent metal ions concentration was 5% of influent metal ion concentration (i.e. 0.03 meq/L). The corresponding breakthrough throughput volumes (V_B) were also estimated. All the estimated service times and breakthrough throughput volumes for uncontrolled and controlled pH conditions have been tabulated in Table 5.61. The breakthrough throughput volumes increased with increase in bed depths at the fixed flow rate as could be seen from Table 5.61. An increase in the service time was observed when the bed depth increased from 3.0 to 6.0 cm. The increase in the metal removal from the bulk metal ion solution with increase in bed depths was possibly due to increase in the amount of adsorbent mass in the larger beds which provided greater opportunities for metal removal.

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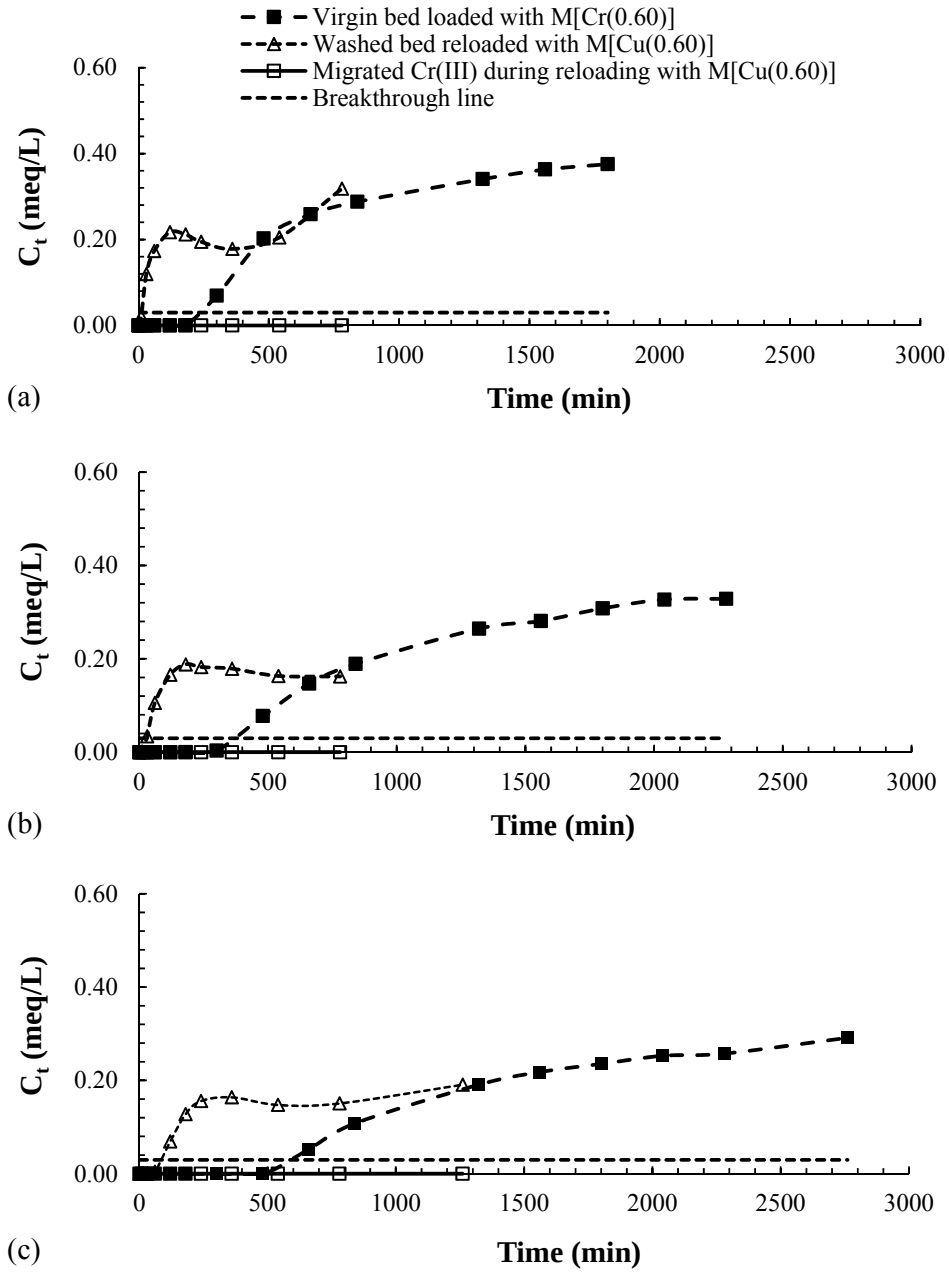

Fig. 5.120: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with M[Cr(0.60)] system and washed bed reloaded with M[Cu(0.60)] system at a flow rate of 2.0 mL/min under uncontrolled pH conditions {Initial metal conc. in M[Cr(0.60)] = 0.58±0.01 meq/L, M[Cu(0.60)] = 0.58±0.01 meq/L, Initial adjusted pH = 5.00±0.03, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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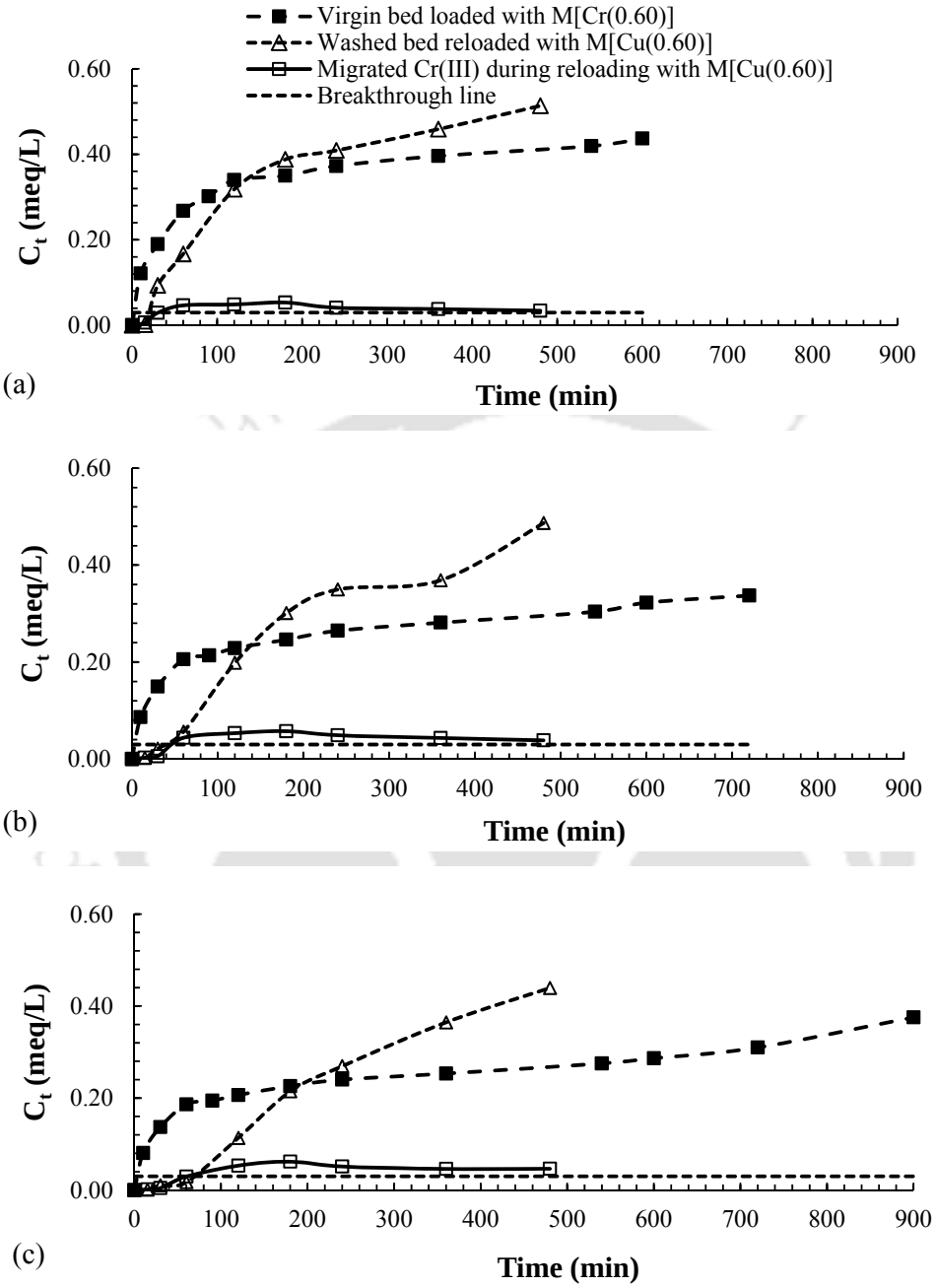

Fig. 5.121: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with M[Cr(0.60)] system and washed bed reloaded with M[Cu(0.60)] system at a flow rate of 2.0 mL/min under controlled pH conditions {Initial metal conc. in M[Cr(0.60)] = 0.58±0.01 meq/L, M[Cu(0.60)] = 0.58±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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Table 5.61: Summary of breakthrough results at a fixed flow rate but varying depths of virgin GAA bed loaded with M[Cr(0.60)] system and washed bed reloaded with M[Cu(0.60)] system under uncontrolled and controlled pH conditions.

pH conditions	Bed depth (cm)	Virgin bed loaded with M[Cr(0.60)] system			Washed bed reloaded with M[Cu(0.60)] system			
		t_B (min)	V_B (mL)	Cr(III) removed (meq)	t_B (min)	V_B (mL)	Cu(II) removed (meq)	Cr(III) migrated (meq)
Uncontrolled	3.0	258	516	0.265	23	46	0.0129	-
	4.5	364	728	0.415	30	60	0.0342	-
	6.0	582	1164	0.668	83	166	0.0954	-
Controlled	3.0	2	4	0.003	19	38	0.0219	0.000
	4.5	3	6	0.004	37	74	0.0424	0.000
	6.0	3	6	0.004	68	136	0.0773	0.002

V_B = Breakthrough throughput volumes at effluent metal concentration equal to 0.03 meq/L; t_B = service time at breakthrough; Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA.

5.7.7 Effect of order of mono-metal ion system loadings on virgin and washed beds on total metal removal under uncontrolled and controlled pH conditions

The column studies for metal removals from virgin and washed beds were carried out with selected mono-metal ion combination of M[Cu(0.60)] and M[Pb(0.60)] in subsections 5.7.1 and 5.7.2. In subsection 5.7.1, metal removals studies were carried out by first loading virgin GAA column beds with M[Cu(0.60)] system, then Cu(II) metal loaded beds were washed and subsequently reloaded with M[Pb(0.60)] system under uncontrolled and controlled pH conditions. However, the order of metal loadings to virgin and washed column beds were changed in subsection 5.7.2 – virgin GAA beds were first loaded with M[Pb(0.60)] system followed by Pb(II) metal loaded washed beds subsequently reloaded with M[Cu(0.60)] system under uncontrolled and controlled pH conditions. Similarly, changed order of mono-metal ion system loadings to virgin and washed column beds were adopted for investigating metal removals from mono-metal ion combination of M[Cr(0.60)] and M[Pb(0.60)] in subsections 5.7.3 and 5.7.4 as well as for mono-metal ion combination of M[Cu(0.60)] and M[Cr(0.60)] in subsections 5.7.5 and 5.7.6. The major objective of these studies was to understand the effect of order of mono-metal ion system loadings on overall metal removals by column beds (virgin and washed beds together) under uncontrolled and controlled pH conditions. While carrying out the studies as presented in subsections 5.7.1 to 5.7.6, it was aimed to operate the virgin as well as washed column beds till the column beds exhausted or yielded effluent metal concentration close to the influent metal concentration (say more than 80% of influent metal concentration). The results of these studies might have

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helped in making an estimate of overall metal removals by the virgin and washed beds together when loaded till the beds might have got exhausted in two different loading orders of combination of selected mono-metal ion systems. While undertaking these studies in the initial phases, operation of column beds till it exhausted or yielded effluent concentration close to 80% of influent metal concentration became a nightmare as the column operations continued for more than 33 h at a stretch. The possible reasons for such a long column operation time might be attributed to selected diameter of the column beds, depth of column beds, linear flow rate through the column and initial influent metal ion concentration. However, it was thought not prudent to alter these selected operational parameters (viz. column diameter, bed depths, flow rate and influent metal ion concentration) to reduce the column operation time to a reasonable length to achieve column exhaustion or to have column effluent concentration close to 80% of the influent metal concentration. Therefore, column studies were carried out with reasonably reduced but different length of time periods for the virgin and washed beds depending upon mono-metal ion system being loaded to the bed and its concentration in the effluent coming out of the column bed as detailed in subsections 5.7.1 to 5.7.6.

The experimental data obtained in subsections 5.7.1 to 5.7.6 were used to estimate overall metal removal by the column beds (virgin and washed beds together) when virgin bed loaded with one mono-metal ion system and washed bed reloaded with another mono-metal ion system under uncontrolled and controlled pH conditions and operated till exhaustion of column beds (virgin and washed beds) or yielded effluent concentration from virgin and washed beds close to predetermined level to the influent metal concentration. These estimates are already presented in Table 5.50, 5.52, 5.54, 5.56, 5.58 and 5.60. An inspection of these tables indicated that columns (virgin as well as washed beds) were operated up to different time periods and, therefore, estimated values of overall metal removals may not be appropriate to assess the effect of order of mono-metal ion system loadings and to arrive at a definite conclusion.

However, the experimental data obtained in subsections 5.7.1 to 5.7.6 were also used to estimate overall metal removal by the column beds (virgin and washed beds together) when virgin bed loaded with one mono-metal ion system and washed bed reloaded with another mono-metal ion system under uncontrolled and controlled pH conditions till

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breakthrough of column beds (virgin and washed beds) when the effluent concentration from virgin and washed beds were 5% of the influent metal concentration (i.e. 0.03 meq/L). Fortunately, all the column studies were able to provide breakthrough results which are available in Table 5.51, 5.53, 5.55, 5.57, 5.59 and 5.61. These results have been compiled and presented in Table 5.62. An inspection of Table 5.62 revealed higher amounts of migrated metal from washed beds compared to metal removed by virgin beds up to respective breakthrough times for (a) mono-metal ion combination of M[Cr(0.60)] and M[Pb(0.60)] when washed bed reloaded with M[Pb(0.60)] system under controlled pH conditions and (b) mono-metal ion combination of M[Cu(0.60)] and M[Cr(0.60)] when washed bed reloaded with M[Cr(0.60)] system under uncontrolled pH conditions. In this respect, it is important to mention that higher amounts of migrated metal ion might be possible from the metal loaded washed beds during its reloading because of the virgin beds had already accumulated higher amounts of metal ion during its loadings up to exhaustion or yielded effluent concentration close to the influent metal concentration.

A closer examination of the last column of Table 5.62 presenting overall metal removed by virgin and washed beds together indicated higher amounts of metal removal for virgin bed loaded with M[Cu(0.60)] system followed by washed bed reloaded with M[Pb(0.60)] system under uncontrolled pH conditions and virgin bed loaded with M[Pb(0.60)] system followed by washed bed reloaded with M[Cu(0.60)] system under controlled pH conditions for mono-metal ion combination of M[Cu(0.60)] and M[Pb(0.60)]. Similarly higher amounts of metal removal observed for virgin bed loaded with M[Cr(0.60)] system followed by washed bed reloaded with M[Pb(0.60)] system under uncontrolled pH conditions and virgin bed loaded with M[Pb(0.60)] system followed by washed bed reloaded with M[Cr(0.60)] system under controlled pH conditions for mono-metal ion combination of M[Cr(0.60)] and M[Pb(0.60)]. However, higher amounts of metal removal observed for virgin bed loaded with M[Cu(0.60)] system followed by washed bed reloaded with M[Cr(0.60)] system under uncontrolled and controlled pH conditions for mono-metal ion combination of M[Cu(0.60)] and M[Cr(0.60)]. It clearly hinted that high amounts of metal removal could be expected if the virgin beds and washed beds were loaded/reloaded with a particular order of loadings with mono-metal ion system as indicated in this analysis. If appropriate order of loadings was not followed, then overall metal removal will be comparatively lower.

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Table 5.62: Column breakthrough results at a glance for fixed flow rate of 2.0 mL/min but varying depths of virgin GAA bed loaded with a mono-metal ion system and washed bed reloaded with another mono-metal ion system under uncontrolled and controlled pH conditions.

Metal combination	pH conditions	Bed depth (cm)	Virgin bed				Washed bed					Overall metal removed by virgin & washed beds (meq)
			Loaded with	t_B (min)	V_B (mL)	Metal removed (meq)	Reloaded with	t_B (min)	V_B (mL)	Metal removed (meq)	Metal migrated (meq)	
M[Cu(0.60)] and M[Pb(0.60)]	Uncontrolled	3.0	M[Cu(0.60)] system	130	260	0.149	M[Pb(0.60)] system	120	240	0.141	0.097	0.193
		4.5		260	520	0.305		175	350	0.203	0.101	0.407
		6.0		390	780	0.437		255	510	0.300	0.129	0.608
	Controlled	3.0		33	66	0.039		38	76	0.044	0.009	0.074
		4.5		68	136	0.079		81	162	0.092	0.029	0.142
		6.0		74	148	0.086		145	290	0.166	0.040	0.212
	Uncontrolled	3.0	M[Pb(0.60)] system	105	210	0.124	M[Cu(0.60)] system	8	16	0.013	0.009	0.128
		4.5		180	360	0.213		40	80	0.047	0.001	0.259
		6.0		260	520	0.304		65	130	0.076	0.003	0.377
	Controlled	3.0		40	80	0.046		27	54	0.032	0.001	0.077
		4.5		143	286	0.163		64	128	0.074	0.011	0.226
		6.0		144	288	0.166		67	134	0.078	0.012	0.232
M[Cr(0.60)] and M[Pb(0.60)]	Uncontrolled	3.0	M[Cr(0.60)] system	216	432	0.256	M[Pb(0.60)] system	67	134	0.079	-	0.335
		4.5		302	604	0.361		122	244	0.143	-	0.504
		6.0		-	-	-		181	362	0.214	-	-
	Controlled	3.0		3	6	0.003		35	70	0.034	0.002	0.035
		4.5		4	8	0.005		97	194	0.110	0.006	0.109
		6.0		7	14	0.009		128	256	0.147	0.012	0.144
	Uncontrolled	3.0	M[Pb(0.60)] system	99	198	0.117	M[Cr(0.60)] system	89	178	0.104	0.031	0.190
		4.5		112	224	0.134		245	490	0.290	0.039	0.385
		6.0		252	504	0.299		257	514	0.303	0.117	0.485
	Controlled	3.0		60	120	0.069		6	12	0.007	0.000	0.076
		4.5		107	214	0.123		7	14	0.008	0.000	0.131
		6.0		180	360	0.207		8	16	0.010	0.000	0.217
M[Cu(0.60)] and M[Cr(0.60)]	Uncontrolled	3.0	M[Cu(0.60)] system	167	334	0.193	M[Cr(0.60)] system	387	774	0.442	0.227	0.407
		4.5		229	458	0.262		780	1560	0.894	0.514	0.642
		6.0		354	708	0.406		1203	2407	1.374	0.735	1.044
	Controlled	3.0		40	80	0.046		3	6	0.003	0.000	0.049
		4.5		60	120	0.068		5	10	0.005	0.000	0.073
		6.0		85	170	0.097		6	12	0.007	0.000	0.104
	Uncontrolled	3.0	M[Cr(0.60)] system	258	516	0.265	M[Cu(0.60)] system	23	46	0.013	-	0.278
		4.5		364	728	0.415		30	60	0.034	-	0.449
		6.0		582	1164	0.668		83	166	0.095	-	0.763
	Controlled	3.0		2	4	0.003		19	38	0.022	0.000	0.024
		4.5		3	6	0.004		37	74	0.042	0.000	0.046
		6.0		3	6	0.004		68	136	0.077	0.002	0.079

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5.7.8 Breakthrough curves for virgin GAA bed loaded with B[Cu(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cu(0.15)+Pb(0.45)] combination under uncontrolled and controlled pH conditions

The studies were carried out by exposing (or loading) the virgin (or fresh) GAA bed with B[Cu(0.45)+Pb(0.15)] combination till the bed exhausted or yielded effluents with more than 50% of total initial metal ion concentration. The loaded bed was then washed with 100 bed volumes of de-mineralized water to remove residual or un-adsorbed metal ions from pore volume of the bed. The washed bed was then again exposed (or reloaded) with B[Cu(0.15)+Pb(0.45)] combination till the bed exhausted or yielded effluents with more than 50% of total initial metal ion concentration. The typical breakthrough curves for Cu(II), Pb(II) and total metal in terms of metal ions remaining in effluent (C_t) versus time for virgin bed loaded with B[Cu(0.45)+Pb(0.15)] combination followed by reloading of washed bed with B[Cu(0.15)+Pb(0.45)] combination for a bed depth of 3.0 cm at a flow rate of 2.0 mL/min along with variation in effluent pH obtained under uncontrolled and controlled pH conditions are presented in Fig. 5.122 and 5.123 respectively.

Under uncontrolled pH conditions (Fig. 5.122), pH of the effluent from the virgin bed of GAA when loaded with B[Cu(0.45)+Pb(0.15)] combination increased to 6.50 in the first 10 min. of operation from initially adjusted pH value of 5.00. After initial 10 min., the effluent pH decreased to around 5.88 within 60 min. of operation. As the operation proceeded beyond 60 min., pH of the effluent further decreased to 5.34 at around 150 min. of operation and finally reached to a value of 4.91 at around 1800 min. of operation. When the washed GAA bed was reloaded with B[Cu(0.15)+Pb(0.45)] combination, pH of the effluent increased to 5.84 in the first 10 min. of operation. After 10 min., pH of the effluent decreased to a value of 5.58 at around 180 min. of operation. The pH of the effluent at the end of 1500 min. of operation was observed as 5.12. The removal of Cu(II) and Pb(II) metal ions by virgin GAA bed up to first 60-150 min. of operation and by washed GAA bed up to approximately first 180 min. of operation might have taken place due to precipitation along with adsorption as pH of the effluent increased above 5.50. The effluent pH from the column beds (virgin as well as washed) observed to initially increase rapidly and then decrease. This aspect of variation in effluent pH from column beds appeared to be unusual which is needed to be investigated in detail.

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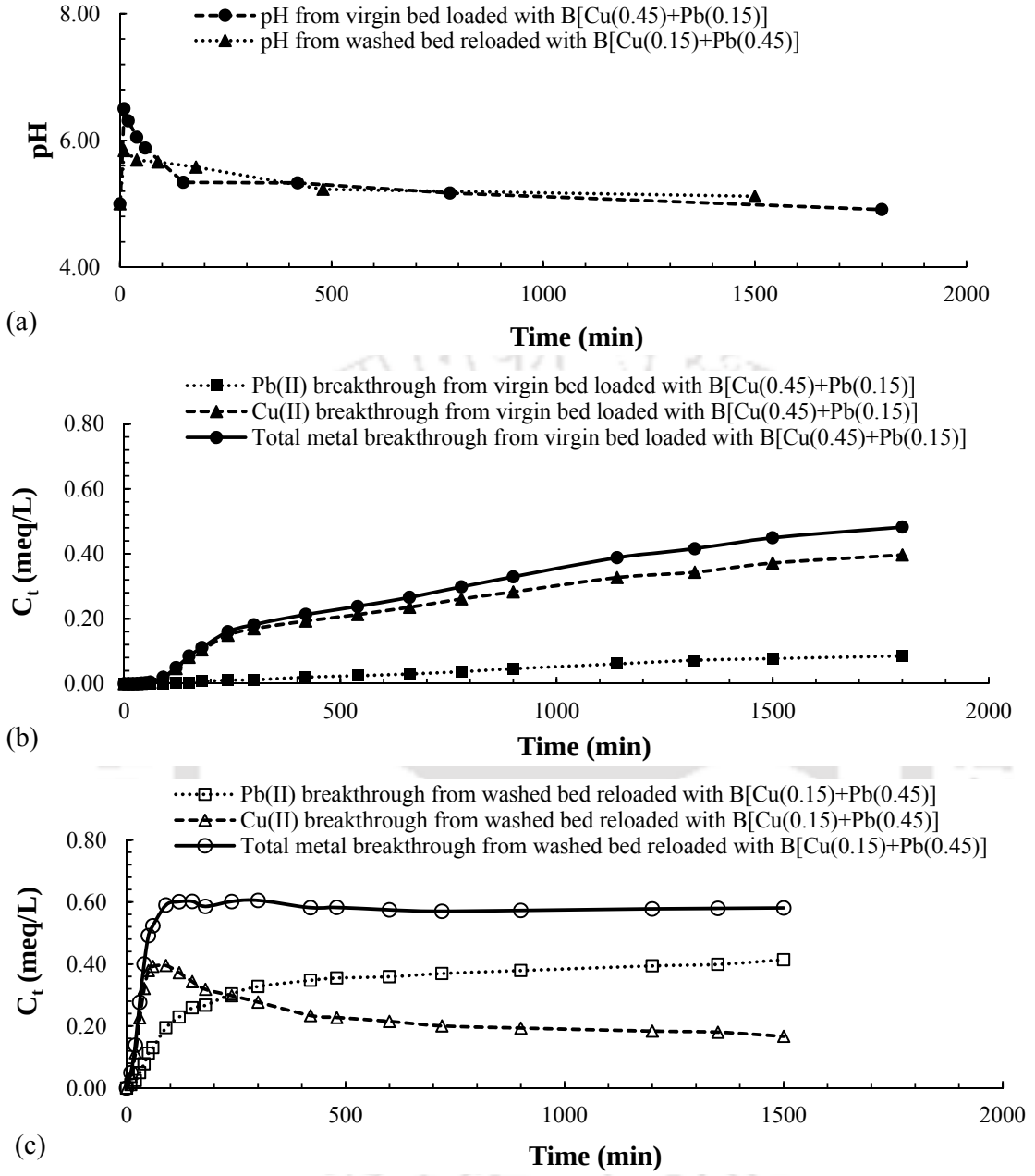

Fig. 5.122: Virgin GAA bed loaded with B[Cu(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cu(0.15)+Pb(0.45)] combination under uncontrolled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cu(0.45)+Pb(0.15)] combination: Cu(II) = 0.45±0.01 meq/L + Pb(II) = 0.15±0.02 meq/L and B[Cu(0.15)+Pb(0.45)] combination: Cu(II) = 0.15±0.00 meq/L + Pb(II) = 0.45±0.01 meq/L, Initial adjusted pH = 5.00±0.04, Temp. = 30±1 °C} (Each data represents an average of two independent experimental values).

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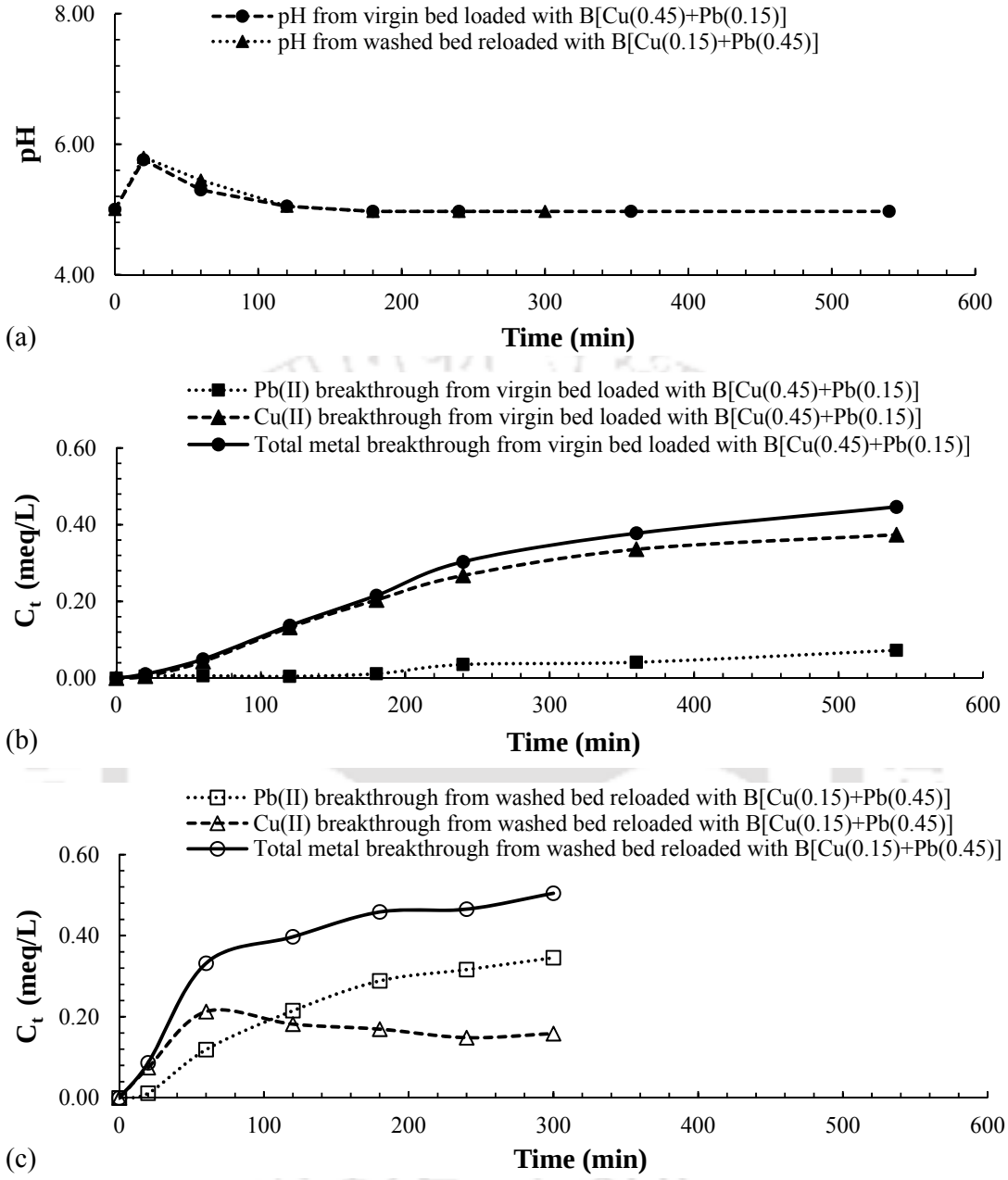

Fig. 5.123: Virgin GAA bed loaded with B[Cu(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cu(0.15)+Pb(0.45)] combination under controlled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cu(0.45)+Pb(0.15)] combination: Cu(II) = 0.43±0.01 meq/L + Pb(II) = 0.16±0.02 meq/L and B[Cu(0.15)+Pb(0.45)] combination: Cu(II) = 0.14±0.00 meq/L + Pb(II) = 0.45±0.01 meq/L, Buffered pH = 5.00±0.04, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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Under uncontrolled pH conditions (Fig. 5.122), when the virgin GAA bed was loaded with B[Cu(0.45)+Pb(0.15)] combination; Cu(II), Pb(II) and total metal ions were not detected in the effluent up to initial 60-90 min. of operation. Thereafter, Cu(II) and total metal ions concentration started to increase and reached to values of 0.170 and 0.182 meq/L respectively at around 300 min. of operation while rise in Pb(II) concentration was very slow and reached to a value of only 0.046 meq/L at around 900 min. of operation. The breakthrough curves for Cu(II) and total metal ions rised further and reached to concentration values of 0.397 and 0.482 meq/L respectively at the end of operation [Fig. 5.122(b)]. When the virgin bed loaded with B[Cu(0.45)+Pb(0.15)] combination was washed and then reloaded with B[Cu(0.15)+Pb(0.45)] combination, it yielded a relatively steeper breakthrough curve for Pb(II) metal [Fig. 5.122(c)] with washed bed appeared to get exhausted with respect to Pb(II) metal in approximately 600 min. of operation. During reloading of the washed bed with B[Cu(0.15)+Pb(0.45)] combination [Fig. 5.122(c)], concentration of Cu(II) metal was observed to rise rapidly in the effluent from a concentration value of zero to a peak value of approximately 0.395 meq/L at around 90 min. of operation. This higher Cu(II) concentration in the effluent compared to Cu(II) concentration in the influent might be due to migration of a part of Cu(II) metal removed and retained during loading of virgin bed with B[Cu(0.45)+Pb(0.15)] combination. After 90 min. of operation, migrated Cu(II) metal concentration started to decrease and reached to a value of around 0.201 meq/L {i.e. higher than influent Cu(II) concentration in B[Cu(0.15)+Pb(0.45)] combination} at 720 min. of operation. When the washed GAA bed was reloaded with B[Cu(0.15)+Pb(0.45)] combination, pH of the effluent increased to 5.84 in the first 10 min. of operation and then decreased to 5.58 at around 180 min. of operation. The increase in pH of the effluent above the precipitation pH value of metal ions during initial time period of washed column operation might have caused Cu(II) metal removal by precipitation and hence Cu(II) concentration in the effluent might be observed less than Cu(II) concentration in influent i.e. 0.15 meq/L. However, pH of the effluent started to decrease as the washed column operation proceeded further with simultaneous removal of Cu(II) and Pb(II) metal ions. Also, higher concentration of Pb(II) metal in B[Cu(0.15)+Pb(0.45)] combination might have caused migration of loosely bound Cu(II) metal ion from the washed bed which consequently resulted in increased concentration of Cu(II) metal ion in effluent than Cu(II) concentration in the influent. Similar breakthrough curves for virgin bed loaded with B[Cu(0.45)+Pb(0.15)] combination followed by reloading with B[Cu(0.15)+Pb(0.45)] combination along with

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variation in effluent pH for bed depths of 4.5 and 6.0 cm at a flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.25 and B.26).

Under controlled pH conditions (Fig. 5.123), pH of the effluent from the virgin bed of GAA when loaded with B[Cu(0.45)+Pb(0.15)] combination increased to 5.76 in the first 20 min. of operation from initially buffered pH value of 5.00. After initial 20 min., the effluent pH decreased to around 5.30 within 60 min. of operation. As the operation proceeded beyond 60 min., pH of the effluent further decreased and finally reached to a value of 4.97 at around 540 min. of operation. When the washed GAA bed was reloaded with B[Cu(0.15)+Pb(0.45)] combination, pH of the effluent increased to 5.80 in the first 20 min. of operation. After 20 min., pH of the effluent decreased to a value of 5.45 at around 60 min. of operation. The pH of the effluent at the end of 300 min. of operation was observed as 4.97. As pH of the effluent increased above 5.50 during the first 20-60 min. of operation of virgin and washed beds, Cu(II) and Pb(II) metal removal might also be possible due to precipitation. The effluent pH from the column beds was observed to initially increase rapidly and then decrease. This aspect of variation in effluent pH from column beds appeared to be unusual which is needed to be investigated in detail.

Under controlled pH conditions (Fig. 5.123), when the virgin GAA bed was loaded with B[Cu(0.45)+Pb(0.15)] combination; Cu(II) and total metal ions were not detected in the effluent up to the first 20 min. of operation. Thereafter, Cu(II) and total metal ions concentration started to increase and reached to values of 0.268 and 0.303 meq/L respectively at around 240 min. of operation while increase in Pb(II) concentration was slow and reached to a value of only 0.073 meq/L at the end of operation. After 240 min. of operation, the breakthrough curves for Cu(II) and total metal ions increased further and reached to concentration values of 0.374 and 0.447 meq/L respectively at the end of operation [Fig. 5.123(b)]. When the virgin bed loaded with B[Cu(0.45)+Pb(0.15)] combination was washed and then reloaded with B[Cu(0.15)+Pb(0.45)] combination, it yielded a relatively steeper breakthrough curve for Pb(II) metal [Fig. 5.123(c)] with washed bed appearing to get exhausted with respect to Pb(II) metal ion in approximately 300 min. of operation. During reloading of the washed bed with B[Cu(0.15)+Pb(0.45)] combination [Fig. 5.123(c)], concentration of Cu(II) metal was observed to rise rapidly in the effluent from a concentration value of zero to a peak value of approximately 0.213 meq/L at around 60 min.

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of operation. This higher Cu(II) concentration in the effluent might be the result of migration of a part of Cu(II) metal removed and retained during loading of virgin bed with B[Cu(0.45)+Pb(0.15)] combination. After the first 60 min. of operation, migrated Cu(II) metal ion concentration started to decrease and reached to a value of 0.159 meq/L {i.e. higher than influent Cu(II) concentration in B[Cu(0.15)+Pb(0.45)] combination} at the end of operation. When the washed GAA bed was reloaded with B[Cu(0.15)+Pb(0.45)] combination, pH of the effluent increased to 5.80 in the first 20 min. of operation and then decreased to 5.45 at around 60 min. of operation. The increase in pH of the effluent above the precipitation pH value of metal ions during initial time period of washed column operation might have caused Cu(II) metal removal by precipitation and hence Cu(II) concentration in the effluent might be observed less than Cu(II) concentration in influent i.e. 0.15 meq/L. However, pH of the effluent started to decrease as the washed column operation proceeded further with simultaneous removal of Cu(II) and Pb(II) metal ions. Also, higher concentration of Pb(II) metal in B[Cu(0.15)+Pb(0.45)] combination might have caused migration of loosely bound Cu(II) metal ion from the washed bed which consequently resulted in increased concentration of Cu(II) metal ion in effluent than Cu(II) concentration in the influent. Similar breakthrough curves for virgin bed loaded with B[Cu(0.45)+Pb(0.15)] combination followed by reloading with B[Cu(0.15)+Pb(0.45)] combination along with variation in effluent pH for bed depths of 4.5 and 6.0 cm at a flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.27 and B.28).

A mass balance was carried out to estimate Cu(II), Pb(II) and total metal removed by column beds under uncontrolled and controlled pH conditions when virgin bed was loaded with B[Cu(0.45)+Pb(0.15)] combination followed by washing and then again reloading with B[Cu(0.15)+Pb(0.45)] combination. Mass balance for metal removal under uncontrolled and controlled pH conditions by the virgin GAA beds when loaded with B[Cu(0.45)+Pb(0.15)] combination was carried out for a time period when the total metal ion concentration in the effluent was equal to or more than 50% of the total metal ion concentration in the influent. As the migration of Cu(II) metal was observed during reloading of washed bed with B[Cu(0.15)+Pb(0.45)] combination, mass balance for metal removal under uncontrolled and controlled pH conditions by washed GAA beds was carried out for a time period when Pb(II) metal ion concentration in the effluent was equal to or more than 50% of the total metal ion concentration in the influent. The summary of mass balance is presented in Table 5.63.

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Table 5.63: Summary of mass balance of metal removed by column beds when virgin GAA bed loaded with B[Cu(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cu(0.15)+Pb(0.45)] combination under uncontrolled and controlled pH conditions.

pH conditions	Flow rate (mL/min)	Bed depth (cm)	Virgin bed loaded with B[Cu(0.45)+Pb(0.15)] combination			Amount of washed out metal (meq)	Washed bed reloaded with B[Cu(0.15)+Pb(0.45)] combination				Total metal removed by bed (meq)	Total metal removed per unit weight of bed (meq/g)
			Initial metal conc. (meq/L)	t_E (min)	Metal removed by bed (meq)		Initial metal conc. (meq/L)	t_E (min)	Metal removed by bed (meq)	Metal migrated from bed (meq) #		
Uncontrolled	2.0	3.0	Cu(II) = 0.45±0.01	780	0.4464	0.0225	Cu(II) = 0.15±0.00	230^	-	0.0749	0.6620	0.0704
			Pb(II) = 0.15±0.02		0.2081	0.0110	Pb(II) = 0.45±0.01		0.1159	-		
			Total = 0.60±0.02		0.6545	0.0335	Total = 0.60±0.01		0.1159	0.0749		
		4.5	Cu(II) = 0.45±0.01	1250	0.6804	0.0117	Cu(II) = 0.15±0.03	660^	-	0.0849	1.2642	0.0958
			Pb(II) = 0.15±0.01		0.3333	0.0078	Pb(II) = 0.45±0.01		0.3549	-		
			Total = 0.60±0.01		1.0137	0.0195	Total = 0.60±0.02		0.3549	0.0849		
		6.0	Cu(II) = 0.46±0.01	1643	0.9886	0.0345	Cu(II) = 0.15±0.00	850^	-	0.2197	1.6903	0.1006
			Pb(II) = 0.15±0.01		0.4684	0.0156	Pb(II) = 0.45±0.02		0.5031	-		
			Total = 0.61±0.01		1.4570	0.0501	Total = 0.60±0.01		0.5031	0.2197		
Controlled	2.0	3.0	Cu(II) = 0.43±0.01	240	0.1468	0.0260	Cu(II) = 0.14±0.00	194^	-	0.0083	0.2708	0.0288
			Pb(II) = 0.16±0.02		0.0692	0.0230	Pb(II) = 0.45±0.01		0.1121	-		
			Total = 0.59±0.02		0.2160	0.0490	Total = 0.59±0.01		0.1121	0.0083		
		4.5	Cu(II) = 0.43±0.01	323	0.1890	0.0140	Cu(II) = 0.14±0.00	300^	-	0.0103	0.4219	0.0320
			Pb(II) = 0.16±0.01		0.0956	0.0100	Pb(II) = 0.45±0.02		0.1716	-		
			Total = 0.59±0.01		0.2846	0.0240	Total = 0.59±0.01		0.1716	0.0103		
		6.0	Cu(II) = 0.43±0.01	392	0.2281	0.0350	Cu(II) = 0.14±0.00	360^	-	0.0062	0.4859	0.0289
			Pb(II) = 0.16±0.01		0.1156	0.0160	Pb(II) = 0.45±0.02		0.1994	-		
			Total = 0.59±0.01		0.3437	0.0510	Total = 0.59±0.01		0.1994	0.0062		

t_E = exhaustion time (effluent total metal concentration equal to 50% of influent total metal concentration from virgin and washed beds respectively, if not specified); ^ = exhaustion time corresponding to Pb(II) effluent concentration equal to 50% of influent total metal concentration; # = total amount of estimated migrated metal ion in the effluent reduced by amount of migrating metal ion loaded onto the washed bed; Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA respectively.

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Under uncontrolled pH conditions, when the column bed of depth 3.0 cm was operated at a flow rate of 2.0 mL/min, exhaustion time (t_E) was estimated as 780 min. for virgin GAA bed loaded with B[Cu(0.45)+Pb(0.15)] combination and 230 min. for washed bed reloaded with B[Cu(0.15)+Pb(0.45)] combination. The Cu(II), Pb(II) and total metal removal by virgin GAA bed up to 780 min. were estimated as 0.4464, 0.2081 and 0.6545 meq respectively. During reloading of the washed bed with B[Cu(0.15)+Pb(0.45)] combination, 0.1159 meq of Pb(II) and 0.6620 meq of total metal removal up to 230 min. was observed along with 0.0749 meq of Cu(II) migrated from the washed bed. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 0.6620 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.0704 meq/g. Under controlled pH conditions, when the column bed of depth 3.0 cm was operated at a flow rate of 2.0 mL/min, exhaustion time (t_E) was estimated as 240 min. for virgin GAA bed loaded with B[Cu(0.45)+Pb(0.15)] combination and 194 min. for washed bed loaded with B[Cu(0.15)+Pb(0.45)] combination. The Cu(II), Pb(II) and total metal removal by virgin GAA bed up to 240 min. were estimated as 0.1468, 0.0692 and 0.2160 meq respectively. During reloading of the washed bed with B[Cu(0.15)+Pb(0.45)] combination, 0.1121 meq of Pb(II) and 0.2708 meq of total metal removal up to 194 min. was observed along with 0.0083 meq of Cu(II) migrated from the washed bed. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 0.2708 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.0288 meq/g.

In order to investigate effect of GAA bed depths on metal removal when the virgin GAA bed was loaded with B[Cu(0.45)+Pb(0.15)] combination and washed bed was again reloaded with B[Cu(0.15)+Pb(0.45)] combination, the breakthrough curves for a linear flow rate of 2.0 mL/min with three different bed depths of 3.0, 4.5 and 6.0 cm of GAA operated under uncontrolled and controlled pH conditions are re-plotted and presented in Fig. 5.124 and 5.125 respectively. It could be observed from these figures that breakthrough curves appear to shift towards right with increase in bed depths. The service times (t_B) for virgin and washed beds were estimated from the breakthrough curves when the effluent metal ion concentration was 5% of influent metal ion concentration (i.e. 0.03 meq/L) with respect to Cu(II), Pb(II) and total metal. The corresponding breakthrough throughput volumes (V_B) were also estimated. All the estimated service times and breakthrough throughput volumes

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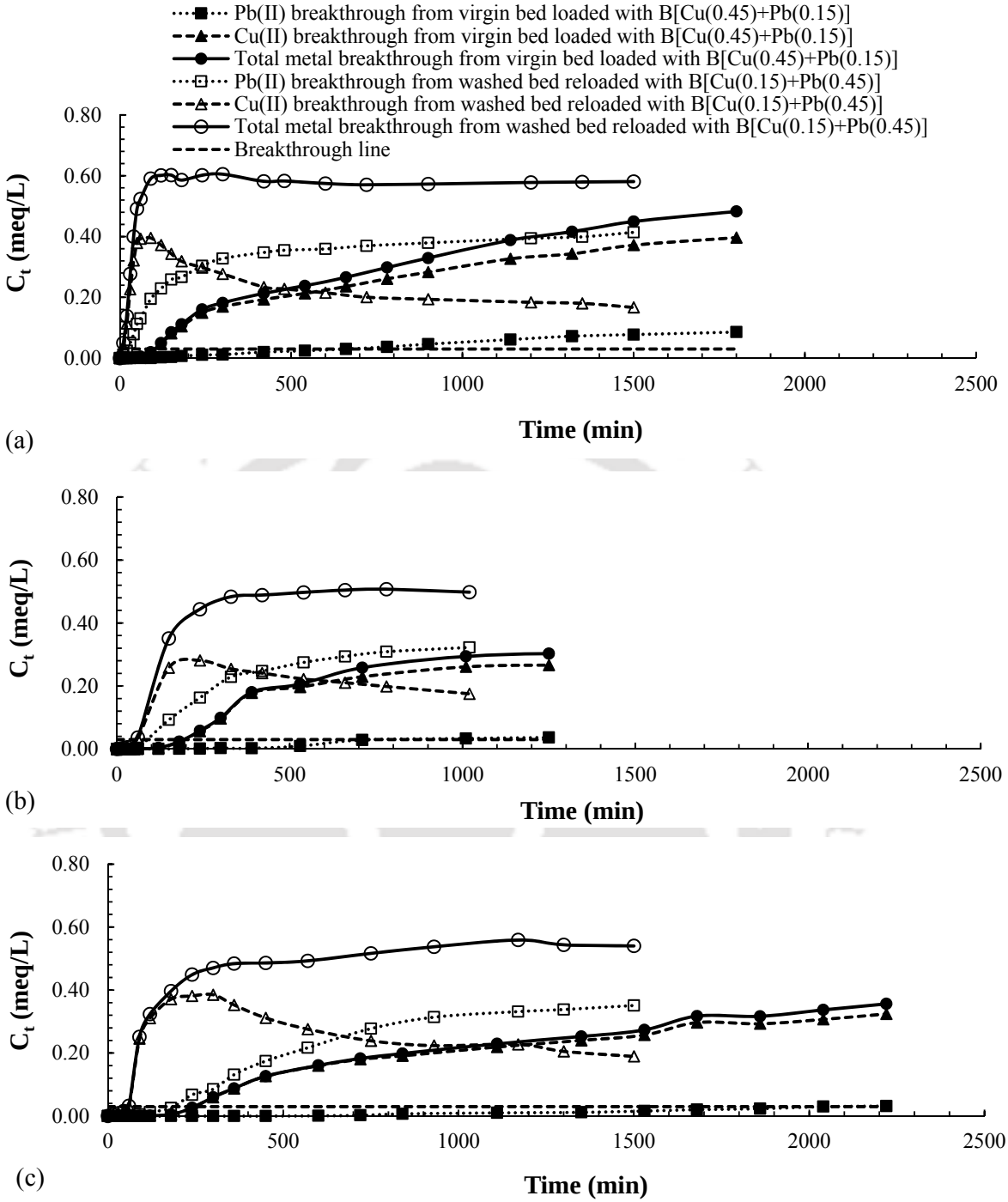

Fig. 5.124: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with B[Cu(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cu(0.15)+Pb(0.45)] combination at a flow rate of 2.0 mL/min under uncontrolled pH conditions {Initial metal conc. in B[Cu(0.45)+Pb(0.15)] combination: Cu(II) = 0.45±0.01 meq/L + Pb(II) = 0.15±0.02 meq/L and B[Cu(0.15)+Pb(0.45)] combination: Cu(II) = 0.15±0.00 meq/L + Pb(II) = 0.45±0.01 meq/L, Initial adjusted pH = 5.00±0.04, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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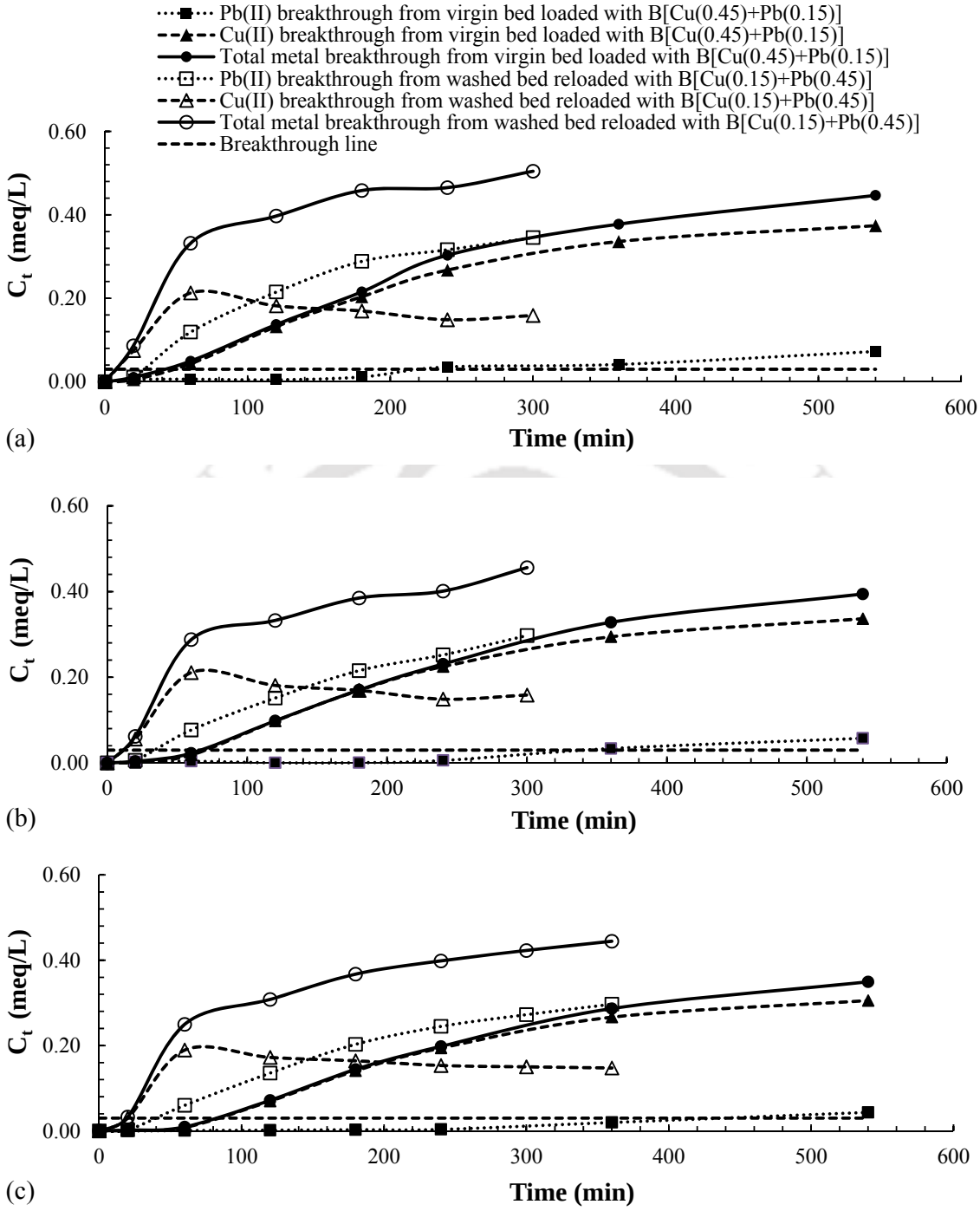

Fig. 5.125: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with B[Cu(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cu(0.15)+Pb(0.45)] combination at a flow rate of 2.0 mL/min under controlled pH conditions {Initial metal conc. in B[Cu(0.45)+Pb(0.15)] combination: Cu(II) = 0.43±0.01 meq/L + Pb(II) = 0.16±0.02 meq/L and B[Cu(0.15)+Pb(0.45)] combination: Cu(II) = 0.14±0.00 meq/L + Pb(II) = 0.45±0.01 meq/L, Buffered pH = 5.00±0.04, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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for uncontrolled and controlled pH conditions have been tabulated in Table 5.64. The breakthrough throughput volumes for Cu(II), Pb(II) and total metal ions increased with increase in bed depths at the fixed flow rate as could be seen from Table 5.64. An increase in the service time was observed when the bed depth increased from 3.0 to 6.0 cm. The increase in Cu(II), Pb(II) and total metal ions removal from the bulk metal ion solution with increase in bed depths were possibly due to increase in the amount of adsorbent mass in the larger beds which provided greater opportunities for metal removal.

5.7.9 Breakthrough curves for virgin GAA bed loaded with B[Cu(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cu(0.45)+Pb(0.15)] combination under uncontrolled and controlled pH conditions

The studies were carried out by exposing (or loading) the virgin (or fresh) GAA bed with B[Cu(0.15)+Pb(0.45)] combination till the bed exhausted or yielded effluents with more than 50% of total initial metal ion concentration. The loaded bed was then washed with 100 bed volumes of de-mineralized water to remove residual or un-adsorbed metal ions from pore volume of the bed. The washed bed was then again exposed (or reloaded) with B[Cu(0.45)+Pb(0.15)] combination till the bed exhausted or yielded effluents with more than 50% of total initial metal ion concentration. The typical breakthrough curves for Cu(II), Pb(II) and total metal ions in terms of metal ions remaining in effluent (C_t) versus time for virgin bed loaded with B[Cu(0.15)+Pb(0.45)] combination followed by reloading of washed bed with B[Cu(0.45)+Pb(0.15)] combination for a bed depth of 3.0 cm at a flow rate of 2.0 mL/min along with variation in effluent pH obtained under uncontrolled and controlled pH conditions are presented in Fig. 5.126 and 5.127 respectively.

Under uncontrolled pH conditions (Fig. 5.126), pH of the effluent from the virgin bed of GAA when loaded with B[Cu(0.15)+Pb(0.45)] combination increased to 6.47 in the first 10 min. of operation from initially adjusted pH value of 5.00. After initial 10 min., the effluent pH decreased to around 5.71 within 60 min. of operation. As operation proceeded beyond 60 min., pH of the effluent further decreased to 5.13 at around 540 min. of operation and finally reached to a value of 4.88 at around 1500 min. of operation. When the washed GAA bed was reloaded with B[Cu(0.45)+Pb(0.15)] combination, pH of the effluent increased to 6.80 in the first 10 min. of operation. After 10 min., pH of the effluent decreased to a value of 5.65 at around 180 min. of operation. The pH of the effluent at the end of 1500 min. of

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Table 5.64: Summary of breakthrough results at a fixed flow rate but varying depths of virgin GAA bed loaded with B[Cu(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cu(0.15)+Pb(0.45)] combination under uncontrolled and controlled pH conditions.

pH conditions	Bed depth (cm)	Virgin bed loaded with B[Cu(0.45)+Pb(0.15)] combination						Washed bed reloaded with B[Cu(0.15)+Pb(0.45)] combination					
		Initial metal conc. (meq/L)	t_B (min)	V_B (mL)	Metal removed (meq)			Initial metal conc. (meq/L)	t_B (min)	V_B (mL)	Metal removed (meq)		
					Cu(II)	Pb(II)	Total				Cu(II)	Pb(II)	Total
Uncontrolled	3.0	Cu(II) = 0.45±0.01	101	202	0.089	0.031	0.120	Cu(II) = 0.15±0.00	8	16	0.002	0.007	0.009
		Pb(II) = 0.15±0.02	660	1320	0.399	0.180	0.579	Pb(II) = 0.45±0.01	22	44	0.004	0.019	0.023
		Total = 0.60±0.02	100	200	0.088	0.030	0.118	Total = 0.60±0.01	6	12	0.002	0.005	0.007
	4.5	Cu(II) = 0.45±0.01	193	386	0.171	0.058	0.229	Cu(II) = 0.15±0.03	57	114	0.016	0.052	0.068
		Pb(II) = 0.15±0.01	710	1420	0.467	0.205	0.672	Pb(II) = 0.45±0.01	86	172	0.016	0.075	0.091
		Total = 0.60±0.01	192	384	0.170	0.058	0.228	Total = 0.60±0.02	54	108	0.015	0.049	0.064
	6.0	Cu(II) = 0.46±0.01	247	494	0.226	0.074	0.300	Cu(II) = 0.15±0.00	60	120	0.017	0.053	0.070
		Pb(II) = 0.15±0.01	2040	4080	1.123	0.568	1.691	Pb(II) = 0.45±0.02	186	372	0.020	0.162	0.182
		Total = 0.61±0.01	247	494	0.226	0.074	0.300	Total = 0.60±0.01	58	116	0.016	0.052	0.068
Controlled	3.0	Cu(II) = 0.43±0.01	46	92	0.039	0.014	0.053	Cu(II) = 0.14±0.00	8	16	0.052	0.007	0.059
		Pb(II) = 0.16±0.02	226	452	0.141	0.066	0.207	Pb(II) = 0.45±0.01	27	54	0.004	0.023	0.027
		Total = 0.59±0.02	40	80	0.034	0.012	0.046	Total = 0.59±0.01	7	14	0.001	0.006	0.007
	4.5	Cu(II) = 0.43±0.01	68	136	0.058	0.021	0.079	Cu(II) = 0.14±0.00	11	22	0.002	0.001	0.003
		Pb(II) = 0.16±0.01	360	720	0.202	0.106	0.308	Pb(II) = 0.45±0.02	33	66	0.005	0.029	0.034
		Total = 0.59±0.01	66	132	0.056	0.020	0.076	Total = 0.59±0.01	9	18	0.002	0.009	0.011
	6.0	Cu(II) = 0.43±0.01	81	162	0.068	0.025	0.093	Cu(II) = 0.14±0.00	20	40	0.005	0.018	0.023
		Pb(II) = 0.16±0.01	436	872	0.241	0.126	0.367	Pb(II) = 0.45±0.02	39	78	0.006	0.034	0.040
		Total = 0.59±0.01	80	160	0.067	0.025	0.092	Total = 0.59±0.01	20	40	0.005	0.018	0.023

V_B = Breakthrough throughput volumes at effluent metal concentration equal to 0.03 meq/L; t_B = service time at breakthrough; Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA respectively.

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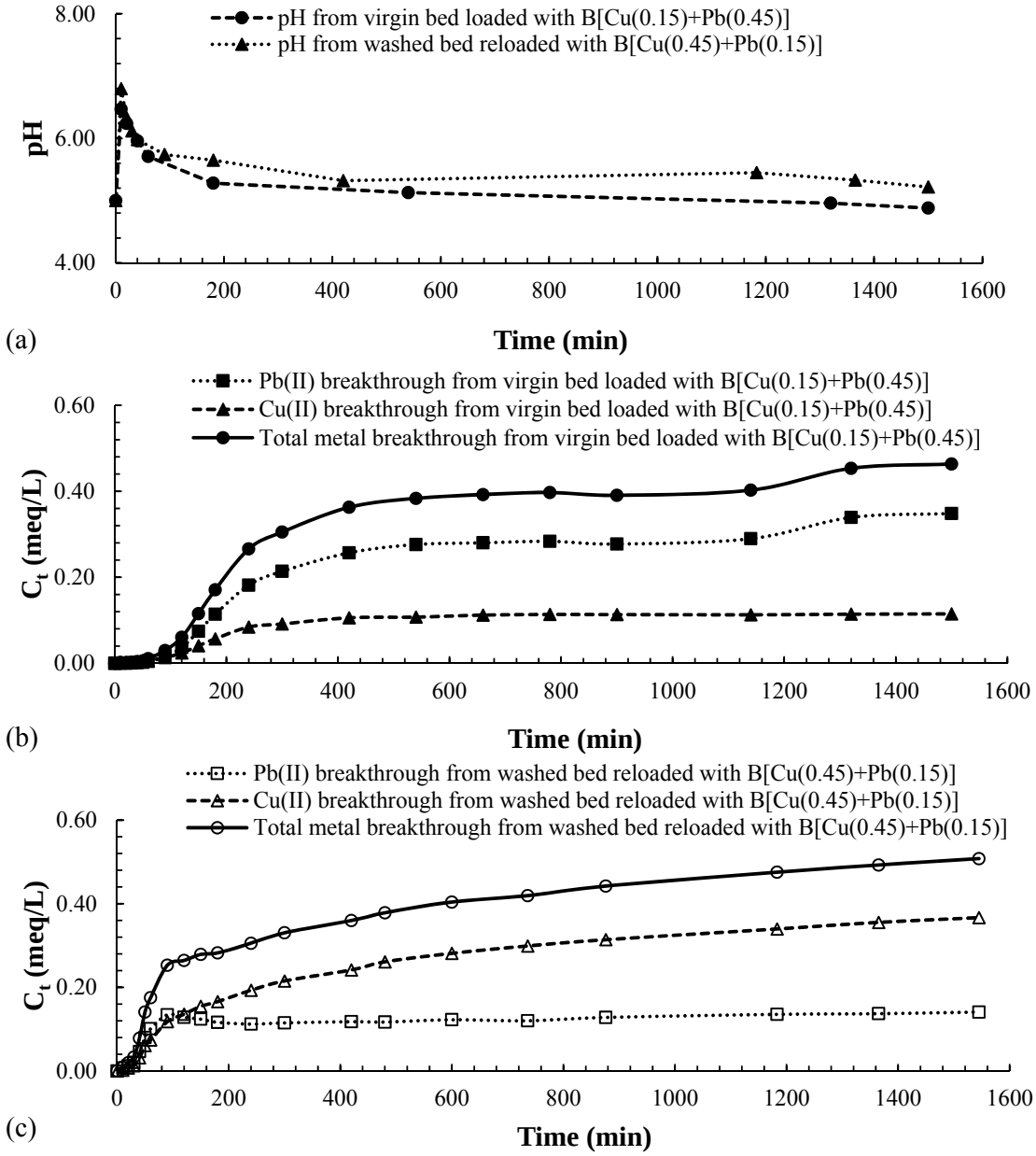

Fig. 5.126: Virgin GAA bed loaded with B[Cu(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cu(0.45)+Pb(0.15)] combination under uncontrolled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cu(0.15)+Pb(0.45)] combination: Cu(II) = 0.15±0.01 meq/L + Pb(II) = 0.44±0.02 meq/L and B[Cu(0.45)+Pb(0.15)] combination: Cu(II) = 0.45±0.00 meq/L + Pb(II) = 0.15±0.01 meq/L, Initial adjusted pH = 5.00±0.05, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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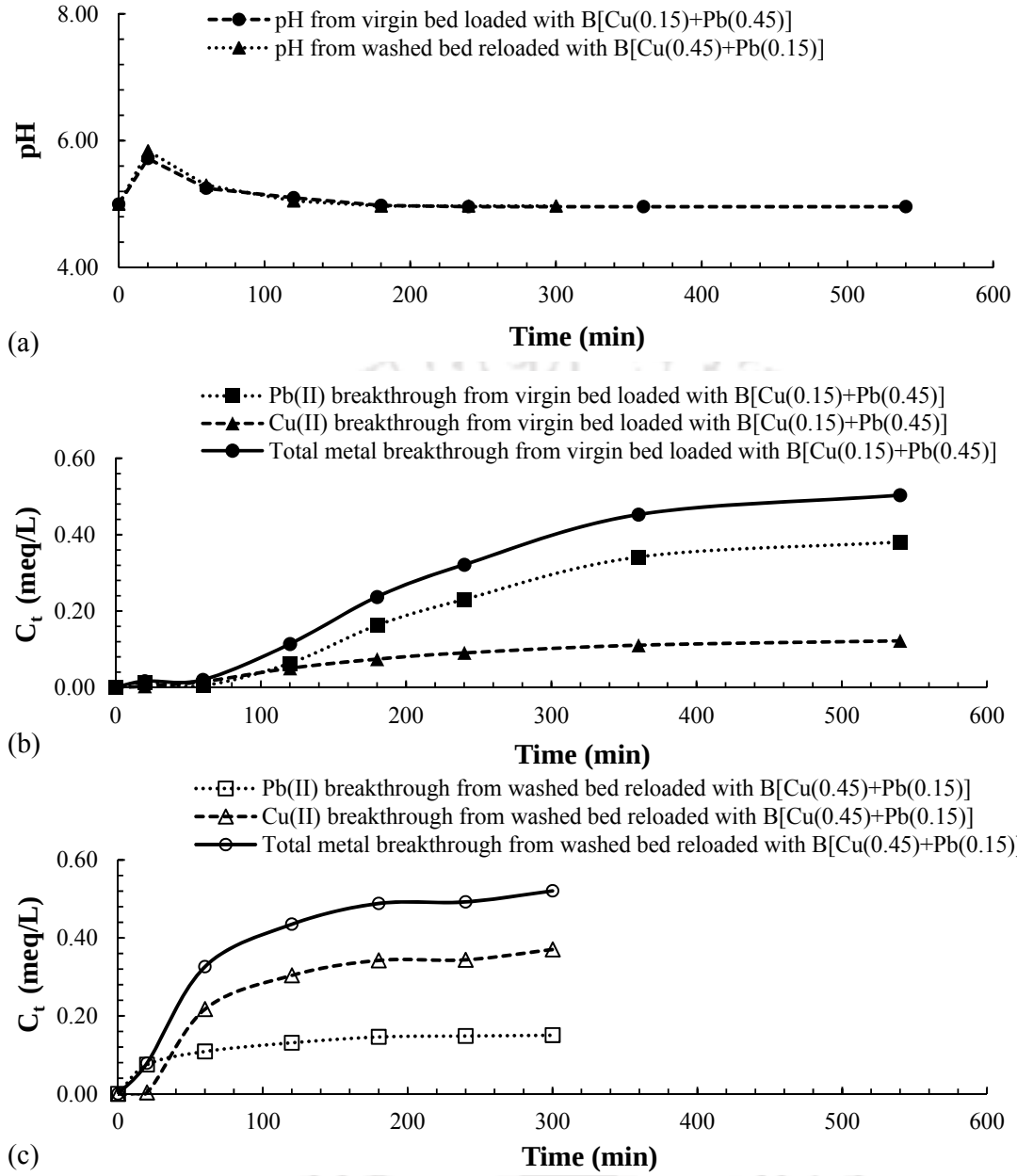

Fig. 5.127: Virgin GAA bed loaded with B[Cu(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cu(0.45)+Pb(0.15)] combination under controlled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cu(0.15)+Pb(0.45)] combination: Cu(II) = 0.14±0.01 meq/L + Pb(II) = 0.45±0.02 meq/L and B[Cu(0.45)+Pb(0.15)] combination: Cu(II) = 0.43±0.01 meq/L + Pb(II) = 0.16±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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operation was observed as 5.22. The removal of Cu(II) and Pb(II) metal ions by virgin GAA bed up to first 60-180 min. of operation and by washed GAA bed up to approximately first 180-420 min. of operation might have taken place due to precipitation along with adsorption as pH of the effluent increased above 5.50 while in the later phase of operation removal of both the metal ions might have taken place due to adsorption only. The effluent pH from the column beds was observed to initially increase rapidly and then decrease. This aspect of variation in effluent pH from column beds appeared to be unusual which is needed to be investigated in detail.

Under uncontrolled pH conditions (Fig. 5.126), when the virgin GAA bed was loaded with B[Cu(0.15)+Pb(0.45)] combination; Cu(II), Pb(II) and total metal ions were not detected in the effluent up to initial 60 min. of operation. After 60 min., the breakthrough curves for Pb(II) and total metal ions started to increase rapidly and reached to values of 0.182 and 0.266 meq/L respectively while Cu(II) breakthrough curve started to rise slowly and reached to a value of only 0.084 meq/L at around 240 min. of operation. After 240 min. of operation, the breakthrough curves increased slowly indicating that the bed was nearing to get exhausted [Fig. 5.126(b)]. When the virgin bed loaded with B[Cu(0.15)+Pb(0.45)] combination was washed and then reloaded with B[Cu(0.45)+Pb(0.15)] combination, it yielded a relatively steeper breakthrough curves for Cu(II), Pb(II) and total metal ions [Fig. 5.126(c)]. The washed GAA bed appeared to get exhausted with Cu(II), Pb(II) and total metal ions in approximately 736, 300 and 736 min. of operation respectively. During reloading of the washed bed with B[Cu(0.45)+Pb(0.15)] combination [Fig. 5.126(c)], concentration of Pb(II) metal was observed to rise in the effluent from a concentration value of zero to a peak value of 0.135 meq/L at around 90 min. of operation, thereafter reached to a value of 0.141 meq/L at around 1545 min. of operation. Did it mean that the washed bed had additional potential for the removal of Pb(II) ion reloaded with lower initial Pb(II) concentration compared to loading of virgin bed with higher initial Pb(II) concentration? It is open for further investigation. Similar breakthrough curves for virgin bed loaded with B[Cu(0.15)+Pb(0.45)] combination followed by reloading with B[Cu(0.45)+Pb(0.15)] combination along with variation in effluent pH for bed depths of 4.5 and 6.0 cm at a flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.29 and B.30).

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Under controlled pH conditions (Fig. 5.127), pH of the effluent from the virgin bed of GAA when loaded with B[Cu(0.15)+Pb(0.45)] combination increased to 5.72 in the first 20 min. of operation from initially buffered pH value of 5.00. After initial 20 min., the effluent pH decreased to around 5.25 within 60 min. of operation. As operation proceeded beyond 60 min., pH of the effluent further decreased and finally reached to a value of 4.96 at around 540 min. of operation. When the washed GAA bed was reloaded with B[Cu(0.45)+Pb(0.15)] combination, pH of the effluent increased to 5.84 in the first 20 min. After initial 20 min., pH of the effluent decreased to 5.30 at around 60 min. of operation. The pH of the effluent at the end of operation was observed as 4.97. The effluent pH was observed to initially increase rapidly and then decrease in the column studies. This aspect is needed to be investigated in detail. As pH of the effluent during first 20-60 min. of virgin GAA bed loading and washed bed reloading went above 5.50, Cu(II) and Pb(II) metals removal might also be possible due to precipitation.

Under controlled pH conditions (Fig. 5.127), when the virgin GAA bed was loaded with B[Cu(0.15)+Pb(0.45)] combination; Cu(II), Pb(II) and total metal ions were not detected in the effluent up to initial 60 min. of operation. After 60 min., the breakthrough curves for Cu(II), Pb(II) and total metal ions started to increase and reached to values of 0.074, 0.163 and 0.237 meq/L respectively at around 180 min. of operation. After 180 min. of operation, the breakthrough curves increased slowly indicating that the bed was nearing to get exhausted [Fig. 5.127(b)]. When the virgin bed loaded with B[Cu(0.15)+Pb(0.45)] combination was washed and then reloaded with B[Cu(0.45)+Pb(0.15)] combination, it yielded a relatively steeper breakthrough curves for Cu(II), Pb(II) and total metal ions [Fig. 5.127(c)]. The washed GAA bed appeared to get exhausted with Cu(II), Pb(II) and total metal ions in approximately 180, 120 and 180 min. of operation respectively. During reloading of the washed bed with B[Cu(0.45)+Pb(0.15)] combination [Fig. 5.127(c)], concentration of Pb(II) metal was observed to rise in the effluent from a concentration value of zero to a value of 0.075 meq/L at around 20 min. of operation, thereafter reached to a value of 0.150 meq/L at around 300 min. of operation. Did it mean that the washed bed had additional potential for the removal of Pb(II) ion reloaded with lower initial Pb(II) concentration compared to loading of virgin bed with higher initial Pb(II) concentration? It is open for further investigation. Similar breakthrough curves for virgin bed loaded with B[Cu(0.15)+Pb(0.45)] combination followed by reloading with B[Cu(0.45)+Pb(0.15)] combination along with

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variation in effluent pH for bed depths of 4.5 and 6.0 cm at a flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.31 and B.32).

A mass balance was carried out to estimate Cu(II), Pb(II) and total metal removal by column beds under uncontrolled and controlled pH conditions when virgin bed was loaded with B[Cu(0.15)+Pb(0.45)] combination followed by washing and then again reloading with B[Cu(0.45)+Pb(0.15)] combination. Mass balance for metal removal under uncontrolled and controlled pH conditions by the column beds when loaded or reloaded with binary-metal ion systems was carried out for a time period when the total metal ion concentration in the effluent was equal to or more than 50% of the total metal ion concentration in the influent for virgin bed loading and washed bed reloading. The summary of mass balance for metal removed under uncontrolled and controlled pH conditions by virgin GAA bed loaded with B[Cu(0.15)+Pb(0.45)] combination, washed and then reloaded with B[Cu(0.45)+Pb(0.15)] combination is presented in Table 5.65.

Under uncontrolled pH conditions, when the column bed of depth 3.0 cm was operated at a flow rate of 2.0 mL/min, exhaustion time (t_E) in terms of total metal concentration in the effluent was estimated as 300 min. for virgin GAA bed loaded with B[Cu(0.15)+Pb(0.45)] combination and 240 min. for washed bed reloaded with B[Cu(0.45)+Pb(0.15)] combination. The Cu(II), Pb(II) and total metal removal by virgin GAA bed up to 300 min. were estimated as 0.0641, 0.2097 and 0.2738 meq respectively. During reloading of the washed bed with B[Cu(0.45)+Pb(0.15)] combination; Cu(II), Pb(II) and total metal removal up to 240 min. were observed as 0.1610, 0.0226 and 0.1836 meq respectively. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 0.4398 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.0468 meq/g. Under controlled pH conditions, when the column bed of depth 3.0 cm was operated at a flow rate of 2.0 mL/min, exhaustion time (t_E) in terms of total metal concentration in the effluent was estimated as 222 min. for virgin GAA bed loaded with B[Cu(0.15)+Pb(0.45)] combination and 55 min. for washed bed reloaded with B[Cu(0.45)+Pb(0.15)] combination. The Cu(II), Pb(II) and total metal removal by virgin GAA bed up to 222 min. of operation were estimated as 0.0427, 0.1659 and 0.2085 meq respectively. During reloading of the washed bed with B[Cu(0.45)+Pb(0.15)] combination; Cu(II), Pb(II) and total metal removal up to 55 min. were observed as 0.0397, 0.0091 and 0.0488 meq respectively. Hence the total metal removal by

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Table 5.65: Summary of mass balance of metal removed by column beds when virgin GAA bed loaded with B[Cu(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cu(0.45)+Pb(0.15)] combination under uncontrolled and controlled pH conditions.

pH conditions	Flow rate (mL/min)	Bed depth (cm)	Virgin bed loaded with B[Cu(0.15)+Pb(0.45)] combination			Amount of washed out metal (meq)	Washed bed reloaded with B[Cu(0.45)+Pb(0.15)] combination			Total metal removed by bed (meq)	Total metal removed per unit weight of bed (meq/g)
			Initial metal conc. (meq/L)	t_E (min)	Metal removed by bed (meq)		Initial metal conc. (meq/L)	t_E (min)	Metal removed by bed (meq)		
Uncontrolled	2.0	3.0	Cu(II) = 0.15±0.01	300	0.0641	0.0130	Cu(II) = 0.45±0.00	240	0.1610	0.4398	0.0468
			Pb(II) = 0.44±0.02		0.2097	0.0046	Pb(II) = 0.15±0.01		0.0226		
			Total = 0.59±0.02		0.2738	0.0176	Total = 0.60±0.01		0.1836		
		4.5	Cu(II) = 0.15±0.01	436	0.0911	0.0189	Cu(II) = 0.45±0.00	780	0.4510	0.9622	0.0729
			Pb(II) = 0.44±0.02		0.3360	0.0055	Pb(II) = 0.15±0.01		0.1485		
			Total = 0.59±0.02		0.4271	0.0244	Total = 0.60±0.01		0.5595		
		6.0	Cu(II) = 0.15±0.01	672	0.1373	0.0254	Cu(II) = 0.45±0.00	540	0.3880	1.0901	0.0649
			Pb(II) = 0.44±0.02		0.5012	0.0063	Pb(II) = 0.15±0.01		0.0953		
			Total = 0.59±0.02		0.6385	0.0317	Total = 0.60±0.01		0.4833		
Controlled	2.0	3.0	Cu(II) = 0.14±0.01	222	0.0427	0.0142	Cu(II) = 0.43±0.01	55	0.0397	0.2392	0.0254
			Pb(II) = 0.45±0.02		0.1659	0.0040	Pb(II) = 0.16±0.01		0.0091		
			Total = 0.59±0.02		0.2086	0.0182	Total = 0.59±0.01		0.0488		
		4.5	Cu(II) = 0.15±0.01	349	0.0717	0.0226	Cu(II) = 0.45±0.00	105	0.0749	0.4008	0.0304
			Pb(II) = 0.44±0.02		0.2706	0.0050	Pb(II) = 0.15±0.01		0.0112		
			Total = 0.59±0.02		0.3423	0.0276	Total = 0.60±0.01		0.0861		
		6.0	Cu(II) = 0.15±0.01	393	0.0859	0.0260	Cu(II) = 0.45±0.00	139	0.0985	0.4608	0.0274
			Pb(II) = 0.44±0.02		0.2947	0.0080	Pb(II) = 0.15±0.01		0.0157		
			Total = 0.59±0.02		0.3806	0.0340	Total = 0.60±0.01		0.1142		

t_E = exhaustion time (effluent total metal concentration equal to 50% of influent total metal concentration from virgin and washed beds respectively, if not specified); Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA respectively.

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the column bed (virgin and washed beds together) was estimated as 0.2392 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.0254 meq/g.

In order to investigate the effect of GAA bed depths on metal removal when the virgin bed was loaded with B[Cu(0.15)+Pb(0.45)] combination and washed bed was again reloaded with B[Cu(0.45)+Pb(0.15)] combination, the breakthrough curves for a linear flow rate of 2.0 mL/min with three different bed depths of 3.0, 4.5 and 6.0 cm operated under uncontrolled and controlled pH conditions are re-plotted and presented in Fig. 5.128 and 5.129 respectively. It could be observed from these figures that breakthrough curves appear to shift towards right with increase in bed depths. The service times (t_B) for virgin beds and washed beds were estimated from the breakthrough curves when the effluent metal ions concentration was 5% of influent metal ion concentration (i.e. 0.03 meq/L) with respect to Cu(II), Pb(II) and total metal. The corresponding breakthrough throughput volumes (V_B) were also estimated. All the estimated service times and breakthrough throughput volumes for uncontrolled and controlled pH conditions have been tabulated in Table 5.66. The breakthrough throughput volumes for Cu(II), Pb(II) and total metal ions increased with increase in bed depths at a fixed flow rate as could be seen from Table 5.66. An increase in the service time was observed when the bed depth increased from 3.0 to 6.0 cm. The increase in Cu(II), Pb(II) and total metal ions removal from the bulk metal ion solution with increase in bed depths were possibly due to increase in the amount of adsorbent mass in the larger beds which provided greater opportunities for metal removal.

5.7.10 Breakthrough curves for virgin GAA bed loaded with B[Cr(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cr(0.15)+Pb(0.45)] combination under uncontrolled and controlled pH conditions

The studies were carried out by exposing (or loading) the virgin (or fresh) GAA bed with B[Cr(0.45)+Pb(0.15)] combination till the bed exhausted or yielded effluents with more than 50% of total initial metal ion concentration. The loaded bed was then washed with 100 bed volumes of de-mineralized water to remove residual or un-adsorbed metal ions from pore volume of the bed. The washed GAA bed was then again exposed (or reloaded) with B[Cr(0.15)+Pb(0.45)] combination till the bed exhausted or yielded effluents with more than 50% of total initial metal ion concentration. The typical breakthrough curves for Cr(III), Pb(II) and total metal ions in terms of metal ions remaining in effluent (C_t) versus

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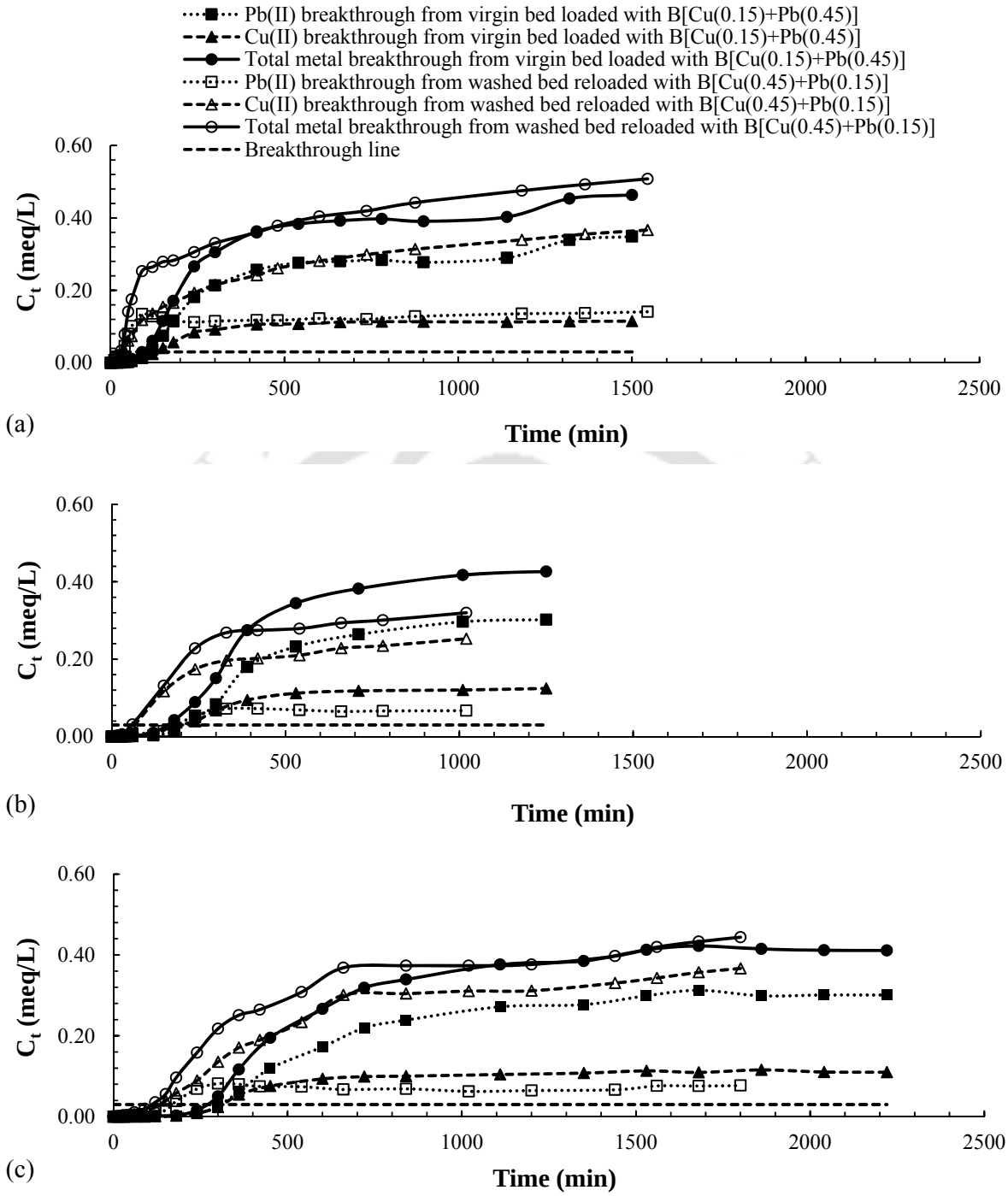

Fig. 5.128: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with B[Cu(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cu(0.45)+Pb(0.15)] combination at a flow rate of 2.0 mL/min under uncontrolled pH conditions {Initial metal conc. in B[Cu(0.15)+Pb(0.45)] combination: Cu(II) = 0.15±0.01 meq/L + Pb(II) = 0.44±0.02 meq/L and B[Cu(0.45)+Pb(0.15)] combination: Cu(II) = 0.45±0.00 meq/L + Pb(II) = 0.15±0.01 meq/L, Initial adjusted pH = 5.00±0.05, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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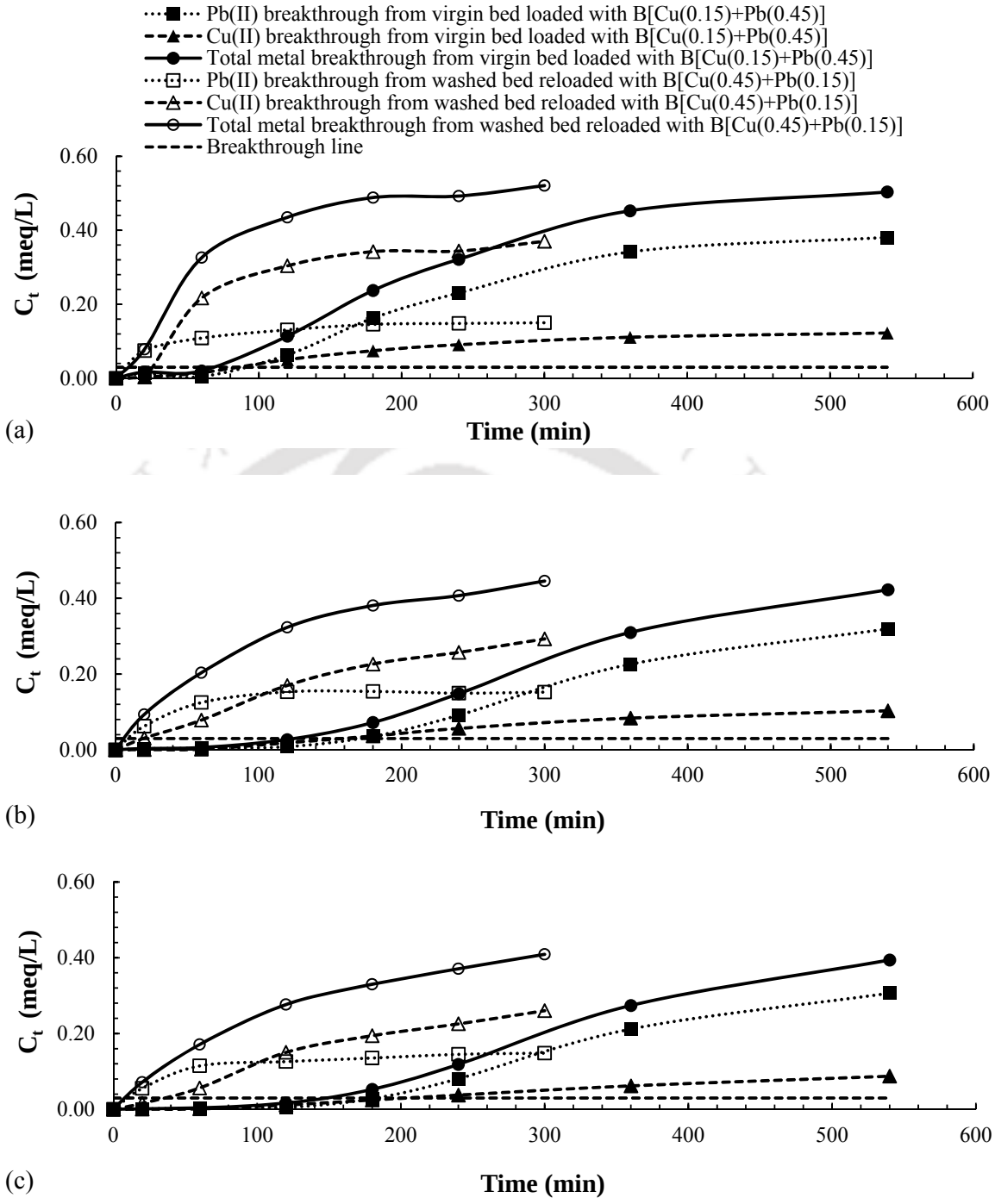

Fig. 5.129: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with B[Cu(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cu(0.45)+Pb(0.15)] combination at a flow rate of 2.0 mL/min under controlled pH conditions {Initial metal conc. in B[Cu(0.15)+Pb(0.45)] combination: Cu(II) = 0.14±0.01 meq/L + Pb(II) = 0.45±0.02 meq/L and B[Cu(0.45)+Pb(0.15)] combination: Cu(II) = 0.43±0.01 meq/L + Pb(II) = 0.16±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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Table 5.66: Summary of breakthrough results at a fixed flow rate but varying depths of virgin GAA bed loaded with B[Cu(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cu(0.45)+Pb(0.15)] combination under uncontrolled and controlled pH conditions.

pH conditions	Bed depth (cm)	Virgin bed loaded with B[Cu(0.15)+Pb(0.45)] combination						Washed bed reloaded with B[Cu(0.45)+Pb(0.15)] combination					
		Initial metal conc. (meq/L)	t_B (min)	V_B (mL)	Metal removed (meq)			Initial metal conc. (meq/L)	t_B (min)	V_B (mL)	Metal removed (meq)		
					Pb(II)	Cu(II)	Total				Pb(II)	Cu(II)	Total
Uncontrolled	3.0	Cu(II) = 0.15±0.01	131	262	0.111	0.037	0.148	Cu(II) = 0.45±0.00	39	78	0.010	0.035	0.045
		Pb(II) = 0.44±0.02	110	220	0.095	0.032	0.127	Pb(II) = 0.15±0.01	33	66	0.009	0.030	0.039
		Total = 0.59±0.02	90	180	0.078	0.026	0.104	Total = 0.60±0.01	30	60	0.008	0.027	0.035
	4.5	Cu(II) = 0.15±0.01	192	384	0.171	0.053	0.224	Cu(II) = 0.45±0.00	65	130	0.019	0.059	0.078
		Pb(II) = 0.44±0.02	206	412	0.182	0.056	0.238	Pb(II) = 0.15±0.01	185	370	0.050	0.147	0.197
		Total = 0.59±0.02	157	314	0.140	0.044	0.184	Total = 0.60±0.01	60	120	0.017	0.054	0.071
	6.0	Cu(II) = 0.15±0.01	312	624	0.274	0.087	0.361	Cu(II) = 0.45±0.00	132	264	0.036	0.122	0.158
		Pb(II) = 0.44±0.02	306	612	0.269	0.086	0.355	Pb(II) = 0.15±0.01	168	336	0.044	0.153	0.197
		Total = 0.59±0.02	265	530	0.234	0.075	0.309	Total = 0.60±0.01	120	240	0.033	0.111	0.144
Controlled	3.0	Cu(II) = 0.14±0.01	85	170	0.075	0.021	0.096	Cu(II) = 0.43±0.01	25	50	0.005	0.020	0.025
		Pb(II) = 0.45±0.02	86	172	0.075	0.021	0.096	Pb(II) = 0.16±0.01	8	16	0.002	0.007	0.009
		Total = 0.59±0.02	66	172	0.059	0.017	0.076	Total = 0.59±0.01	7	14	0.002	0.007	0.009
	4.5	Cu(II) = 0.15±0.01	180	360	0.159	0.046	0.205	Cu(II) = 0.45±0.00	20	40	0.005	0.017	0.022
		Pb(II) = 0.44±0.02	180	360	0.159	0.046	0.205	Pb(II) = 0.15±0.01	18	36	0.002	0.008	0.010
		Total = 0.59±0.02	124	248	0.111	0.033	0.144	Total = 0.60±0.01	6	12	0.002	0.005	0.007
	6.0	Cu(II) = 0.15±0.01	205	410	0.181	0.053	0.234	Cu(II) = 0.45±0.00	34	68	0.007	0.028	0.035
		Pb(II) = 0.44±0.02	182	364	0.162	0.048	0.210	Pb(II) = 0.15±0.01	11	22	0.003	0.009	0.012
		Total = 0.59±0.02	142	284	0.128	0.038	0.166	Total = 0.60±0.01	8	16	0.002	0.007	0.009

V_B = Breakthrough throughput volumes at effluent metal concentration equal to 0.03 meq/L; t_B = service time at breakthrough; Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA respectively.

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time for virgin bed loaded with B[Cr(0.45)+Pb(0.15)] combination followed by reloading of washed bed with B[Cr(0.15)+Pb(0.45)] combination for a bed depth of 3.0 cm at a flow rate of 2.0 mL/min along with variation in effluent pH obtained under uncontrolled and controlled pH conditions are presented in Fig. 5.130 and 5.131 respectively.

Under uncontrolled pH conditions (Fig. 5.130), pH of the effluent from the virgin bed of GAA when loaded with B[Cr(0.45)+Pb(0.15)] combination increased to 6.84 in the first 15 min. of operation from initially adjusted pH value of 5.00. After initial 15 min., the effluent pH decreased to around 6.04 within 120 min. of operation. As operation proceeded beyond 120 min., pH of the effluent further decreased to 5.39 at around 300 min. of operation and finally reached to a value of 4.35 at around 1080 min. of operation. When the washed GAA bed was reloaded with B[Cr(0.15)+Pb(0.45)] combination, pH of the effluent increased to 5.40 in the first 10 min. of operation. After 10 min., pH of the effluent decreased to a value of 5.00 at around 120 min. of operation. The pH of the effluent at the end of 660 min. of operation was observed as 4.50. Hence the removal of Cr(III) and Pb(II) metal ions by virgin GAA bed up to first 60-180 min. of operation might have been due to precipitation along with adsorption as pH of the effluent increased above 5.50. Since pH of the effluent did not increase above 5.50 during reloading of washed bed with B[Cr(0.15)+Pb(0.45)], the removal of Cr(III) and Pb(II) metal ions might have been due to adsorption only. However, the effluent pH from the column beds was observed to initially increase rapidly and then decrease. This aspect of variation in effluent pH from column beds appeared to be unusual which is needed to be investigated in detail.

Under uncontrolled pH conditions, when the virgin bed was loaded with B[Cr(0.45)+Pb(0.15)] combination; Cr(III), Pb(II) and total metal ions were not detected in the effluent up to initial 120 min. of operation [Fig. 5.130(b)]. After 120 min., the breakthrough curves for Cr(III), Pb(II) and total metal ions gradually increased and reached to values of 0.127, 0.118 and 0.246 meq/L respectively at around 480 min. of operation. After 480 min. of operation, the breakthrough curves increased slowly indicating that the bed was nearing to get exhausted [Fig. 5.130(b)]. When the virgin bed loaded with B[Cr(0.45)+Pb(0.15)] combination was washed and then reloaded with B[Cr(0.15)+Pb(0.45)] combination, it yielded a relatively steeper breakthrough curves for Pb(II) and total metal ions while Cr(III) breakthrough curve was observed to be flat [Fig. 5.130(c)]. The washed

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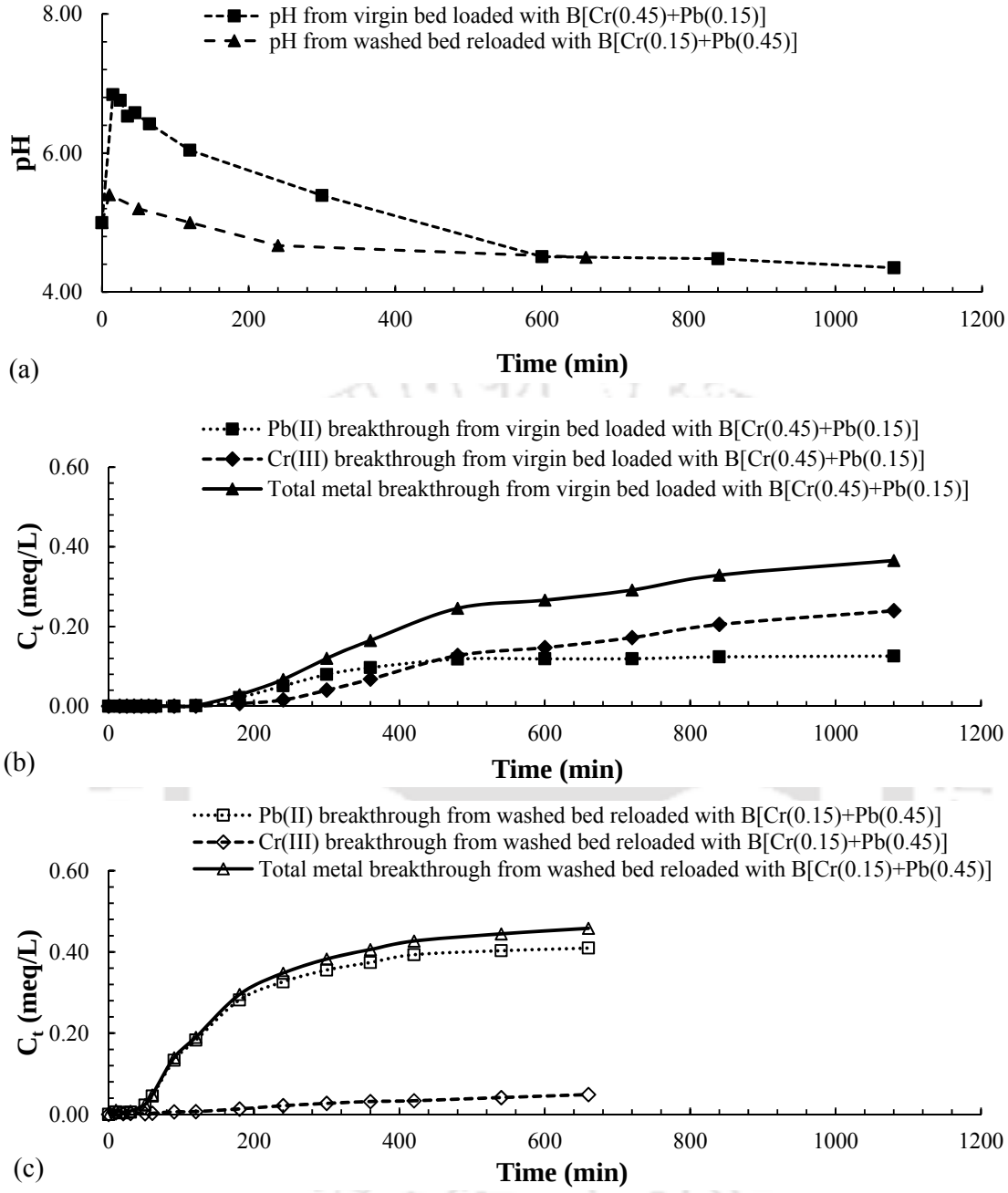

Fig. 5.130: Virgin GAA bed loaded with B[Cr(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cr(0.15)+Pb(0.45)] combination under uncontrolled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cr(0.45)+Pb(0.15)] combination: Cr(III) = 0.44±0.01 meq/L + Pb(II) = 0.15±0.02 meq/L and B[Cr(0.15)+Pb(0.45)] combination: Cr(III) = 0.15±0.00 meq/L + Pb(II) = 0.45±0.01 meq/L, Initial adjusted pH = 5.00±0.04, Temp. = 30±1 °C} (Each data represents an average of two independent experimental values).

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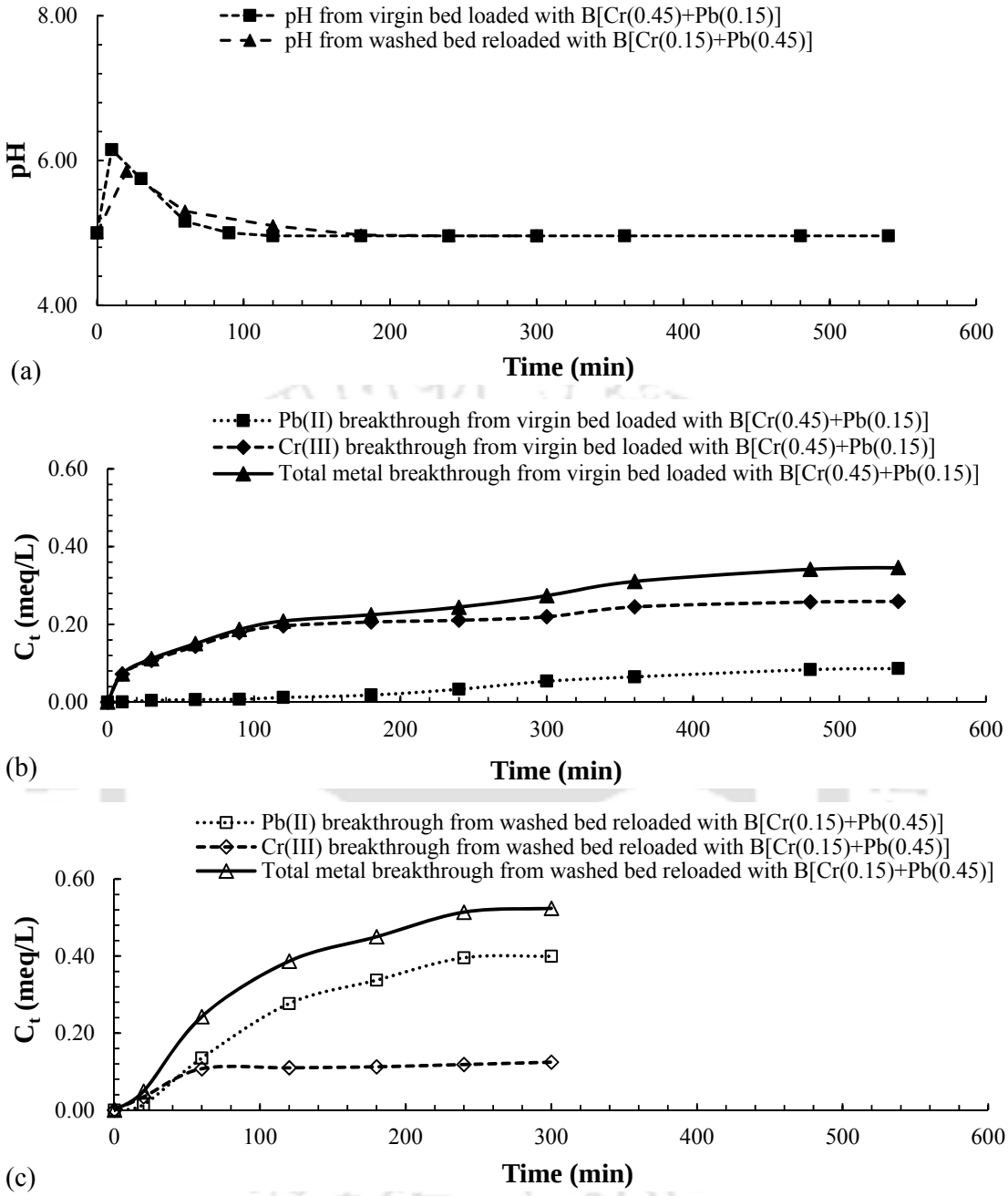

Fig. 5.131: Virgin GAA bed loaded with B[Cr(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cr(0.15)+Pb(0.45)] combination under controlled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cr(0.45)+Pb(0.15)] combination: Cr(III) = 0.46±0.01 meq/L + Pb(II) = 0.16±0.02 meq/L and B[Cr(0.15)+Pb(0.45)] combination: Cr(III) = 0.16±0.02 meq/L + Pb(II) = 0.47±0.02 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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GAA bed appeared to get exhausted with respect to Pb(II) and total metal ions in approximately 540 min. of operation. Similar breakthrough curves for virgin bed loaded with B[Cr(0.45)+Pb(0.15)] combination followed by reloading with B[Cr(0.15)+Pb(0.45)] combination along with variation in effluent pH for bed depths of 4.5 and 6.0 cm at a flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.33 and B.34).

Under controlled pH conditions (Fig. 5.131), pH of the effluent from the virgin bed of GAA when loaded with B[Cr(0.45)+Pb(0.15)] combination increased to 6.15 in the first 10 min. of operation from initially buffered pH value of 5.00. After initial 10 min., the effluent pH decreased to around 5.16 within 60 min. of operation. As the operation proceeded beyond 60 min., pH of the effluent further decreased and finally reached to a value of 4.96 in the later phase of operation. When the washed GAA bed was reloaded with B[Cr(0.15)+Pb(0.45)] combination, pH of the effluent increased to 5.85 in the first 20 min. After initial 20 min., pH of the effluent decreased to 5.10 at around 120 min. of operation. The pH of the effluent at the end of operation was observed as 4.96. The effluent pH observed to initially increase rapidly and then decrease in the column studies. This aspect is needed to be investigated in detail. Since pH of the effluent during initial 20-60 min. of virgin GAA bed loading and washed bed reloading increased above 5.50, Cr(III) and Pb(II) metals removal cannot be ruled out due to precipitation.

Under controlled pH conditions, when the virgin GAA bed was loaded with B[Cr(0.45)+Pb(0.15)] combination, Cr(III) and total metal ions breakthrough curves increased rapidly in the beginning of operation and reached to values of 0.144 and 0.150 meq/L respectively at around 60 min. of operation while Pb(II) breakthrough curve was observed to be flat and gradually reached to a value of only 0.065 meq/L at around 360 min. of operation [Fig. 5.131(b)]. The virgin GAA bed appeared to get exhausted with respect to Cr(III) and total metal in approximately 360 min. of operation [Fig. 5.131(b)]. When the virgin bed loaded with B[Cr(0.45)+Pb(0.15)] combination was washed and then reloaded with B[Cr(0.15)+Pb(0.45)] combination, Pb(II) breakthrough curve increased rapidly after initial 20 min. of operation and reached to a value of 0.338 meq/L at 180 min. of operation [Fig. 5.131(c)]. During reloading of the washed bed with B[Cr(0.15)+Pb(0.45)] combination [Fig. 5.131(c)], concentration of Cr(III) metal was observed to rise in the effluent from a concentration value of zero to a value of approximately 0.108 meq/L at around 60 min. of

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operation, thereafter remained at the same level till the end of the operation. Did it mean that the washed bed had additional potential for the removal of Cr(III) ion reloaded with lower initial Cr(III) concentration compared to loading of virgin bed with higher initial Cr(III) concentration? It is open for further investigation. The washed GAA bed appeared to get exhausted with respect to Pb(II) and total metal in approximately 240 min. of operation. Similar breakthrough curves for virgin bed loaded with B[Cr(0.45)+Pb(0.15)] combination followed by reloading with B[Cr(0.15)+Pb(0.45)] combination along with variation in effluent pH for bed depths of 4.5 and 6.0 cm at a flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.35 and B.36).

A mass balance was carried out to estimate Cr(III), Pb(II) and total metal removal by column beds under uncontrolled and controlled pH conditions when virgin bed was loaded with B[Cr(0.45)+Pb(0.15)] combination followed by washing and then again reloading with B[Cr(0.15)+Pb(0.45)] combination. Mass balance for metal removal under uncontrolled and controlled pH conditions by the column beds when loaded or reloaded with binary-metal ion systems was carried out for a time period when the total metal ion concentration in the effluent was equal to or more than 50% of the total metal ion concentration in the influent. Since the total metal breakthrough curve from the column study with 6.0 cm bed depth under uncontrolled pH condition hardly reached to 14% of total initial metal ion concentration, the mass balance analysis for the same was not carried out. Mass balance for metal removed under uncontrolled and controlled pH conditions by virgin GAA bed loaded with B[Cr(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cr(0.15)+Pb(0.45)] combination is presented in Table 5.67.

Under uncontrolled pH conditions, when the column bed of depth 3.0 cm was operated at a flow rate of 2.0 mL/min, exhaustion time (t_E) in terms of total metal concentration in the effluent was estimated as 720 min. for virgin GAA bed loaded with B[Cr(0.45)+Pb(0.15)] combination and 180 min. for washed bed reloaded with B[Cr(0.15)+Pb(0.45)] combination. The Cr(III), Pb(II) and total metal removal by virgin GAA bed up to 720 min. were estimated as 0.5317, 0.1086 and 0.6403 meq respectively. During reloading of the washed bed with B[Cr(0.15)+Pb(0.45)] combination; Cr(III), Pb(II) and total metal removal up to 180 min. were observed as 0.0520, 0.1165 and 0.1684 meq respectively. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 0.7028 meq and the

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Table 5.67: Summary of mass balance of metal removed by column beds when virgin GAA bed loaded with B[Cr(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cr(0.15)+Pb(0.45)] combination under uncontrolled and controlled pH conditions.

pH conditions	Flow rate (mL/min)	Bed depth (cm)	Virgin bed loaded with B[Cr(0.45)+Pb(0.15)] combination			Amount of washed out metal (meq)	Washed bed reloaded with B[Cr(0.15)+Pb(0.45)] combination			Total metal removed by bed (meq)	Total metal removed per unit weight of bed (meq/g)
			Initial metal conc. (meq/L)	t_E (min)	Metal removed by bed (meq)		Initial metal conc. (meq/L)	t_E (min)	Metal removed by bed (meq)		
Uncontrolled	2.0	3.0	Pb(II) = 0.15±0.02	720	0.1086	0.066	Pb(II) = 0.45±0.01	180	0.1165	0.7028	0.0748
			Cr(III) = 0.44±0.01		0.5317	0.040	Cr(III) = 0.15±0.00		0.0520		
			Total = 0.59±0.02		0.6403	0.106	Total = 0.60±0.01		0.1685		
		4.5	Pb(II) = 0.15±0.02	947*	0.1481	0.056	Pb(II) = 0.45±0.01	360*	0.2240	1.1675	0.0884
			Cr(III) = 0.44±0.01		0.7641	0.016	Cr(III) = 0.15±0.00		0.1033		
			Total = 0.59±0.02		0.9122	0.072	Total = 0.60±0.01		0.3273		
		6.0	Pb(II) = 0.15±0.02	-	-	-	Pb(II) = 0.45±0.01	-	-	-	-
			Cr(III) = 0.44±0.01		-	-	Cr(III) = 0.15±0.00		-		
			Total = 0.59±0.02		-	-	Total = 0.60±0.01		-		
Controlled	2.0	3.0	Pb(II) = 0.16±0.02	360	0.0925	0.030	Pb(II) = 0.47±0.02	89	0.0646	0.2945	0.0313
			Cr(III) = 0.46±0.01		0.1970	0.042	Cr(III) = 0.16±0.02		0.0124		
			Total = 0.62±0.02		0.2895	0.072	Total = 0.63±0.02		0.0770		
		4.5	Pb(II) = 0.16±0.02	360^	0.1058	0.043	Pb(II) = 0.45±0.01	202^	0.1496	0.4505	0.0341
			Cr(III) = 0.44±0.01		0.2335	0.032	Cr(III) = 0.15±0.00		0.0366		
			Total = 0.60±0.02		0.3393	0.075	Total = 0.60±0.01		0.1862		
		6.0	Pb(II) = 0.15±0.02	540^	0.1575	0.040	Pb(II) = 0.45±0.01	229^	0.1668	0.6590	0.0392
			Cr(III) = 0.44±0.01		0.3780	0.055	Cr(III) = 0.15±0.00		0.0517		
			Total = 0.59±0.02		0.5355	0.095	Total = 0.60±0.01		0.2185		

t_E = exhaustion time (effluent total metal concentration equal to 50% of influent total metal concentration from virgin and washed beds respectively, if not specified); * = total effluent conc. equal to 40% of total influent concentration; ^ = total effluent concentration equal to 30% of total influent concentration; Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA respectively.

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total metal removal per unit weight of the adsorbent was estimated as 0.0748 meq/g. Under controlled pH conditions, when the column bed of depth 3.0 cm was operated at a flow rate of 2.0 mL/min, exhaustion time (t_E) in terms of total metal concentration in the effluent was estimated as 360 min. for virgin GAA bed loaded with B[Cr(0.45)+Pb(0.15)] combination and 89 min. for washed bed reloaded with B[Cr(0.15)+Pb(0.45)] combination. The Cr(III), Pb(II) and total metal removal by virgin GAA bed up to 360 min. were estimated as 0.1970, 0.0925 and 0.2895 meq respectively. During reloading of the washed bed with B[Cr(0.15)+Pb(0.45)] combination; Cr(III), Pb(II) and total metal removal up to 89 min. were observed as 0.0124, 0.0646 and 0.0770 meq respectively. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 0.2945 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.0313 meq/g.

In order to investigate the effect of GAA bed depths on metal removal when the virgin GAA bed was loaded with B[Cr(0.45)+Pb(0.15)] combination and washed bed was again reloaded with B[Cr(0.15)+Pb(0.45)] combination, the breakthrough curves for a linear flow rate of 2.0 mL/min with three different bed depths of 3.0, 4.5 and 6.0 cm operated under uncontrolled and controlled pH conditions are re-plotted and presented in Fig. 5.132 and 5.133 respectively. It could be observed from these figures that breakthrough curves appear to shift towards right with increase in bed depths. The service times (t_B) for virgin beds and washed beds were estimated from the breakthrough curves when the effluent metal ions concentration was 5% of influent metal ion concentration (i.e. 0.03 meq/L) with respect to Cr(III), Pb(II) and total metal. The corresponding breakthrough throughput volumes (V_B) were also estimated. All the estimated service times and breakthrough throughput volumes for uncontrolled and controlled pH conditions have been tabulated in Table 5.68. The breakthrough throughput volumes for Cr(III), Pb(II) and total metal ions increased with increase in bed depths at the fixed flow rate as could be seen from Table 5.68. An increase in the service time was observed when the bed depth increased from 3.0 to 6.0 cm. The increase in Cr(III), Pb(II) and total metal ions removal from the bulk metal ion solution with increase in bed depths were possibly due to increase in the amount of adsorbent mass in the larger beds which provided greater opportunities for metal removal. Further, estimated breakthrough time for Cr(III) metal during loading of virgin GAA bed with B[Cr(0.45)+Pb(0.15)] combination under uncontrolled pH conditions were higher than for Pb(II) metal. However, estimated breakthrough time for Cr(III) metal during loading of virgin

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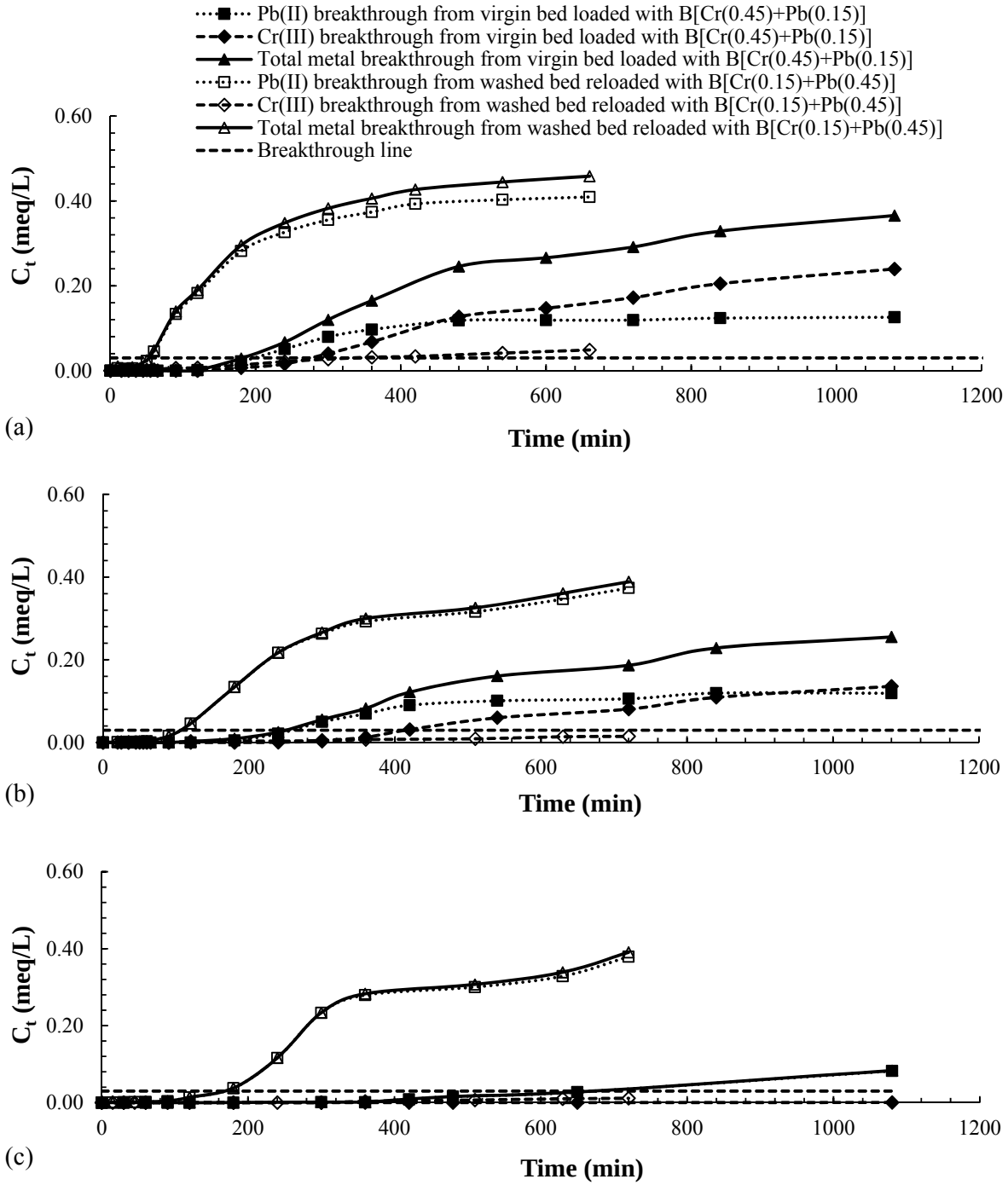

Fig. 5.132: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with B[Cr(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cr(0.15)+Pb(0.45)] combination at a flow rate of 2.0 mL/min under uncontrolled pH conditions {Initial metal conc. in B[Cr(0.45)+Pb(0.15)] combination: Cr(III) = 0.44±0.01 meq/L + Pb(II) = 0.15±0.02 meq/L and B[Cr(0.15)+Pb(0.45)] combination: Cr(III) = 0.15±0.00 meq/L + Pb(II) = 0.45±0.01 meq/L, Initial adjusted pH = 5.00±0.04, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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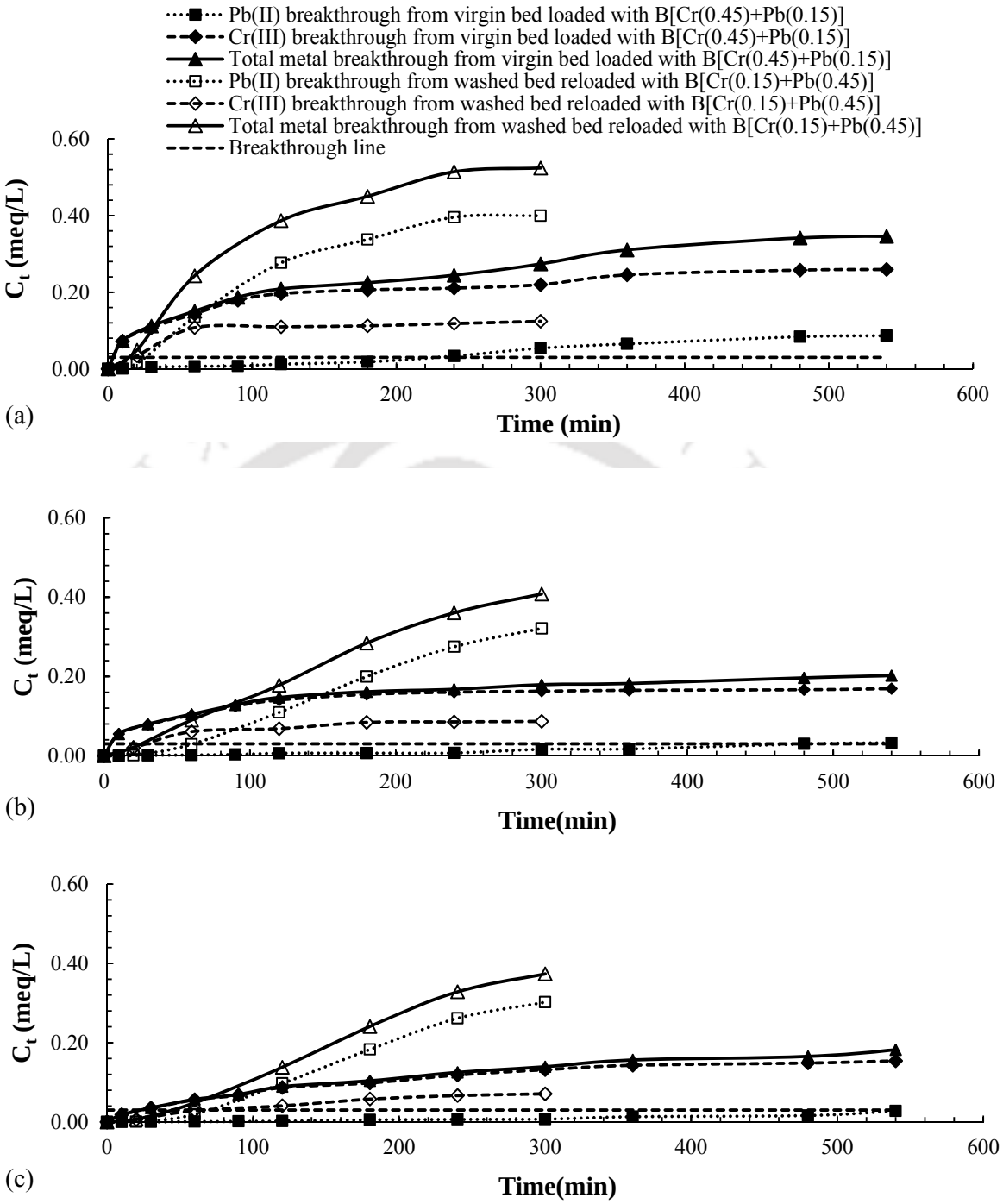

Fig. 5.133: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with B[Cr(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cr(0.15)+Pb(0.45)] combination at a flow rate of 2.0 mL/min under controlled pH conditions {Initial metal conc. in B[Cr(0.45)+Pb(0.15)] combination: Cr(III) = 0.46±0.01 meq/L + Pb(II) = 0.16±0.02 meq/L and B[Cr(0.15)+Pb(0.45)] combination: Cr(III) = 0.16±0.02 meq/L + Pb(II) = 0.47±0.02 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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Table 5.68: Summary of breakthrough results at fixed flow rate but varying depths of virgin GAA bed loaded with B[Cr(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cr(0.15)+Pb(0.45)] combination under uncontrolled and controlled pH conditions.

pH conditions	Bed depth (cm)	Virgin bed loaded with B[Cr(0.45)+Pb(0.15)] combination						Washed bed reloaded with B[Cr(0.15)+Pb(0.45)] combination					
		Initial metal conc. (meq/L)	t_B (min)	V_B (mL)	Metal removed (meq)			Initial metal conc. (meq/L)	t_B (min)	V_B (mL)	Metal removed (meq)		
					Cr(III)	Pb(II)	Total				Cr(III)	Pb(II)	Total
Uncontrolled	3.0	Pb(II) = 0.15±0.02	196	392	0.173	0.056	0.229	Pb(II) = 0.45±0.01	53	106	0.016	0.047	0.063
		Cr(III) = 0.44±0.01	274	549	0.240	0.072	0.312	Cr(III) = 0.15±0.00	360	720	0.098	0.156	0.254
		Total = 0.59±0.02	180	360	0.159	0.053	0.212	Total = 0.60±0.01	52	104	0.016	0.046	0.062
	4.5	Pb(II) = 0.15±0.02	258	516	0.232	0.074	0.306	Pb(II) = 0.45±0.01	104	208	0.030	0.091	0.121
		Cr(III) = 0.44±0.01	420	840	0.374	0.103	0.477	Cr(III) = 0.15±0.00	720*	1440	0.200	0.309	0.509
		Total = 0.59±0.02	249	498	0.224	0.072	0.296	Total = 0.60±0.01	104	208	0.030	0.091	0.121
	6.0	Pb(II) = 0.15±0.02	670	1340	0.605	0.189	0.794	Pb(II) = 0.45±0.01	161	322	0.047	0.140	0.187
		Cr(III) = 0.44±0.01	1139	2278	1.025	0.273	1.298	Cr(III) = 0.15±0.00	720*	1440	0.203	0.350	0.553
		Total = 0.59±0.02	670	1340	0.605	0.189	0.794	Total = 0.60±0.01	161	322	0.047	0.140	0.187
Controlled	3.0	Pb(II) = 0.16±0.02	240	480	0.140	0.068	0.208	Pb(II) = 0.47±0.02	25	50	0.003	0.022	0.025
		Cr(III) = 0.46±0.01	4	8	0.004	0.001	0.005	Cr(III) = 0.16±0.02	20	40	0.003	0.018	0.021
		Total = 0.62±0.02	4	8	0.004	0.001	0.005	Total = 0.63±0.02	12	24	0.002	0.011	0.013
	4.5	Pb(II) = 0.16±0.02	480	960	0.305	0.137	0.442	Pb(II) = 0.45±0.01	60	120	0.055	0.012	0.067
		Cr(III) = 0.44±0.01	5	10	0.005	0.002	0.007	Cr(III) = 0.15±0.00	30	60	0.005	0.027	0.032
		Total = 0.60±0.02	5	10	0.005	0.002	0.007	Total = 0.60±0.01	25	50	0.004	0.023	0.027
	6.0	Pb(II) = 0.15±0.02	540	1080	0.378	0.158	0.536	Pb(II) = 0.45±0.01	68	136	0.016	0.062	0.078
		Cr(III) = 0.44±0.01	24	48	0.021	0.007	0.028	Cr(III) = 0.15±0.00	66	132	0.016	0.060	0.076
		Total = 0.59±0.02	23	46	0.021	0.007	0.028	Total = 0.60±0.01	42	84	0.009	0.039	0.048

V_B = Breakthrough throughput volumes at effluent metal concentration equal to 0.03 meq/L; t_B = service time at breakthrough; * = time when effluent conc. less than 0.03 meq/L, Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA respectively.

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GAA bed with B[Cr(0.45)+Pb(0.15)] combination under controlled pH conditions was lower than for Pb(II) metal. It revealed the early breakthrough for Pb(II) metal under uncontrolled pH conditions and early breakthrough for Cr(III) under controlled pH conditions. Larger size of Cr(III)-acetate complexes [due to higher coordination number associated with Cr(III) metal] formed in controlled pH conditions compared to Pb(II)-acetate complexes might be the possible reason for early breakthrough for Cr(III) metal under controlled pH conditions. for uncontrolled and controlled pH conditions have been tabulated in Table 5.68. The breakthrough throughput volumes for Cr(III), Pb(II) and total metal ions increased with increase in bed depths at the fixed flow rate as could be seen from Table 5.68. An increase in the service time was observed when the bed depth increased from 3.0 to 6.0 cm. The increase in Cr(III), Pb(II) and total metal ions removal from the bulk metal ion solution with increase in bed depths were possibly due to increase in the amount of adsorbent mass in the larger beds which provided greater opportunities for metal removal. Further, estimated breakthrough time for Cr(III) metal during loading of virgin GAA bed with B[Cr(0.45)+Pb(0.15)] combination under uncontrolled pH conditions were higher than for Pb(II) metal. However, estimated breakthrough time for Cr(III) metal during loading of virgin GAA bed with B[Cr(0.45)+Pb(0.15)] combination under controlled pH conditions was lower than for Pb(II) metal. It revealed the early breakthrough for Pb(II) metal under uncontrolled pH conditions and early breakthrough for Cr(III) under controlled pH conditions. Larger size of Cr(III)-acetate complexes [due to higher coordination number associated with Cr(III) metal] formed in controlled pH conditions compared to Pb(II)-acetate complexes might be the possible reason for early breakthrough for Cr(III) metal under controlled pH conditions.

5.7.11 Breakthrough curves for virgin GAA bed loaded with B[Cr(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cr(0.45)+Pb(0.15)] combination under uncontrolled and controlled pH conditions

The studies were carried out by exposing (or loading) the virgin (or fresh) GAA bed with B[Cr(0.15)+Pb(0.45)] combination till the bed exhausted or yielded total metal ion concentration in the effluent more than 50% of total initial metal ion concentration in the influent. The loaded bed was then washed with 100 bed volumes of de-mineralized water to remove residual or un-adsorbed metal ions from pore volume of the bed. The washed bed was then again exposed (or reloaded) with B[Cr(0.45)+Pb(0.15)] combination till the bed again exhausted or yielded total metal ion concentration in the effluent more than 40% of total

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initial metal ion concentration in the influent. The typical breakthrough curves for Cr(III), Pb(II) and total metal in terms of metal ions remaining in effluent (C_t) versus time for virgin bed loaded with B[Cr(0.15)+Pb(0.45)] combination followed by reloading of washed bed with B[Cr(0.45)+Pb(0.15)] combination for a bed depth of 3.0 cm at a flow rate of 2.0 mL/min along with variation in effluent pH obtained under uncontrolled and controlled pH conditions are presented in Fig. 5.134 and 5.135 respectively.

Under uncontrolled pH conditions (Fig. 5.134), pH of the effluent from the virgin bed of GAA when loaded with B[Cr(0.15)+Pb(0.45)] combination increased to 6.87 within first 15 min. of operation from initially adjusted pH value of 5.00. After initial 15 min., the effluent pH decreased to around 6.02 within 120 min. of operation. As operation proceeded beyond 120 min., pH of the effluent further decreased to 5.45 at around 300 min. of operation and finally reached to a value of 4.68 at around 1080 min. of operation. When the washed GAA bed was reloaded with B[Cr(0.45)+Pb(0.15)] combination, pH of the effluent increased to 5.68 in the first 10 min. of operation. After 10 min., pH of the effluent decreased to a value of 5.00 at around 90 min. of operation. The pH of the effluent at the end of 660 min. of operation was observed as 4.55. The removal of Cr(III) and Pb(II) metal ions by virgin GAA bed up to first 120-300 min. of operation and by washed GAA bed up to approximately first 30 min. of operation might have been due to precipitation along with adsorption as pH of the effluent increased above 5.50, while in the later phase of the operation removal of both the metal ions might have been due to adsorption only. The effluent pH from the column beds was observed to initially increase rapidly and then decrease. This aspect of variation in effluent pH from column beds appeared to be unusual which is needed to be investigated in detail.

Under uncontrolled pH conditions [Fig. 5.134(b)], when the virgin GAA bed was loaded with B[Cr(0.15)+Pb(0.45)] combination, no Pb(II) and total metal ion concentrations were observed in the effluent up to 90 min. of operation. The breakthrough curves for Pb(II) and total metal started to increase after 90 min. of operation. The breakthrough curves for Pb(II) and total metal reached to values of 0.363 and 0.368 meq/L respectively at around 360 min. of operation. After 360 min. of operation, the breakthrough curves increased slowly indicating that the bed was nearing to get exhausted [Fig. 5.134(b)]. The Cr(III) breakthrough curve was observed to be flat and approximately 0.024 meq/L of Cr(III) was detected in the

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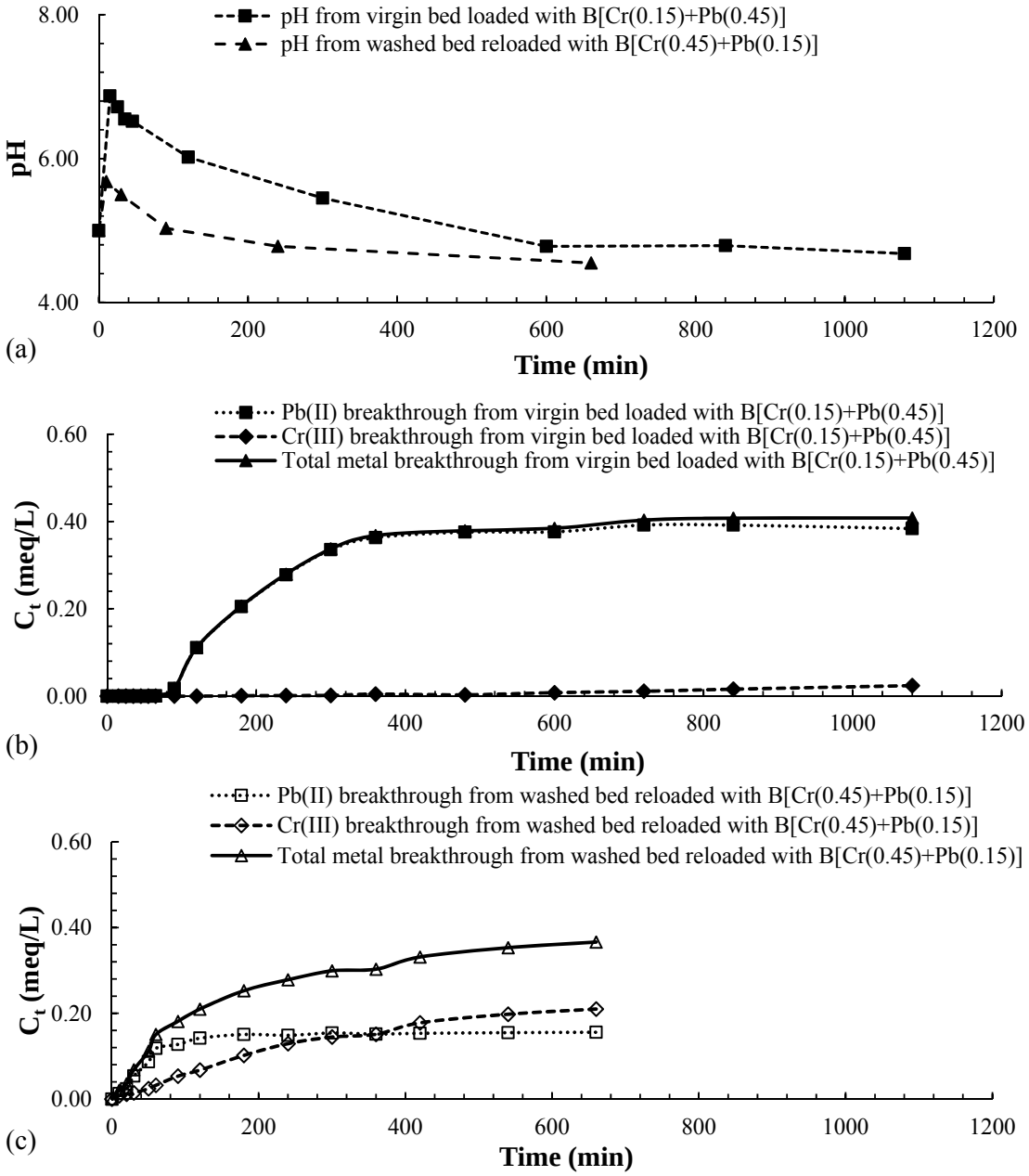

Fig. 5.134: Virgin GAA bed loaded with B[Cr(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cr(0.45)+Pb(0.15)] combination under uncontrolled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cr(0.15)+Pb(0.45)] combination: Cr(III) = 0.15±0.01 meq/L + Pb(II) = 0.45±0.02 meq/L and B[Cr(0.45)+Pb(0.15)] combination: Cr(III) = 0.44±0.00 meq/L + Pb(II) = 0.15±0.01 meq/L, Initial adjusted pH = 5.00±0.05, Temp. = 30±1 °C} (Each data represents an average of two independent experimental values).

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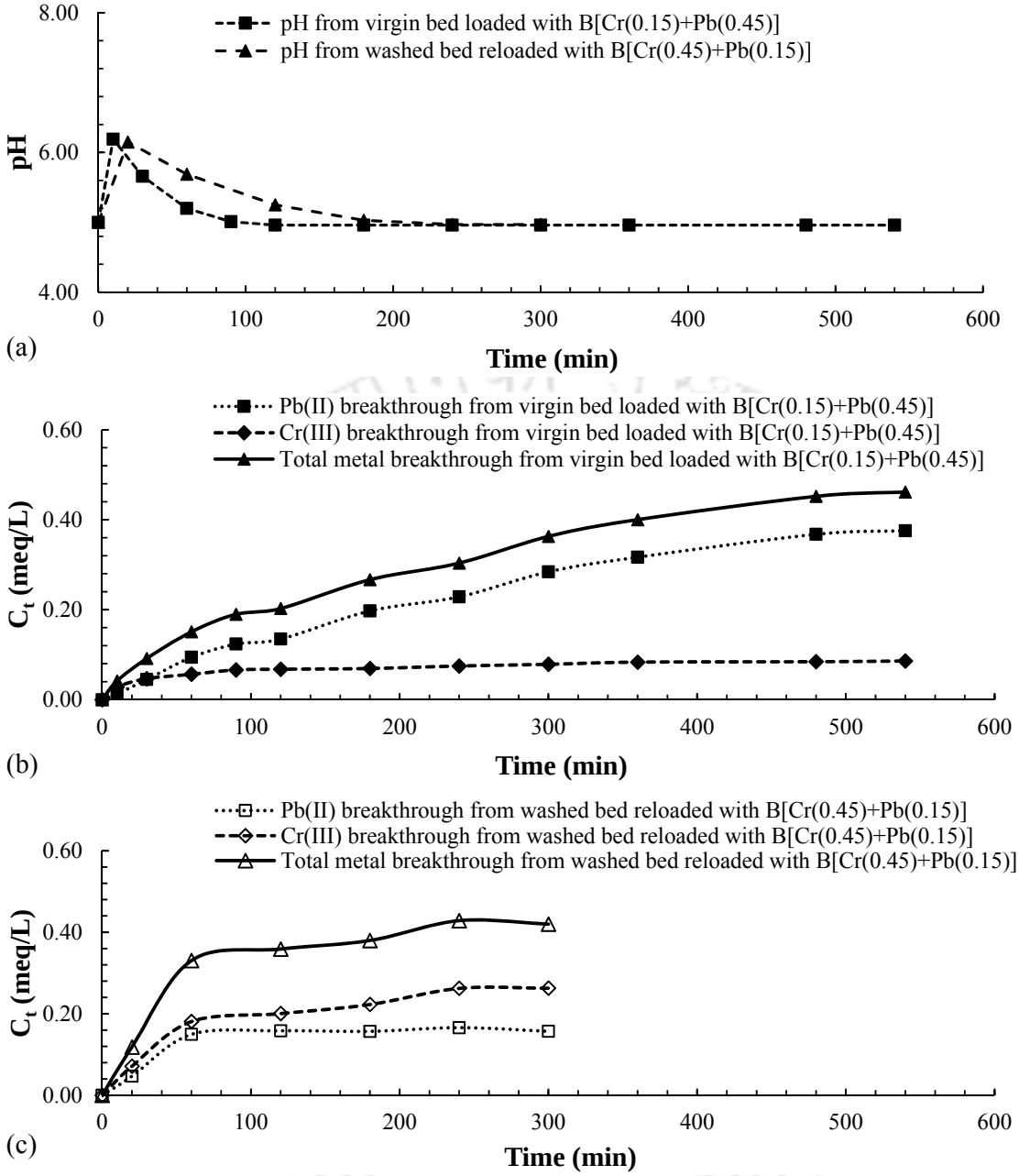

Fig. 5.135: Virgin GAA bed loaded with B[Cr(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cr(0.45)+Pb(0.15)] combination under controlled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 3.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cr(0.15)+Pb(0.45)] combination: Cr(III) = 0.16±0.01 meq/L + Pb(II) = 0.48±0.02 meq/L and B[Cr(0.45)+Pb(0.15)] combination: Cr(III) = 0.46±0.00 meq/L + Pb(II) = 0.16±0.01 meq/L, Buffered pH = 5.00±0.05, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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effluent at around 1080 min. of operation. When the virgin bed loaded with B[Cr(0.15)+Pb(0.45)] combination was washed and then reloaded with B[Cr(0.45)+Pb(0.15)] combination, the breakthrough curves for Cr(III), Pb(II) and total metal observed to increase with start of operation and reached to values of 0.068, 0.142 and 0.210 meq/L respectively at around 120 min. of operation [Fig. 5.134(c)]. The washed bed appeared to get exhausted with respect to Cr(III), Pb(II) and total metal in approximately 660, 240 and 660 min. of operation respectively. During reloading of the washed bed with B[Cr(0.45)+Pb(0.15)] combination [Fig. 5.134(c)], concentration of Pb(II) metal was observed to rise in the effluent from a concentration value of zero to a value of 0.128 meq/L at around 90 min. of operation, thereafter reached to 0.156 meq/L at the end of the operation. Did it mean that the washed bed had additional potential for the removal of Pb(II) ion reloaded with lower initial Pb(II) concentration compared to loading of virgin bed with higher initial Pb(II) concentration? It is open for further investigation. Similar breakthrough curves for virgin bed loaded with B[Cr(0.15)+Pb(0.45)] combination followed by reloading with B[Cr(0.45)+Pb(0.15)] combination along with variation in effluent pH for bed depths of 4.5 and 6.0 cm at a flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.37 and B.38).

Under controlled pH conditions (Fig. 5.135), pH of the effluent from the virgin bed of GAA when loaded with B[Cr(0.15)+Pb(0.45)] combination increased to 6.19 within first 10 min. of operation from initially buffered pH value of 5.00. After initial 10 min., the effluent pH decreased to around 5.20 within 60 min. of operation. As operation proceeded beyond 60 min., pH of the effluent further decreased slowly and became constant to value of 4.96 in the later phase of operation. When the washed GAA bed was reloaded with B[Cr(0.45)+Pb(0.15)] combination, pH of the effluent increased to 6.15 in the first 20 min. After initial 20 min., pH of the effluent decreased to 5.25 at around 120 min. of operation. The pH of the effluent at the end of operation was observed as 4.96. As pH of the effluent increased above 5.50 during the first 30-60 min. of operation of virgin GAA bed and 60-120 min. of operation of washed bed, Cr(III) and Pb(II) metals reduction cannot be ruled out due to precipitation. The effluent pH was observed to initially increase rapidly and then decrease in the column studies. This aspect is needed to be investigated in detail.

Under controlled pH conditions [Fig. 5.135(b)], when the virgin GAA bed was loaded with B[Cr(0.15)+Pb(0.45)] combination; Cr(III), Pb(II) and total metal breakthrough curves

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observed to increase with the start of operation and reached to values of 0.066, 0.124 and 0.190 meq/L respectively at around 90 min. of operation [Fig. 5.135(b)]. The virgin GAA bed was observed to get exhausted with respect to Cr(III), Pb(II) and total metal in approximately 90, 480 and 480 min. of operation respectively [Fig. 5.135(b)]. When the virgin bed loaded with B[Cr(0.15)+Pb(0.45)] combination was washed and then reloaded with B[Cr(0.45)+Pb(0.15)] combination; Cr(III), Pb(II) and total metal breakthrough curves observed to increase with the start of operation and reached to values of 0.181, 0.150 and 0.331 meq/L respectively at around 60 min. of operation [Fig. 5.135(c)]. The washed bed appeared to get exhausted with respect to Cr(III), Pb(II) and total metal in approximately 180 min. of operation. During reloading of the washed bed with B[Cr(0.45)+Pb(0.15)] combination [Fig. 5.135(c)], concentration of Pb(II) metal was observed to rise in the effluent from a concentration value of zero to a value of 0.150 meq/L at around 60 min. of operation, thereafter reached to value of 0.157 at the end of the operation. Did it mean that the washed bed had additional potential for the removal of Pb(II) ion reloaded with lower initial Pb(II) concentration compared to loading of virgin bed with higher initial Pb(II) concentration? It is open for further investigation. Similar breakthrough curves for virgin bed loaded with B[Cr(0.15)+Pb(0.45)] combination followed by reloading with B[Cr(0.45)+Pb(0.15)] combination along with variation in effluent pH for bed depths of 4.5 and 6.0 cm at a flow rate of 2.0 mL/min have been developed and presented in Appendix B (Fig. B.39 and B.40).

A mass balance was carried out to estimate Cr(III), Pb(II) and total metal removal by column beds under uncontrolled and controlled pH conditions when virgin bed was loaded with B[Cr(0.15)+Pb(0.45)] combination followed by washing and then again reloading with B[Cr(0.45)+Pb(0.15)] combination. Mass balance for metal removal under uncontrolled and controlled pH conditions by the column beds when loaded or reloaded with binary-metal ion systems was carried out for a time period when the total metal ion concentration in the effluent was equal to or more than 50% of the total metal ion concentration in the influent. A summary of mass balance for metal removed under uncontrolled and controlled pH conditions by virgin GAA bed loaded with B[Cr(0.15)+Pb(0.45)] combination, washed and then reloaded with B[Cr(0.45)+Pb(0.15)] combination is presented in Table 5.69.

Under uncontrolled pH conditions, when the virgin column bed of depth 3.0 cm was operated at a flow rate of 2.0 mL/min, exhaustion time (t_E) in terms of total metal

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Table 5.69: Summary of mass balance of metal removed by column beds when virgin GAA bed loaded with B[Cr(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cr(0.45)+Pb(0.15)] combination under uncontrolled and controlled pH conditions.

pH conditions	Flow rate (mL/min)	Bed depth (cm)	Virgin bed loaded with B[Cr(0.15)+Pb(0.45)] combination			Amount of washed out metal (meq)	Washed bed reloaded with B[Cr(0.45)+Pb(0.15)] combination			Total metal removed by bed (meq)	Total metal removed per unit weight of bed (meq/g)
			Initial metal conc. (meq/L)	t_E (min)	Metal removed by bed (meq)		Initial metal conc. (meq/L)	t_E (min)	Metal removed by bed (meq)		
Uncontrolled	2.0	3.0	Pb(II) = 0.45±0.02	261	0.1697	0.078	Pb(II) = 0.15±0.01	300	0.0132	0.3921	0.0417
			Cr(III) = 0.15±0.01		0.0784	0.004	Cr(III) = 0.44±0.00		0.2128		
			Total = 0.60±0.02		0.2481	0.082	Total = 0.59±0.01		0.2260		
		4.5	Pb(II) = 0.45±0.02	387	0.2460	0.015	Pb(II) = 0.15±0.01	470*	0.0313	0.7686	0.0582
			Cr(III) = 0.15±0.01		0.1221	0.004	Cr(III) = 0.44±0.00		0.3882		
			Total = 0.60±0.02		0.3681	0.019	Total = 0.59±0.01		0.4195		
		6.0	Pb(II) = 0.45±0.02	1080	0.6550	0.015	Pb(II) = 0.15±0.01	720*	0.5807	1.6045	0.0955
			Cr(III) = 0.15±0.01		0.3427	0.004	Cr(III) = 0.44±0.00		0.0451		
			Total = 0.60±0.02		0.9977	0.019	Total = 0.59±0.01		0.6258		
Controlled	2.0	3.0	Pb(II) = 0.48±0.02	248	0.1618	0.025	Pb(II) = 0.16±0.01	56	0.0319	0.2111	0.0225
			Cr(III) = 0.16±0.01		0.0481	0.015	Cr(III) = 0.46±0.00		0.0093		
			Total = 0.64±0.02		0.2099	0.040	Total = 0.62±0.01		0.0412		
		4.5	Pb(II) = 0.45±0.02	376	0.2863	0.040	Pb(II) = 0.15±0.01	180	0.0212	0.4308	0.0326
			Cr(III) = 0.15±0.01		0.0858	0.035	Cr(III) = 0.44±0.00		0.1125		
			Total = 0.60±0.02		0.3721	0.075	Total = 0.59±0.01		0.1337		
		6.0	Pb(II) = 0.44±0.00	418	0.3106	0.017	Pb(II) = 0.15±0.01	265	0.0283	0.5950	0.0354
			Cr(III) = 0.15±0.01		0.1029	0.006	Cr(III) = 0.44±0.00		0.1762		
			Total = 0.60±0.02		0.4135	0.023	Total = 0.62±0.01		0.2045		

t_E = exhaustion time (effluent total metal concentration equal to 50% of influent total metal concentration from virgin and washed beds respectively, if not specified); * = total effluent conc. equal to 40% of total influent concentration; Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA respectively.

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concentration in the effluent was estimated as 261 min. for virgin GAA bed loaded with B[Cr(0.15)+Pb(0.45)] combination and 300 min. for washed bed reloaded with B[Cr(0.45)+Pb(0.15)] combination. The Cr(III), Pb(II) and total metal removal by virgin GAA bed up to 261 min. were estimated as 0.0784, 0.1697 and 0.2481 meq respectively. During reloading of the washed bed with B[Cr(0.45)+Pb(0.15)] combination; Cr(III), Pb(II) and total metal removal up to 300 min. were observed as 0.2128, 0.0132 and 0.2260 meq respectively. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 0.3921 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.0417 meq/g. Under controlled pH conditions, when the virgin column bed of depth 3.0 cm was operated at a flow rate of 2.0 mL/min, exhaustion time (t_E) in terms of total metal concentration in the effluent was estimated as 248 min. for virgin GAA bed loaded with B[Cr(0.15)+Pb(0.45)] combination and 56 min. for washed bed reloaded with B[Cr(0.45)+Pb(0.15)] combination. The Cr(III), Pb(II) and total metal removal by virgin GAA bed up to 248 min. were estimated as 0.0481, 0.1618 and 0.2099 meq respectively. During reloading of the washed bed with B[Cr(0.45)+Pb(0.15)] combination; Cr(III), Pb(II) and total metal removal up to 56 min. were observed as 0.0093, 0.0319 and 0.0412 meq respectively. Hence the total metal removal by the column bed (virgin and washed beds together) was estimated as 0.2111 meq and the total metal removal per unit weight of the adsorbent was estimated as 0.0225 meq/g.

In order to investigate the effect of GAA bed depths on metal removal when the virgin GAA bed was loaded with B[Cr(0.15)+Pb(0.45)] combination and washed bed was again reloaded with B[Cr(0.45)+Pb(0.15)] combination, the breakthrough curves for a linear flow rate of 2.0 mL/min with three different bed depths of 3.0, 4.5 and 6.0 cm of GAA operated under uncontrolled and controlled pH conditions are re-plotted and presented in Fig. 5.136 and 5.137 respectively. It could be observed from these figures that breakthrough curves appear to shift towards right with increase in bed depths. The service times (t_B) for virgin beds and washed beds were estimated from the breakthrough curves when the effluent metal ions concentration was 5% of influent metal ion concentration (i.e. 0.03 meq/L) in terms of Cr(III), Pb(II) and total metal. The service times for virgin beds and washed beds were not estimated for column depth of 6.0 cm under uncontrolled pH conditions as effluent concentration did not yield value of 0.03 meq/L. The corresponding breakthrough throughput volumes (V_B) were also estimated. All the estimated service times and breakthrough

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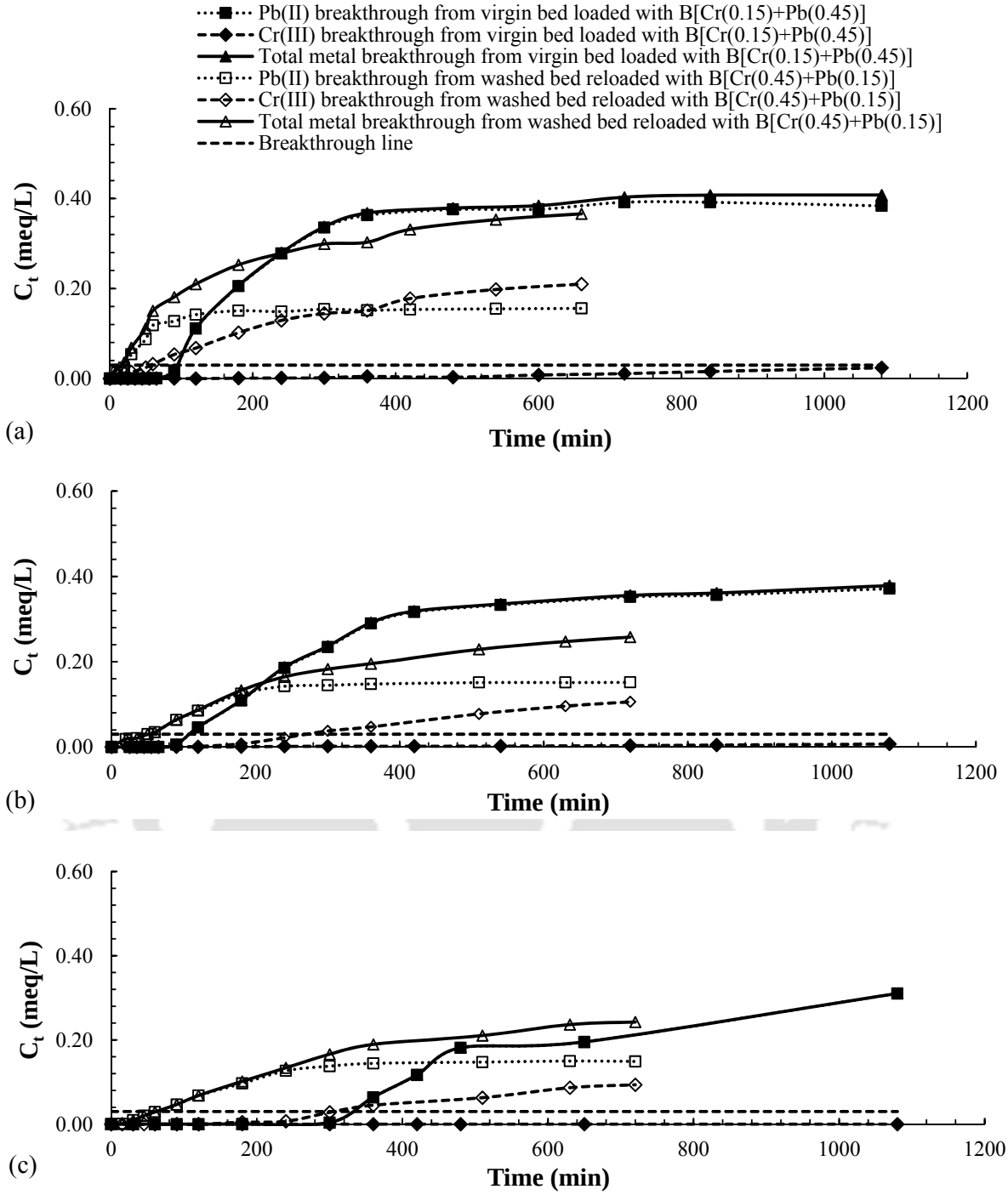

Fig. 5.136: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with B[Cr(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cr(0.45)+Pb(0.15)] combination at a flow rate of 2.0 mL/min under uncontrolled pH conditions {Initial metal conc. in B[Cr(0.15)+Pb(0.45)] combination: Cr(III) = 0.15±0.01 meq/L + Pb(II) = 0.45±0.02 meq/L and B[Cr(0.45)+Pb(0.15)] combination: Cr(III) = 0.44±0.00 meq/L + Pb(II) = 0.15±0.01 meq/L, Initial adjusted pH = 5.00±0.05, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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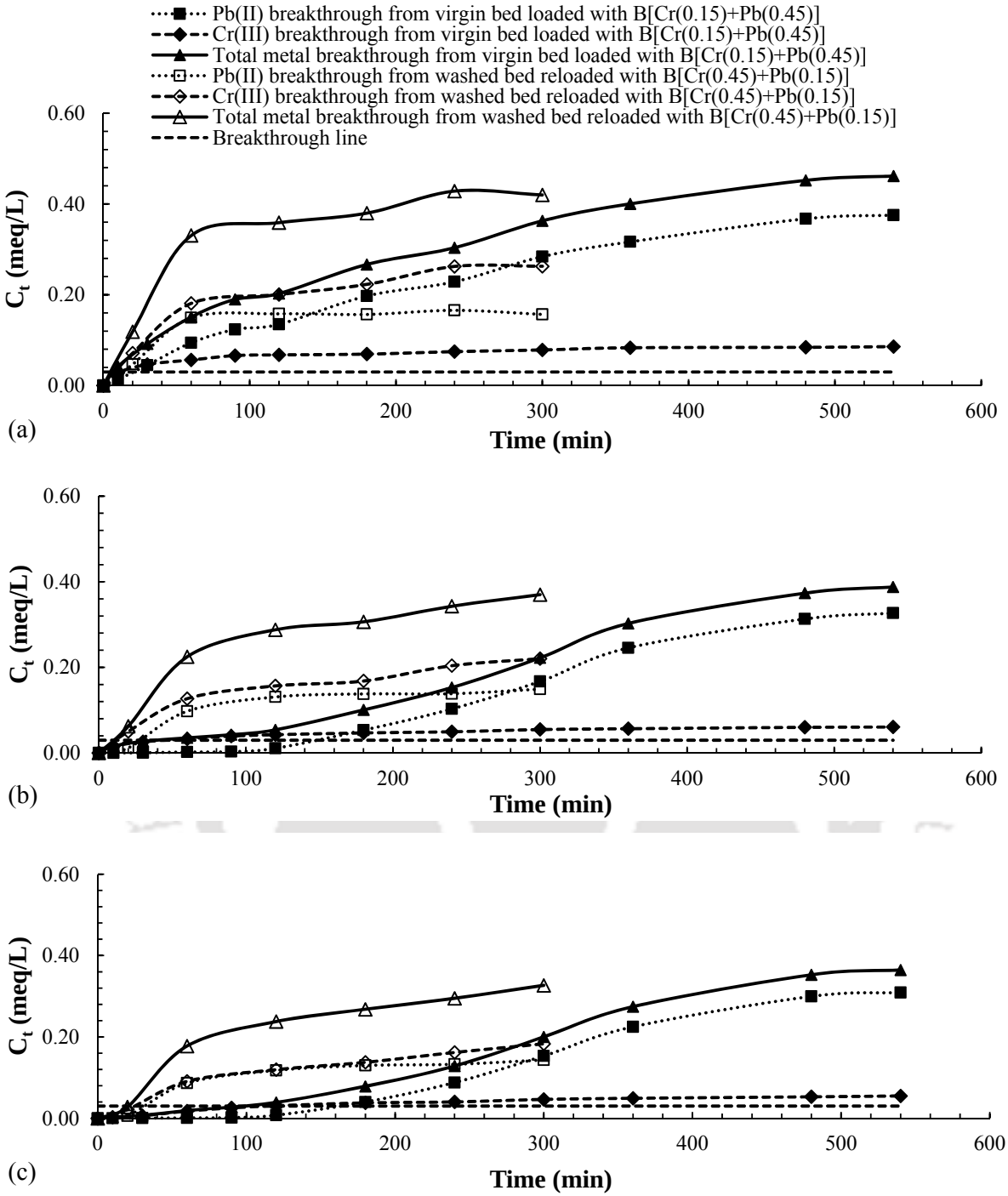

Fig. 5.137: Breakthrough curves for virgin GAA bed depths of (a) 3.0 cm (b) 4.5 cm and (c) 6.0 cm loaded with B[Cr(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cr(0.45)+Pb(0.15)] combination at a flow rate of 2.0 mL/min under controlled pH conditions {Initial metal conc. in B[Cr(0.15)+Pb(0.45)] combination: Cr(III) = 0.15±0.01 meq/L + Pb(II) = 0.45±0.02 meq/L and B[Cr(0.45)+Pb(0.15)] combination: Cr(III) = 0.44±0.00 meq/L + Pb(II) = 0.15±0.01 meq/L, Buffered pH = 5.00±0.05, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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throughput volumes for uncontrolled and controlled pH conditions have been tabulated in Table 5.70. The breakthrough throughput volumes for Cr(III), Pb(II) and total metal ions increased with increase in bed depths at the fixed flow rate as could be seen from Table 5.70. An increase in the service time was observed when the bed depth increased from 3.0 to 6.0 cm. The increase in Cr(III), Pb(II) and total metal ions removal from the bulk metal ion solution with increase in bed depths were possibly due to increase in the amount of adsorbent mass in the larger beds which provided greater opportunities for metal removal. Further, estimated breakthrough time for Cr(III) metal during loading of virgin GAA bed with B[Cr(0.15)+Pb(0.45)] combination under uncontrolled pH conditions were higher than for Pb(II) metal. However, estimated breakthrough time for Cr(III) metal during loading of virgin GAA bed with B[Cr(0.15)+Pb(0.45)] combination under controlled pH conditions was lower than for Pb(II) metal. It revealed the early breakthrough for Pb(II) metal under uncontrolled pH conditions and early breakthrough for Cr(III) under controlled pH conditions. Larger size of Cr(III)-acetate complexes [due to higher coordination number associated with Cr(III) metal] formed in controlled pH conditions compared to Pb(II)-acetate complexes might be the reason for the early breakthrough of Cr(III) metal under controlled pH conditions.

5.7.12 Effect of order of binary-metal ion system loadings on virgin and washed beds on total metal removal under uncontrolled and controlled pH conditions

The column studies for Cu(II) and Pb(II) metal removals from virgin and washed beds were carried out with selected combinations of Cu(II)+Pb(II) binary-metal ion system in subsections 5.7.8 and 5.7.9. In subsection 5.7.8, metal removals studies were carried out by first loading virgin GAA column beds with B[Cu(0.45)+Pb(0.15)] combination, then B[Cu(0.45)+Pb(0.15)] combination loaded beds were washed and subsequently reloaded with B[Cu(0.15)+Pb(0.45)] combination under uncontrolled and controlled pH conditions. However, the order of metal combination loadings to virgin and washed column beds were changed in subsection 5.7.9 – virgin GAA beds were first loaded with B[Cu(0.15)+Pb(0.45)] combination followed by B[Cu(0.15)+Pb(0.45)] combination loaded washed beds subsequently were reloaded with B[Cu(0.45)+Pb(0.15)] combination under uncontrolled and controlled pH conditions. Similarly, changed order of binary-metal ion system loadings to virgin and washed column beds were adopted for investigating Cr(III) and Pb(II) metal removals from combinations of Cr(III)+Pb(II) binary-metal ion systems in subsections 5.7.10 and 5.7.11. The major objective of these studies was to understand the effect of order of

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Table 5.70: Summary of breakthrough results at a fixed flow rate but varying depths of virgin GAA bed loaded with B[Cr(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cr(0.45)+Pb(0.15)] combination under uncontrolled and controlled pH conditions.

pH conditions	Bed depth (cm)	Virgin bed loaded with B[Cr(0.15)+Pb(0.45)] combination						Washed bed reloaded with B[Cr(0.45)+Pb(0.15)] combination					
		Initial metal conc. (meq/L)	t_B (min)	V_B (mL)	Metal removed (meq)			Initial metal conc. (meq/L)	t_B (min)	V_B (mL)	Metal removed (meq)		
					Cr(III)	Pb(II)	Total				Cr(III)	Pb(II)	Total
Uncontrolled	3.0	Pb(II) = 0.45±0.02	94	188	0.028	0.084	0.112	Pb(II) = 0.15±0.01	22	44	0.015	0.006	0.021
		Cr(III) = 0.15±0.01	1260	2520	0.351	0.312	0.663	Cr(III) = 0.44±0.00	60	120	0.047	0.012	0.059
		Total = 0.60±0.02	94	188	0.028	0.084	0.112	Total = 0.59±0.01	20	40	0.013	0.005	0.018
	4.5	Pb(II) = 0.45±0.02	108	216	0.034	0.096	0.130	Pb(II) = 0.15±0.01	50	100	0.036	0.013	0.049
		Cr(III) = 0.15±0.01	1080*	2160	0.336	0.387	0.723	Cr(III) = 0.44±0.00	270	540	0.228	0.032	0.260
		Total = 0.60±0.02	108	216	0.034	0.096	0.130	Total = 0.59±0.01	50	100	0.036	0.013	0.049
	6.0	Pb(II) = 0.45±0.02	-	-	-	-	-	Pb(II) = 0.15±0.01	-	-	-	-	-
		Cr(III) = 0.15±0.01	-	-	-	-	-	Cr(III) = 0.44±0.00	-	-	-	-	-
		Total = 0.60±0.02	-	-	-	-	-	Total = 0.59±0.01	-	-	-	-	-
Controlled	3.0	Pb(II) = 0.48±0.02	20	40	0.005	0.018	0.023	Pb(II) = 0.16±0.01	13	26	0.005	0.003	0.008
		Cr(III) = 0.16±0.01	12	24	0.003	0.011	0.014	Cr(III) = 0.46±0.00	8	16	0.003	0.002	0.005
		Total = 0.64±0.02	7	14	0.002	0.007	0.009	Total = 0.62±0.01	5	10	0.002	0.001	0.003
	4.5	Pb(II) = 0.45±0.02	147	294	0.037	0.134	0.171	Pb(II) = 0.15±0.01	28	56	0.015	0.008	0.023
		Cr(III) = 0.15±0.01	60	120	0.016	0.056	0.072	Cr(III) = 0.44±0.00	12	24	0.005	0.004	0.009
		Total = 0.60±0.02	60	120	0.016	0.056	0.072	Total = 0.59±0.01	9	18	0.004	0.003	0.007
	6.0	Pb(II) = 0.44±0.00	161	322	0.044	0.148	0.192	Pb(II) = 0.15±0.01	32	64	0.018	0.009	0.027
		Cr(III) = 0.15±0.01	120	240	0.034	0.111	0.145	Cr(III) = 0.44±0.00	25	50	0.013	0.007	0.020
		Total = 0.60±0.02	96	192	0.028	0.090	0.118	Total = 0.62±0.01	21	42	0.001	0.007	0.008

V_B = Breakthrough throughput volumes at effluent metal concentration equal to 0.03 meq/L; t_B = service time at breakthrough, * = effluent metal concentration equal to 0.007 meq/L; Bed depths of 3.0, 4.5 and 6.0 cm contained 9.4, 13.2 and 16.8 g of GAA respectively.

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binary-metal ion system loadings on overall metal removals by column beds (virgin and washed beds together) under uncontrolled and controlled pH conditions. While carrying out the studies as presented in subsections 5.7.8 to 5.7.11, it was aimed to operate the virgin as well as washed column beds till the column beds exhausted or yielded total effluent metal concentration close to the total influent metal concentration (say more than 80% of total influent metal concentration). The results of these studies might have helped in making an estimate of overall metal removals by the virgin and washed beds together when loaded till the beds might have got exhausted in two different loading orders of combination of selected binary-metal ion systems. While undertaking these studies in the initial phases, operation of column beds till it exhausted or yielded total effluent metal concentration close to 80% of total influent metal concentration became a nightmare as the column operations continued for more than 30 h at a stretch. The possible reasons for such a long column operation time might be attributed to selected diameter of the column beds, depth of column beds, linear flow rate through the column and initial influent metal ion concentration. However, it was thought not prudent to alter these selected operational parameters (viz. column diameter, bed depths, flow rate and influent metal ion concentration) to reduce the column operation time to a reasonable length to achieve column exhaustion or to have column total effluent metal concentration close to 80% of the total influent metal concentration. Therefore, column studies were carried out with reasonably reduced but different length of time periods for the virgin and washed beds depending upon binary-metal ion system being loaded to the bed and its concentration in the effluent coming out of the column bed as detailed in subsections 5.7.8 to 5.7.11.

The experimental data obtained in subsections 5.7.8 to 5.7.11 were used to estimate overall metal removal by the column beds (virgin and washed beds together) when virgin bed loaded with a combination of binary-metal ion system and washed bed reloaded with another combination of binary-metal ion system under uncontrolled and controlled pH conditions and operated till the column beds (virgin and washed beds) yielded total effluent metal concentration from virgin and washed beds close to or predetermined level to the total influent metal concentration. These estimates are already presented in Table 5.63, 5.65, 5.67 and 5.69. An inspection of these tables indicated that columns (virgin as well as washed beds) were operated up to different time periods and, therefore, estimated values of overall metal removals may not be appropriate to assess the effect of order of binary-metal ion system loadings and to arrive at a definite conclusion.

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However, the experimental data obtained in subsections 5.7.8 to 5.7.11 were also used to estimate overall metal removal by the column beds (virgin and washed beds together) when virgin bed loaded with a combination of binary-metal ion system and washed bed reloaded with another combination of binary-metal ion system under uncontrolled and controlled pH conditions till breakthrough of column beds (virgin and washed beds) when the total effluent concentration from virgin and washed beds were 5% of the total influent metal concentration (i.e. 0.03 meq/L). Fortunately, all the column studies were able to provide breakthrough results which are available in Table 5.64, 5.66, 5.68 and 5.70. These results for column breakthrough time for total metal ions have been compiled and presented in Table 5.71. A closer examination of the last column of Table 5.71 presenting overall metal removed by virgin and washed beds together indicated higher amounts of metal removal for virgin bed loaded with B[Cr(0.45)+Pb(0.15)] combination followed by washed bed reloaded with B[Cr(0.15)+Pb(0.45)] combination under uncontrolled pH conditions for binary-metal ion systems comprising of Cr(III)+Pb(II) (Table 5.71). However, generally higher amounts of metal removal observed for virgin bed loaded with B[Cr(0.15)+Pb(0.45)] combination followed by washed bed reloaded with B[Cr(0.45)+Pb(0.15)] combination under controlled pH conditions for binary-metal ion systems comprising of Cr(III)+Pb(II). It clearly hinted that higher amounts of metal removal could be expected if the virgin beds and washed beds were loaded/reloaded with a particular order of loadings with Cr(III)+Pb(II) binary-metal ion system as indicated in the analysis. If appropriate order of loadings was not followed, then overall metal removal will be comparatively lower. However in case of Cu(II)+Pb(II) binary-metal ion system, definite trend for higher metal removal was not observed when virgin bed loaded with B[Cu(0.45)+Pb(0.15)] combination followed by washed bed reloaded with B[Cu(0.15)+Pb(0.45)] combination and vice-versa under uncontrolled pH conditions while higher amounts of metal removal observed for virgin bed loaded with B[Cu(0.15)+Pb(0.45)] combination followed by washed bed reloaded with B[Cu(0.45)+Pb(0.15)] combination under controlled pH conditions.

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Table 5.71: Column breakthrough results at a glance for fixed flow rate of 2.0 mL/min but varying depths of virgin GAA bed loaded with a binary-metal ion combination and washed bed reloaded with another binary-metal ion combination under uncontrolled and controlled pH conditions.

Binary combinations	pH conditions	Bed depth (cm)	Virgin bed						Washed bed						Overall metal removed by virgin & washed beds (meq)
			Loaded with	t_B* (min)	V_B (mL)	Metal removed (meq)			Loaded with	t_B* (min)	V_B (mL)	Metal removed (meq)			
						Cu(II)	Pb(II)	Total				Cu(II)	Pb(II)	Total	
B[Cu(0.45)+Pb(0.15)] & B[Cu(0.15)+Pb(0.45)]	Uncontrolled	3.0	B[Cu(0.45)+Pb(0.15)]	100	200	0.088	0.030	0.118	B[Cu(0.15)+Pb(0.45)]	6	12	0.002	0.005	0.007	0.125
		4.5		192	384	0.170	0.058	0.228		54	108	0.015	0.049	0.064	0.292
		6.0		247	494	0.226	0.074	0.300		58	116	0.016	0.052	0.068	0.368
	Controlled	3.0		40	80	0.034	0.012	0.046		7	14	0.001	0.006	0.007	0.053
		4.5		66	132	0.056	0.020	0.076		9	18	0.002	0.009	0.011	0.087
		6.0		80	160	0.067	0.025	0.092		20	40	0.005	0.018	0.023	0.115
	Uncontrolled	3.0	B[Cu(0.15)+Pb(0.45)]	90	180	0.078	0.026	0.104	B[Cu(0.45)+Pb(0.15)]	30	60	0.008	0.027	0.035	0.139
		4.5		157	314	0.140	0.044	0.184		60	120	0.017	0.054	0.071	0.255
		6.0		265	530	0.234	0.075	0.309		120	240	0.033	0.111	0.144	0.453
	Controlled	3.0		66	172	0.059	0.017	0.076		7	14	0.002	0.007	0.009	0.085
		4.5		124	248	0.111	0.033	0.144		6	12	0.002	0.005	0.007	0.151
		6.0		142	284	0.128	0.038	0.166		8	16	0.002	0.007	0.009	0.175

Table continued on next page…….

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Table 5.71 continues…….

Binary combinations	pH conditions	Bed depth (cm)	Virgin bed						Washed bed						Overall metal removed by virgin & washed beds (meq)
			Loaded with	t_B* (min)	V_B (mL)	Metal removed (meq)			Loaded with	t_B* (min)	V_B (mL)	Metal removed (meq)			
						Cr(III)	Pb(II)	Total				Cr(III)	Pb(II)	Total	
B[Cr(0.45)+Pb(0.15)] & B[Cr(0.15)+Pb(0.45)]	Uncontrolled	3.0	B[Cr(0.45)+Pb(0.15)]	180	360	0.159	0.053	0.212	B[Cr(0.15)+Pb(0.45)]	52	104	0.016	0.046	0.062	0.274
		4.5		249	498	0.224	0.072	0.296		104	208	0.030	0.091	0.121	0.417
		6.0		670	1340	0.605	0.189	0.794		161	322	0.047	0.140	0.187	0.981
	Controlled	3.0		4	8	0.004	0.001	0.005		12	24	0.002	0.011	0.013	0.018
		4.5		5	10	0.005	0.002	0.007		25	50	0.004	0.023	0.027	0.034
		6.0		23	46	0.021	0.007	0.028		42	84	0.009	0.039	0.048	0.076
	Uncontrolled	3.0	B[Cr(0.15)+Pb(0.45)]	94	188	0.028	0.084	0.112	B[Cr(0.45)+Pb(0.15)]	20	40	0.013	0.005	0.018	0.130
		4.5		108	216	0.034	0.096	0.130		50	100	0.036	0.013	0.049	0.179
		6.0		-	-	-	-	-		-	-	-	-	-	
	Controlled	3.0		7	14	0.002	0.007	0.009		5	10	0.002	0.001	0.003	0.012
		4.5		60	120	0.016	0.056	0.072		9	18	0.004	0.003	0.007	0.079
		6.0		96	192	0.028	0.090	0.118		21	42	0.001	0.007	0.008	0.126

* = Breakthrough time correspondence to total effluent metal conc. equal to 0.03 meq/L.

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5.7.13 Summary

The continuous mode column studies for metal removals from mono- and binary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions were investigated under uncontrolled and controlled pH conditions. (1) The effluent solution pH coming out of the virgin and washed beds were observed to increase rapidly from initially adjusted pH of 5.00 under uncontrolled pH conditions and initially buffered pH of 5.00 under controlled pH conditions to higher levels and then decreased back close to initially adjusted and buffered pH levels during initial phases (first 100 min.) of column operation when virgin beds loaded and washed beds reloaded with mono- and binary-metal ion systems. This aspect of variation in effluent solution pH from column beds appeared to be unusual requiring further detail investigation. (2) The rise in effluent solution pH above 5.50 might have led to metal removals from mono- and binary-metal ion systems due to combined effects of precipitation and adsorption under uncontrolled and controlled pH conditions of column operations. (3) In general, the column beds had shown additional metal removal capability when virgin beds loaded with a mono-metal ion system or a combination of binary-metal ion system followed by reloading of washed beds with another mono-metal ion system or another combination of binary-metal ion system under uncontrolled and controlled pH conditions. (4) When the virgin beds loaded with mono-metal ion system (termed as the first metal) were washed and then reloaded with another mono-metal ion system (termed as the second metal) under uncontrolled and controlled pH conditions, migration of the first metal ion {either Cu(II) or Pb(II) or Cr(III) as the case may be} from the washed beds to the effluent solution took place. Generally, the breakthrough of the second metal ion in the effluent solution was observed after the peak of the migrating first metal ion had occurred. This might be due to possible occupation by the second metal ion of the spaces/sites vacated by the migrating first metal ion from the column beds. (5) When the virgin beds of depth 3.0, 4.5 and 6.0 cm loaded with M[Pb(0.60)] systems; washed and then reloaded with M[Cu(0.60)] systems under uncontrolled pH conditions of column operations, an unusual trend in breakthrough curves for Cu(II) metal ions from the washed beds were observed – first a rising trend with a peak, then a declining trend with a flat dip and then again a rising trend till the end of column operation. The migration of Pb(II) metal ions from the washed beds might have aided in the unusual trend of breakthrough curves of Cu(II) metal ions. Similar unusual trends in breakthrough curves for Cu(II) metal ions were also observed from washed beds reloaded

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with M[Cu(0.60)] system {but virgin beds previously loaded with M[Cr(0.60)] system} under uncontrolled pH conditions without migration of Cr(III) metal ion from the washed beds to the solution during reloading. (6) When virgin beds loaded with B[Cu(0.45)+Pb(0.15)] combination were washed and reloaded with B[Cu(0.15)+Pb(0.45)] combination under uncontrolled and controlled pH conditions, the effluent Cu(II) concentration was observed to be higher than 0.15 meq/L after initial period of column operation. It indicated migration of Cu(II) from the washed beds which was previously loaded with B[Cu(0.45)+Pb(0.15)] combination. However, (7) when virgin beds loaded with B[Cu(0.15)+Pb(0.45)] combination were washed and reloaded with B[Cu(0.45)+Pb(0.15)] combination under uncontrolled and controlled pH conditions, the effluent Pb(II) concentration was observed to be lower than 0.15 meq/L during the column operation indicating no migration of Pb(II) from washed beds. Similarly, when virgin beds loaded with B[Cr(0.45)+Pb(0.15)] and B[Cr(0.15)+Pb(0.45)] combinations were washed and reloaded respectively with B[Cr(0.15)+Pb(0.45)] and B[Cr(0.45)+Pb(0.15)] combinations under uncontrolled and controlled pH conditions, the effluent Cr(III) and Pb(II) concentrations were observed to be lower than 0.15 meq/L during the column operation. Did it mean that the washed beds had additional potential for removal of Pb(II) and Cr(III) ions reloaded with lower initial concentrations of Pb(II) and Cr(III) ions in the respective binary-metal ion combinations compared to loading of the virgin beds with higher initial concentrations of Pb(II) and Cr(III) in the binary-metal ion combinations? This aspect is also open for further investigation. (8) With the increase in bed depths from 3.0 cm to 6.0 cm, the breakthrough curves with mono- and binary-metal ion systems under uncontrolled and controlled pH conditions appeared to shift to the right yielding an increased service times and breakthrough throughput volumes. (9) The order of loading and reloading of virgin and washed beds with mono- and binary-metal ion systems under uncontrolled and controlled pH conditions appeared to have bearing on higher amounts of metals removals by the column beds.

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CHAPTER 6

SUMMARY AND CONCLUSIONS

The kinetics and equilibrium studies for metal removals under uncontrolled pH conditions and metal uptakes under controlled pH conditions and column studies for metal removals under uncontrolled and controlled pH conditions have been investigated for selected combinations of mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) metal ions. The major conclusions obtained from this research work have been summarized below.

The availability of metal ions in soluble form with variation in solution pH from mono-, binary- and ternary-metal ion systems was experimentally and theoretically investigated. The conclusions from the study are:

1. Cu(II), Pb(II) and Cr(III) metal ions were 100% available in solution up to pH 5.50 from mono-metal ion systems of M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)]. At higher pH than 5.50, the availability of metal ions in solution started to reduce due to precipitation.
2. Cu(II), Pb(II) and Cr(III) metal ions were 100% available in solution up to pH 5.50 in all the four selected combinations of binary-metal ion systems comprising of Cu(II)+Pb(II), Cr(III)+Pb(II). With increase in pH above 5.50, the availability of metal ions in solution started to reduce due to precipitation.
3. The availability of Cu(II) and Cr(III) metal ions drastically reduced in all the four combinations of binary-metal ion system comprising of Cu(II)+Cr(III) and two combinations of ternary-metal ion systems comprising of Cu(II)+Pb(II)+Cr(III) at solution pH of 5.00 or higher due to precipitation or co-precipitation of metal ions.
4. The theoretical analysis indicated reduction of some of the metal ion concentration in the mono-, binary- and ternary-metal ion systems even at lower pH level of 5.00.

The effect of contact time on the metal ions remaining in aqueous phase from mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) have been

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investigated under uncontrolled and controlled pH conditions. The conclusions from the study are:

1. All the selected combinations of mono-, binary- and ternary-metal ion systems investigated for effect of contact time on the metal ions concentration remaining in aqueous phase under uncontrolled pH conditions had shown increase in solution pH with contact time leading to removal of metal ions from the aqueous phase due to combined effects of precipitation and adsorption.
2. All the selected combinations of mono-, binary-, and ternary-metal ion systems investigated for effect of contact time on the metal ions concentration remaining in aqueous phase under controlled pH conditions had shown that bulk solution pH remained unchanged throughout the contact time and hence the removal of all the three metal ions was due to adsorption only.
3. The reduction in residual metal ions concentrations from all selected combinations of mono-, binary- and ternary-metal ion systems were lower under controlled pH conditions compared to uncontrolled pH conditions. The GAA had ability to alter solution pH to higher levels under uncontrolled pH conditions thereby aiding metal removals due to combined effects of precipitation and adsorption while under controlled pH conditions, the acetate buffer reagent formed metal complexes thereby making complexed metal less available for adsorption.
4. The total residual metal ions concentrations remaining in solution from selected combinations of Cu(II)+Pb(II), Cr(III)+Pb(II) and Cu(II)+Cr(III) binary-metal ion systems having total initial metal ion concentration of approximately 0.60 meq/L overlapped within 95% confidence interval. It indicated that the concentration of total metal ion remaining in aqueous phase was fairly independent of proportion of initial metal ion concentration in selected binary-metal ion systems as long as total initial metal ion concentration was approximately the same.
5. Increase in total initial metal ions concentrations in solution resulted in increased total residual metal ions concentration except for the combination of Cu(II)+Cr(III) binary-metal ion system under uncontrolled pH conditions.

The kinetics of metal uptake under controlled pH conditions and metal removal (or reduction) under uncontrolled pH conditions have been studied from selected combinations

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of mono-, binary- and ternary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) metal ions. The conclusions from the study are:

1. The total metal uptakes under controlled pH conditions was observed to be similar and fairly independent of proportion of initial metal ion concentrations present in selected combinations of binary- and ternary-metal ion systems as long as total initial metal ion concentration in the combinations was near to 0.60 meq/L even though ionic radius, valence, and atomic weights of the metal ions were different from each other. Similar results were observed for total metal removals under uncontrolled pH conditions from selected combinations of binary- and ternary-metal ion systems investigated.
2. Doubling of total initial metal ion concentrations i.e. 1.20 meq/L in the three combinations of binary-metal ion systems and tripling of total initial metal ion concentrations i.e. 1.80 meq/L in a combination of ternary-metal ion system enhanced total metal uptakes compared to uptakes from combinations of mono-, binary- and ternary-metal ion systems having total initial metal ion concentration of approximately 0.60 meq/L. It indicated additional metal uptake capacity of the GAA with increase in total initial metal ion concentration. Similar results were observed for total metal removals for combinations of binary-metal ion systems with doubled total initial metal ion concentrations compared to combinations of mono- and binary-metal ion systems having total initial metal ion concentration approximately 0.60 meq/L indicating additional metal removal capability of GAA used.
3. The kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions followed pseudo-second-order rate and kinetic models respectively for the combinations of mono-, binary- and ternary-metal ion systems investigated.
4. The adsorption of target metal ions by GAA under controlled pH conditions from different combinations of mono-, binary- and ternary-metal ions was observed to be a complex process involving surface adsorption as well as intra-particle diffusion contributing to rate controlling steps.

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Batch tests to investigate additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions by GAA when exposed to metal ions repeatedly with mono-metal ion systems of M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)] were carried out. The conclusions from the study are:

1. Target metal loaded adsorbent GAA when exposed only once to a non-target mono-metal ion system indicated additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions. The displacement of target mono-metal ions into solution was observed possibly due to displacement of target mono-metal ions loosely bound to the surface of GAA possibly via outer-sphere complexation mechanism.
2. Repeated exposures of GAA to 6-10 loading cycles to target mono-metal ions concentration of 0.60 meq/L indicated additional metal removal capacity under uncontrolled pH conditions and additional metal uptake capacity under controlled pH conditions in each cycles. After 6-10 cycles, target mono-metal loaded GAA was again exposed to a non-target mono-metal ion once, additional removal of non-target mono-metal ion under uncontrolled pH conditions and additional uptake of non-target mono-metal ion under controlled pH conditions were observed along with displacement of target mono-metal ion into the solution.

Kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for four loading cycles with mono- and binary-metal ions systems comprising of Cu(II), Pb(II) and Cr(III) metal ions were investigated. The conclusions from the study are:

1. During the first three loading cycles with a mono-metal ion system, additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions was observed in each loading cycle. Additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions decreased with increase in number of loading cycles during the first three loading cycles.
2. When GAA loaded with a mono-metal ion system during first three loading cycles was exposed to another mono-metal ion system in the fourth loading cycle, additional

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metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions of the other metal ion was observed. The migration of metal ions loaded onto GAA during the first three loading cycles to bulk solution was observed during the fourth loading cycle.

3. The cumulative metal removal under uncontrolled pH conditions and cumulative metal uptake under controlled pH conditions from mono-metal ion systems increased with number of loading cycles.
4. Based upon cumulative metal mass removed, a definite preference of metal removal by GAA was observed when loaded with mono-metal ion systems in different cycles. However, based upon cumulative metal mass uptaken, no definite preference of metal uptake by GAA was observed when loaded with mono-metal ion systems in different cycles.
5. During the first three loading cycles with a combination of binary-metal ion system, metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions for the metal ions with higher concentration in the combination decreased with increase in number of loading cycles {except for Cr(III) metal removal under uncontrolled pH condition from B[Cr(0.45)+Pb(0.15)] combination}.
6. When GAA loaded with first three loading cycles of a combination of binary-metal ion system was exposed to another combination in the fourth loading cycle, the metal ion having lower concentration in combination had insignificant removal under uncontrolled pH conditions and insignificant uptake under controlled pH conditions {except for Pb(II) metal removal under uncontrolled pH conditions from B[Cu(0.45)+Pb(0.15)] combination and Cr(III) metal removal and metal uptake from B[Cr(0.15)+Pb(0.45)] combination} while the metal ion having higher concentration in combination had shown higher removal under uncontrolled pH conditions and higher uptake under controlled pH conditions compared to its removal and uptake from previous three loading cycles.
7. The variation in total metal removals under uncontrolled pH conditions and total metal uptakes under controlled pH conditions generally decreased with increase in number of loading cycles except for the fourth loading cycle with B[Cr(0.45)+Pb(0.15)] combination wherein total metal removals from the cycle were higher than that obtained during the second and third loading cycles with B[Cr(0.15)+Pb(0.45)] combination.

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8. The cumulative metal removal under uncontrolled pH conditions and cumulative metal uptake under controlled pH conditions increased with number of loading cycles of binary-metal ion systems indicating additional metal removal and additional metal uptake potential of GAA.

The equilibrium studies for metal ions removal under uncontrolled pH conditions and metal ions uptake under controlled pH conditions for the selected combinations of mono-, binary- and ternary-metal ion systems have been carried out. The conclusions from the study are:

1. Average equilibrium pH of solutions was more than 5.50 at lower C_e values causing metal removals at equilibrium under uncontrolled pH conditions due to precipitation as well as adsorption. While the metal uptakes at equilibrium from the solutions under controlled pH conditions were mainly due to adsorption.
2. Two mathematical relationships i.e. power and polynomial curves well predicted individual and total metal ion removals at equilibrium from the selected combinations of mono-, binary- and ternary-metal ion systems under uncontrolled pH conditions.
3. The higher R^2 values obtained for Freundlich isotherm model indicated its better suitability to represent the experimental equilibrium metal uptake data from the selected combinations of mono-, binary- and ternary-metal ion systems.
4. The variations in metal removals at equilibrium from mono-metal ion systems generally appeared to overlap at 95% confidence intervals with variations in total metal removals at equilibrium from the combinations of binary-metal ion systems and varied within a small band with the ternary-metal ion system having total initial metal ion concentration of 0.60 meq/L. Similarly total metal uptakes at equilibrium from mono-, binary- and ternary-metal ion systems having total initial metal ion concentration of 0.60 meq/L varied within small band. These results suggested that the metal removals at equilibrium and metal uptakes at equilibrium depend on the total initial metal ion concentration present in the solution rather than on ionic radius, valence and atomic weights of individual metal ions.
5. Two of the competitive metal uptake models – namely Extended Freundlich Isotherm model and SRS model were able to fit closely the experimental data from binary- and

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ternary-metal ion combinations having initial metal ion concentration of participating metal ions approximately to 0.60 meq/L obtained under controlled pH conditions.

The continuous mode column studies for metal removal under uncontrolled and controlled pH conditions were carried out for the selected combinations of mono- and binary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) metals. The conclusions from the study are:

1. The effluent solution pH coming out of the virgin and washed beds were observed to increase rapidly from initially adjusted pH of 5.00 under uncontrolled pH conditions and initially buffered pH of 5.00 under controlled pH conditions to higher levels and then decreased back close to initially adjusted and buffered pH levels during initial phases (first 100 min.) of column operation when virgin beds loaded and washed beds reloaded with mono- and binary-metal ion systems.
2. The rise in effluent solution pH above 5.50 might have caused metal removals from mono- and binary-metal ion systems due to combined effects of precipitation and adsorption under uncontrolled and controlled pH conditions of column operations.
3. The column beds had shown additional metal removal capability when virgin beds loaded with a mono-metal ion system or a combination of binary-metal ion system followed by reloading of washed beds with another mono-metal ion system or another combination of binary-metal ion system under uncontrolled and controlled pH conditions.
4. When the virgin beds loaded with mono-metal ion system (termed as the first metal) were washed and then reloaded with another mono-metal ion system (termed as the second metal) under uncontrolled and controlled pH conditions, migration of the first metal ion {either Cu(II) or Pb(II) or Cr(III) as the case may be} from the washed beds to the effluent solution took place. The breakthrough of the second metal ion in the effluent solution was observed after the peak of the migrating first metal ion had occurred. This might be due to possible occupation by the second metal ion of the spaces/sites vacated by the migrating first metal ion from the column beds.
5. When the virgin beds of depth 3.0, 4.5 and 6.0 cm loaded with M[Pb(0.60)] systems; washed and then reloaded with M[Cu(0.60)] systems under uncontrolled pH conditions of column operations, an unusual trend in breakthrough curves for Cu(II)

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metal ions from the washed beds were observed – first a rising trend with a peak, then a declining trend with a flat dip and then again a rising trend till the end of column operation. The migration of Pb(II) metal ions from the washed beds might have aided in the unusual trend of breakthrough curves of Cu(II) metal ions. Similar unusual trends in breakthrough curves for Cu(II) metal ions were also observed from washed beds reloaded with M[Cu(0.60)] system {but virgin beds previously loaded with M[Cr(0.60)] system} under uncontrolled pH conditions without migration of Cr(III) metal ion from the washed beds to the solution during reloading.

6. When virgin beds loaded with B[Cu(0.45)+Pb(0.15)] combination were washed and reloaded with B[Cu(0.15)+Pb(0.45)] combination under uncontrolled and controlled pH conditions, the effluent Cu(II) concentration was observed to be higher than 0.15 meq/L after initial period of column operation. It indicated migration of Cu(II) from the washed beds which was previously loaded with B[Cu(0.45)+Pb(0.15)] combination. However, when virgin beds loaded with B[Cu(0.15)+Pb(0.45)] combination were washed and reloaded with B[Cu(0.45)+Pb(0.15)] combination under uncontrolled and controlled pH conditions, the effluent Pb(II) concentration was observed to be lower than 0.15 meq/L during the column operation indicating no migration of Pb(II) from washed beds.
7. When virgin beds loaded with B[Cr(0.45)+Pb(0.15)] and B[Cr(0.15)+Pb(0.45)] combinations were washed and reloaded respectively with B[Cr(0.15)+Pb(0.45)] and B[Cr(0.45)+Pb(0.15)] combinations under uncontrolled and controlled pH conditions, the effluent Cr(III) and Pb(II) concentrations were observed to be lower than 0.15 meq/L during the column operation.
8. With the increase in bed depths from 3.0 cm to 6.0 cm, the breakthrough curves with mono- and binary-metal ion systems under uncontrolled and controlled pH conditions appeared to shift to the right yielding an increased service times and breakthrough throughput volumes.
9. The order of loading and reloading of virgin and washed beds with mono- and binary-metal ion systems under uncontrolled and controlled pH conditions appeared to have bearing on higher amounts of metals removals by the column beds.

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CHAPTER 7

FUTURE SCOPE OF RESEARCH

The present research work was focused to understand metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions from selected combinations of mono-, binary- and ternary-metal ion systems through kinetics and equilibrium studies in batch modes and column studies in continuous mode. All these studies were performed while maintaining similar sets of experimental conditions in majority of selected combinations in terms of total initial metal ion concentrations in the metal ion systems, same initial adjusted pH levels using diluted HCl or NaOH for uncontrolled pH conditions but acetate buffers for controlled pH conditions and room temperatures for all the combinations, using a particular adsorbent (GAA), use of particular mode of mixing with a fixed mixing speed, etc. Though the present works have helped in improving understanding of the metal removal and metal uptake from selected combinations of mono-, binary- and ternary-metal ion systems under uncontrolled and controlled pH conditions. However, it has also generated many questions/queries which need logical answer after thorough investigation. Some of the questions/queries are listed below which may be considered as future scope as additional outcome of this research work.

1. The metal availability in aqueous phase at different selected solution pH estimated using MINEQL+ software were not in agreement with the experimental metal availability results. This needs detailed investigation and appropriate resolution.
2. The presence of Cu(II) and Cr(III) metal ions together in solutions of binary-metal ion systems of Cu(II)+Cr(III) and ternary-metal ion systems of Cu(II)+Pb(II)+Cr(III) had profound effect on its availability in aqueous phase around solution pH of 5.00 or higher. A few preliminary studies were carried out for concentrations of Cu(II) and Cr(III) metal ions remaining in solution with variation in contact time using a fixed dose of 0.6 g GAA/50 mL at a lower pH values of 3.50 and 4.30 under uncontrolled pH conditions with an aim to keep most of the metal ions in aqueous phase. However, quick rise in solution pH levels above 5.00 observed in the beginning of experiments leading to sharp reduction in metal availability in aqueous phase due to precipitation. On the other hand, no metal precipitation was observed under controlled pH

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conditions with initial solution pH buffered to 3.50 and 4.30 using additional amounts of acetate buffers, but it did not show any reduction of metal ion concentration remaining in solution with variation in contact time using a fixed dose of 0.6 g GAA/50 mL. Therefore, the aspect of quick rise in pH levels and precipitation of metal ions under uncontrolled pH conditions and no reduction in metal ion concentration remaining in aqueous phase with variation in contact time under controlled pH conditions needs investigation.

3. The metal ion concentrations remaining in aqueous phase from all the selected combinations of mono-, binary- and ternary-metal ion systems were higher under controlled pH conditions compared to uncontrolled pH conditions. This was attributed to metal-complex formation with acetate buffer components thereby making a part of metal ion unavailable for adsorption. This needs to be confirmed by additional investigation.
4. The kinetics of metal removal from selected combinations of mono-, binary- and ternary-metal ion systems under uncontrolled pH conditions have been dealt with in this thesis by modifying the existing expressions of pseudo-first-order and pseudo-second-order kinetic models for metal uptakes with giving appropriate interpretations to modified kinetic constants. It is important to point out that the metal removals under uncontrolled pH conditions have been attributed to combined effects of precipitation and adsorption in this thesis, while the existing kinetic models are applicable only for metal uptake by the adsorbent. However, the modified expressions for kinetics of metal removal under uncontrolled pH conditions need rigorous verification from published data for its applicability and wide acceptance by researchers.
5. The kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions have been carried out for four loading cycles with selected combinations of mono- and binary-metal ion systems comprising of Cu(II), Pb(II) and Cr(III) ions – the first three loading cycles with a mono-metal ion system or combination of binary-metal ion system while the fourth loading cycle with another mono-metal ion system or another combination of binary-metal ion system. In each of the first three loading cycles, additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions were observed. However, during the fourth loading cycle, additional removal and additional uptake of

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the loaded metal ion was observed while migration of metal ion loaded in the first three cycles to the aqueous phase was also observed. Hence, there is need to further loading of the adsorbent of the fourth cycle to estimate additional removal and additional uptake of loaded metal ion and further migration of the metal ion loaded in the first three cycles.

6. The data obtained for variation in metal uptake with equilibrium metal concentrations from selected combinations of mono-, binary- and ternary-metal ion systems under controlled pH conditions have been analyzed using well known adsorption isotherms – Langmuir and Freundlich. However, the data obtained for variation in metal removal with equilibrium metal concentration from selected combinations of mono-, binary- and ternary-metal ion systems under uncontrolled pH conditions cannot be analyzed using adsorption isotherms as the metal removals have been attributed due to combined effects of precipitation and adsorption. However, mathematical relationships in terms of power and polynomial curves have been developed between metal removals at equilibrium with the equilibrium metal concentration. There is a need to develop appropriate mathematical models for the analysis of metal removal data obtained under uncontrolled pH conditions.
7. The experimental equilibrium metal uptake data obtained under competitive environment from three combinations of binary-metal ion systems {B[Cu(0.60)+Pb(0.60)], B[Cr(0.60)+Pb(0.60)] and B[Cu(0.60)+Cr(0.60)]} and one combination of ternary-metal ion system {T[Cu(0.60)+Pb(0.60)+Cr(0.60)]} have been analyzed using identified competitive metal uptake models namely modified competitive Langmuir model, extended Langmuir isotherm model, extended Freundlich isotherm model and SRS model as experimental equilibrium metal uptake data from single or mono-metal ion systems {M[Cu(0.60)], M[Pb(0.60)] and M[Cr(0.60)]} under non-competitive environments were available. However, the identified competitive metal uptake models could not be applied to the other combinations of binary- and ternary-metal ion systems due to non-availability of non-competitive experimental equilibrium data for single or mono-metal ion systems having initial metal ion concentrations of 0.15 meq/L, 0.20 meq/L, 0.30 meq/L and 0.45 meq/L.
8. The equilibrium studies for metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions with selected combinations of mono-,

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binary- and ternary-metal ion systems comprising of Cu(II), Pb(II), and Cr(III) ions have been carried out by exposing the adsorbent GAA only once to the metal ion system. However, the kinetics of metal removal under uncontrolled pH conditions and metal uptake under controlled pH conditions have been carried out for four loading cycles with selected combinations of metal ion systems which yielded additional metal removal and additional metal uptake in each of the loading cycles. These interesting kinetic experimental results have made a strong case for carrying out similar equilibrium studies. There is a need to carry out equilibrium studies for assessing the capability of the adsorbent for additional metal removal under uncontrolled pH conditions and additional metal uptake under controlled pH conditions from mono-, binary- and ternary-metal systems comprising of Cu(II), Pb(II) and Cr(III) ions when the adsorbent is exposed repeatedly with the same metal ion (or same combination of metal ions) or a different metal ion (or a different combination of same metal ions but with a different initial metal ion concentrations).

9. The effluent solution pH coming out of the virgin and washed beds were observed to increase rapidly from initially adjusted pH of 5.00 under uncontrolled pH conditions and initially buffered pH of 5.00 under controlled pH conditions to higher levels and then decreased back close to initially adjusted and buffered pH levels during initial phases (first 100 min.) of column operation when virgin beds loaded and washed beds reloaded with mono- and binary-metal ion systems. This aspect of variation in effluent solution pH from column beds appeared to be unusual requiring further detailed investigation.
10. The rise in effluent solution pH coming out of the virgin and washed beds were observed to be above 5.50 which might have led to metal removals from mono- and binary-metal ion systems due to combined effects of precipitation and adsorption under uncontrolled and controlled pH conditions of column operations. Whether column breakthroughs results could still be analyzed using bed depth service time (BDST) model (Bohart & Adams, 1920) and Thomas model (Naddafi et al., 2007; Thomas, 1944)?
11. When the virgin beds of depth 3.0, 4.5 and 6.0 cm loaded with M[Pb(0.60)] systems; washed and then reloaded with M[Cu(0.60)] systems under uncontrolled pH conditions of column operation, an unusual trend in breakthrough curves for Cu(II) metal ions from the washed beds were observed – first a rising trend with a peak, then

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a declining trend with a flat dip and then again a rising trend till the end of column operation. The migration of Pb(II) metal ions from the washed beds might have aided in the unusual trend of breakthrough curves of Cu(II) metal ions. Similar unusual trends in breakthrough curves for Cu(II) metal ions were also observed from washed beds reloaded with M[Cu(0.60)] system {but virgin beds previously loaded with M[Cr(0.60)] system} under uncontrolled pH conditions without migration of Cr(III) metal ion from the washed beds to the solution during reloading. This aspect is open for further investigation.

12. When virgin beds loaded with B[Cu(0.15)+Pb(0.45)] combination were washed and reloaded B[Cu(0.45)+Pb(0.15)] combination under uncontrolled and controlled pH conditions, the effluent Pb(II) concentration was observed to be lower than 0.15 meq/L during the column operation indicating no migration of Pb(II) from washed beds. Similarly, when virgin beds loaded with B[Cr(0.45)+Pb(0.15)] and B[Cr(0.15)+Pb(0.45)] combinations were washed and reloaded respectively with B[Cr(0.15)+Pb(0.45)] and B[Cr(0.45)+Pb(0.15)] combinations under uncontrolled and controlled pH conditions, the effluent Cr(III) and Pb(II) concentrations were observed to be lower than 0.15 meq/L during the column operation. Did it mean that the washed beds had additional potential for the removal of Pb(II) and Cr(III) ions reloaded with lower initial concentrations of Pb(II) and Cr(III) ions in the respective binary-metal ion combinations compared to loading of the virgin beds with higher initial concentrations of Pb(II) and Cr(III) in the binary-metal ion combinations? This aspect is also open for further investigation.
13. The effect of order of mono- and binary-metal ion system loadings on virgin and washed beds on total metal removal under uncontrolled and controlled pH conditions have been carried out by comparing the column performance up to breakthrough time only as the columns could not be in operation till its exhaustion. In order to compare the total metal removal from the virgin and washed beds together, it is important to operate the column beds (virgin as well as washed) till it get exhausted with the loaded metal ion system.
14. Is it possible to simulate column breakthrough curves using batch kinetic and equilibrium data as presented in this thesis? An effort in this direction will serve the cause of metal removal through column operation tremendously.

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15. In addition, change in adsorbent type, selection of different adsorbates and its combinations, changes in experimental conditions such as initial pH levels, adsorbent doses, temperature, method of mixing and its speed may require separate in-depth studies.

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Appendix A

Estimation of q_e and k_1 of pseudo-first-order rate expression using Least Squares Method

A.1 Background

The pseudo-first-order rate expression with regard to adsorption of ions on solid surface systems is expressed as:

$$q_t = q_e (1 - e^{-k_1 \times t}) \tag{A.1}$$

and its linearized form is represented as:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \tag{A.2}$$

where q_e and q_t are the amounts of metal ions adsorbed on adsorbent (meq/g) at equilibrium and at time t respectively and k_1 is the rate constant of first order adsorption (1/min). The linearized form of rate equation (Eq. A.2) had been used to only evaluate k_1 value graphically, provided q_e value had already been evaluated experimentally. However, in the absence of experimentally determined q_e value, the evaluation of k_1 value graphically appeared to be difficult. However the values of k_1 and q_e could be determined simultaneously and independently using the experimental values of various q_t obtained at different 't' by applying the method of least squares to Eq. (A.1).

A.2 Method

The pseudo-first-order rate expression of adsorption process represented by Eq. (A.1) is similar to the biochemical oxygen demand (BOD) exerted which is represented as:

$$y = y_u (1 - e^{-kt}) \tag{A.3}$$

where y_u and y_t are the ultimate BOD (mg/L) and BOD exerted (mg/L) at time t respectively and k is the BOD rate constant (1/d). Eq. (A.1) and (A.3) are similar in nature.

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Tchobanoglous et al. (2003) proposed the least squares method for the estimation of BOD constants namely y_u (ultimate BOD) and k (BOD rate constant). Applying the similar technique of least squares method, the pseudo-first-order rate expression constants namely q_e and k_1 were also estimated.

The least square method involves fitting a curve through a set of data points, so that the sum of the squares of the residuals (the difference between the observed value and the value of the fitted curve) must be a minimum. Using this method, a curve can be fitted through a set of data points. For example, for a time series of q_t (amount of metal adsorbed at the given time t), the following equation may be written for each of the various n data points:

$$\left.\frac{dq_t}{dt}\right|_{t=n} = k_1(q_e - q_t) \tag{A.4}$$

In Eq. (A.4), both q_e and k_1 are unknown. If it is assumed that dq_t/dt represents the value of the slope of the curve to be fitted through all the data points for a given k_1 and q_e value, then because of experimental error, the two sides of Eq. (A.4) will not be equal but will differ by an amount R. Rewriting Eq. (A.4) in terms of R for the general case yields

$$R = k_1(q_e - q_t) - \frac{dq_t}{dt} \tag{A.5}$$

Simplifying and using the notation q_t' for $\frac{dq_t}{dt}$ gives

$$R = k_1 q_e - k_1 q_t - q_t' \tag{A.6}$$

Substituting a for $k_1 q_e$ and $-b$ for k_1 gives

$$R = a + bq_t - q_t' \tag{A.7}$$

Now, if the sum of squares of the residuals R is to be a minimum, the following must hold:

$$\frac{\partial}{\partial a}\sum R^2 = \sum \frac{\partial R}{\partial a} \tag{A.8}$$

$$\frac{\partial}{\partial b}\sum R^2 = \sum 2R\frac{\partial R}{\partial b} \tag{A.9}$$

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If the indicated operations in Eq.(A.8) and (A.9) are carried out using the value of the residual *R* defined by Eq.(A.7), the following set of equations result:

$$na + b\sum q_t - \sum q_t' = 0 \tag{A.10}$$

$$a\sum q_t + b\sum q_t^2 - \sum q_t q_t' = 0 \tag{A.11}$$

where *n* is number of data points

$$a = -bq_e$$

$$b = -k_1(base\ e)$$

$$q_e = -\frac{a}{b}$$

$$\frac{dq_t}{dt} = q_t' = \frac{q_{t,n+1} - q_{t,n-1}}{2\Delta t}$$

A.3 Objective

Estimation of q_e and k_1 values of pseudo-first-order rate expression using the method of least squares for the kinetic data as shown in Table A.1 obtained using GAA for initial Cu(II) concentration of 0.59 meq/L.

A.4 Procedure Adopted

1. Set up a computation table for values of q_t^2, q_t' and $q_t \times q_t'$ as shown in Table A.2. The slope q_t' is computed as follows:

$$\frac{dq_t}{dt} = q_t' = \frac{q_{t,n+1} - q_{t,n-1}}{2\Delta t}$$

2. Substituting the values computed in Step 1 in the following equations, and solving it for *a* and *b*

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Table A.1: Kinetic data obtained using GAA for initial Cu(II) conc. of 0.59 meq/L.

Time (min)	q_t (meq/g)
0	0.0000
5	0.0221
10	0.0222
20	0.0272
30	0.0287
60	0.0318
90	0.0365
120	0.0386
180	0.0421
240	0.0467

Table A2: Computation table with values of q^2t, q_t' and $q_t \times q_t'$.

Time (min)	q_t	q_t^2	q_t'	$q_t \times q_t'$
0	0.0000			
5	0.0221	0.0004867	0.0022152	0.0000489
10	0.0222	0.0004907	0.0003393	0.0000075
20	0.0272	0.0007372	0.0003252	0.0000088
30	0.0287	0.0008212	0.0001168	0.0000033
60	0.0318	0.0010126	0.0001304	0.0000041
90	0.0365	0.0013307	0.0001128	0.0000041
120	0.0386	0.0014894	0.0000620	0.0000024
180	0.0421	0.0017686	0.0000680	0.0000029
240	0.0467[a]			
Sums	0.2492	0.0081371	0.0033697	0.0000820

[a]value not included in the total

$$na + b\sum q_t - \sum q_t' = 0 \qquad \text{(A.12)}$$

$$a\sum q_t + b\sum q_t^2 - \sum q_t q_t' \qquad \text{(A.13)}$$

=> $8a + 0.2492b - 0.0033697 = 0$

$0.2492a + 0.0081371b - 0.0000820 = 0$

Solving this, $b = -0.0585$ and $a = 0.0022$

3. Determine the values of k_1 and q_e

$$k_1 = -b = -(-0.0585) = 0.0585$$

$$q_e = -\frac{a}{b} = 0.0376$$

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Appendix B

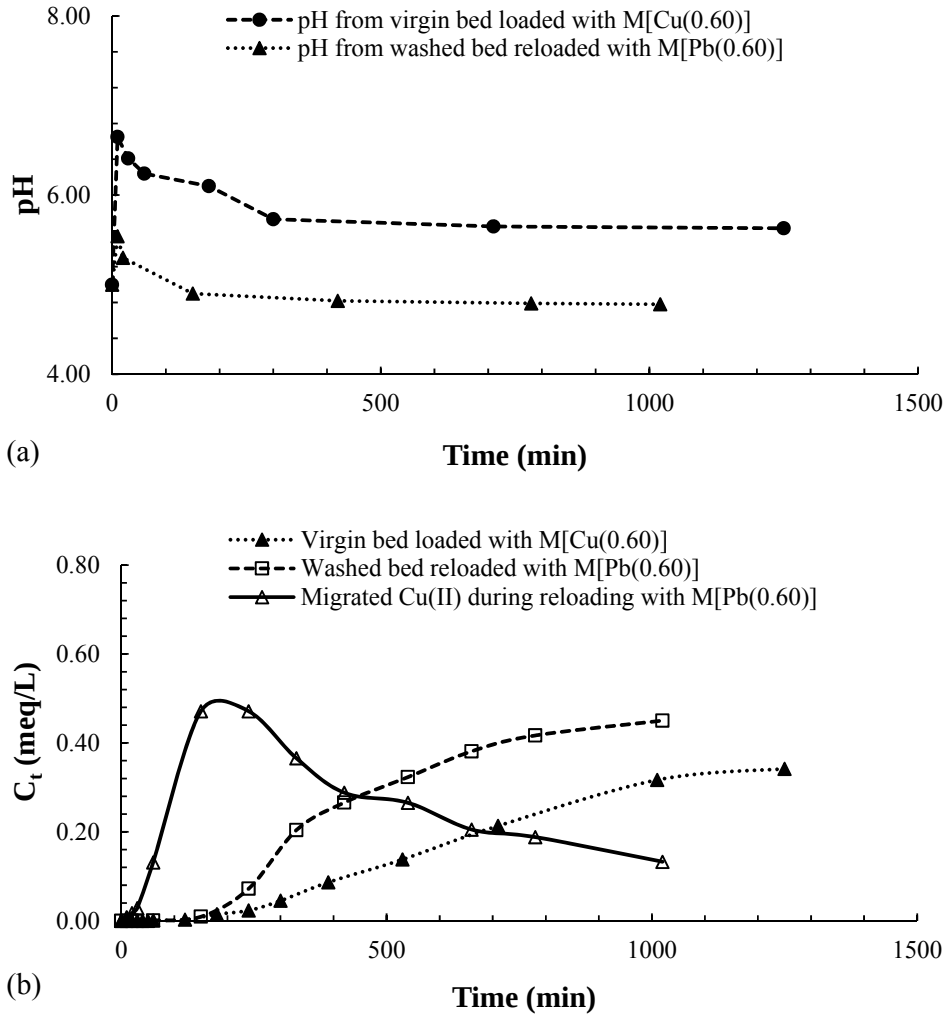

Fig. B.1: Virgin GAA bed loaded with M[Cu(0.60)] system and washed bed reloaded with M[Pb(0.60)] system under uncontrolled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cu(0.60)] = 0.60±0.03 meq/L, M[Pb(0.60)] = 0.59±0.01 meq/L, Initial adjusted pH = 5.00±0.04, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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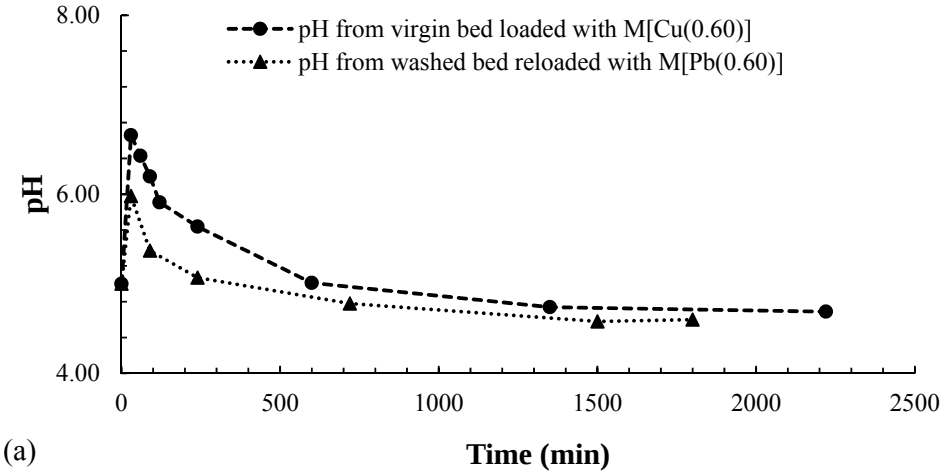
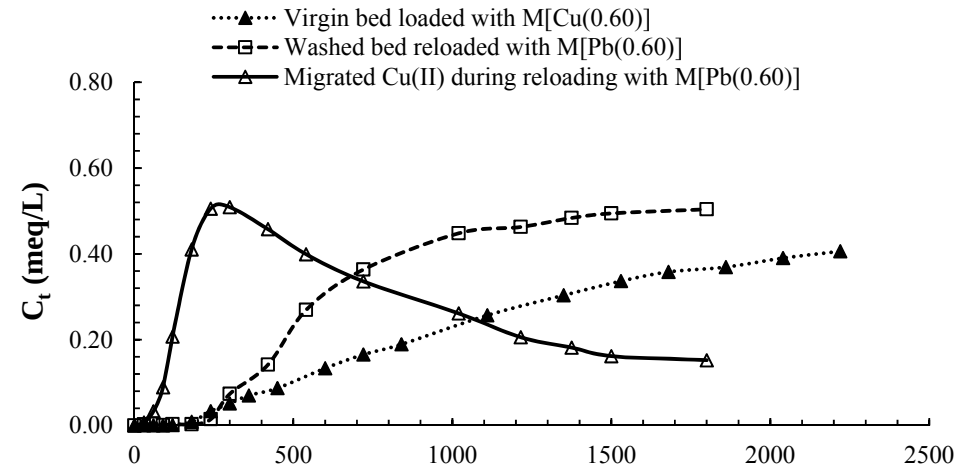


(a)



(b)

Fig. B.2: Virgin GAA bed loaded with M[Cu(0.60)] system and washed bed reloaded with M[Pb(0.60)] system under uncontrolled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cu(0.60)] = 0.62±0.00 meq/L, M[Pb(0.60)] = 0.59±0.00 meq/L, Initial adjusted pH = 5.00±0.04, Temp. = 30±1 °C} (Each data represents an average of two independent experimental values).

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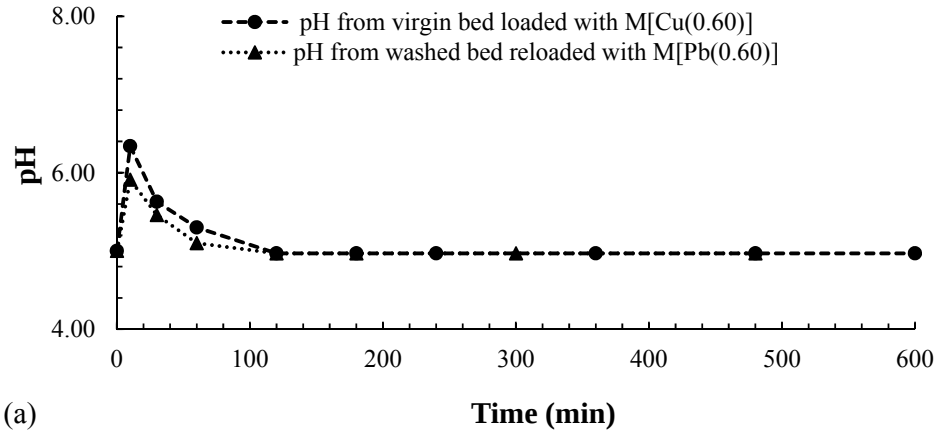
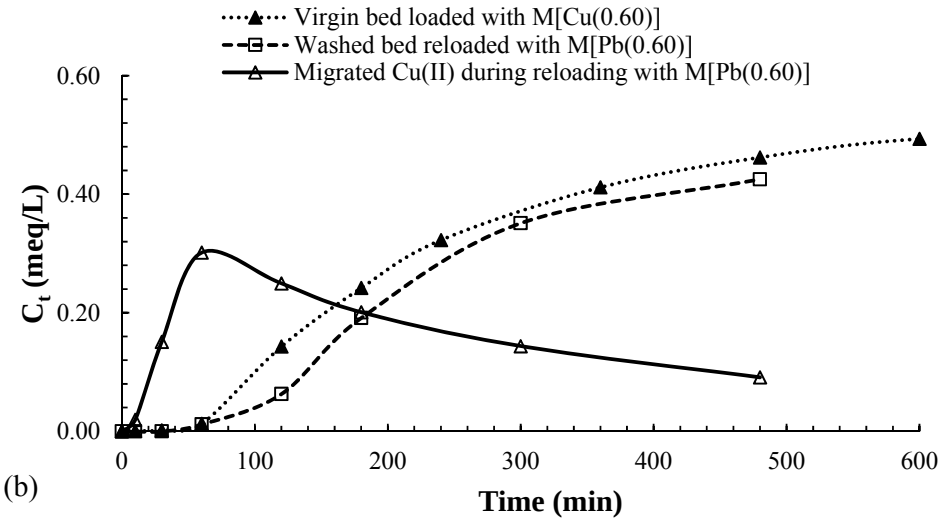


(a)



(b)

Fig. B.3: Virgin GAA bed loaded with M[Cu(0.60)] system and washed bed reloaded with M[Pb(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cu(0.60)] = 0.60±0.01 meq/L, M[Pb(0.60)] = 0.58±0.02 meq/L, Buffered pH = 5.00±0.05, Temp. = 30±1 °C} (Each data represents an average of two independent experimental values).

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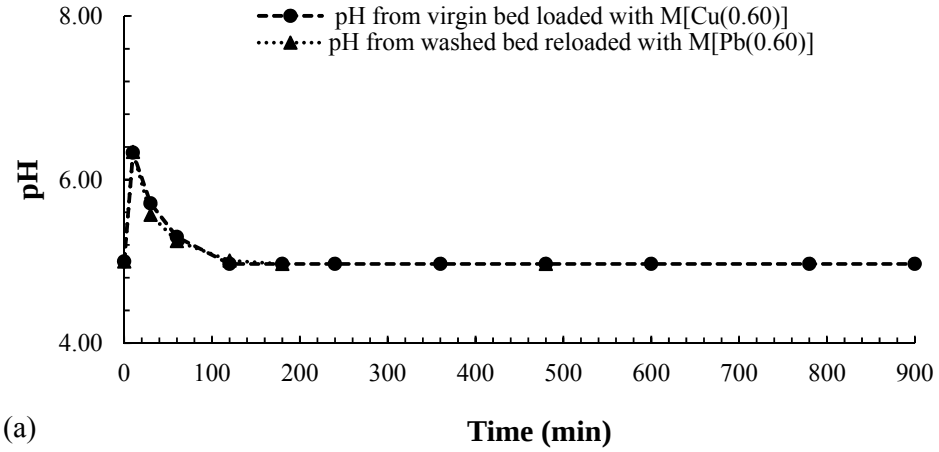
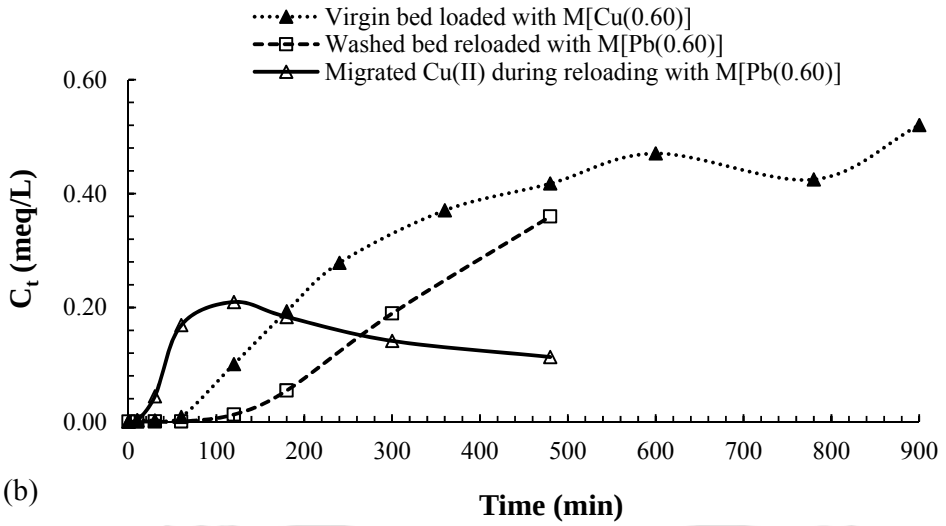


(a)



(b)

Fig. B.4: Virgin GAA bed loaded with M[Cu(0.60)] system and washed bed reloaded with M[Pb(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cu(0.60)] = 0.60±0.01 meq/L, M[Pb(0.60)] = 0.58±0.02 meq/L, Buffered pH = 5.00±0.05, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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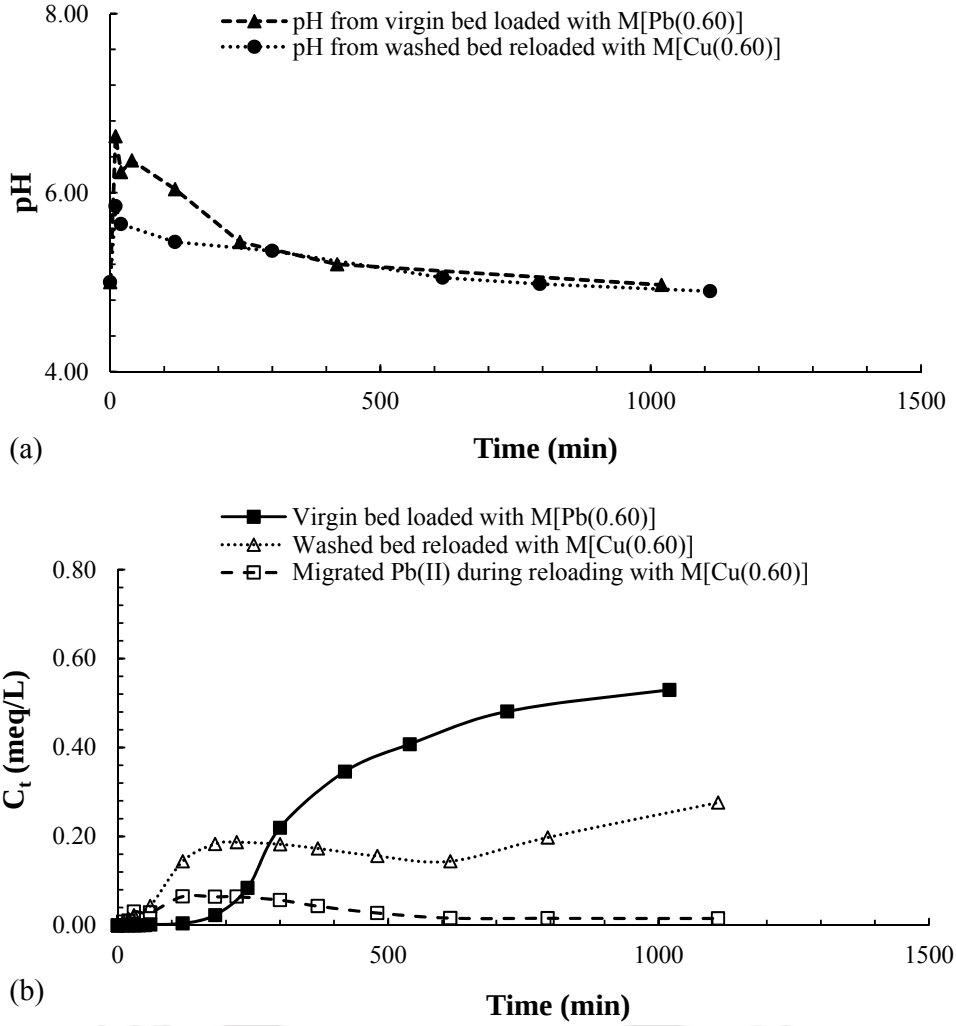

Fig. B.5: Virgin GAA bed loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cu(0.60)] system under uncontrolled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Pb(0.60)] = 0.60±0.01 meq/L, M[Cu(0.60)] = 0.60±0.00 meq/L, Initial adjusted pH = 5.00±0.03, Temp. = 30±1°C} (Each data represents an average of two independent experimental values).

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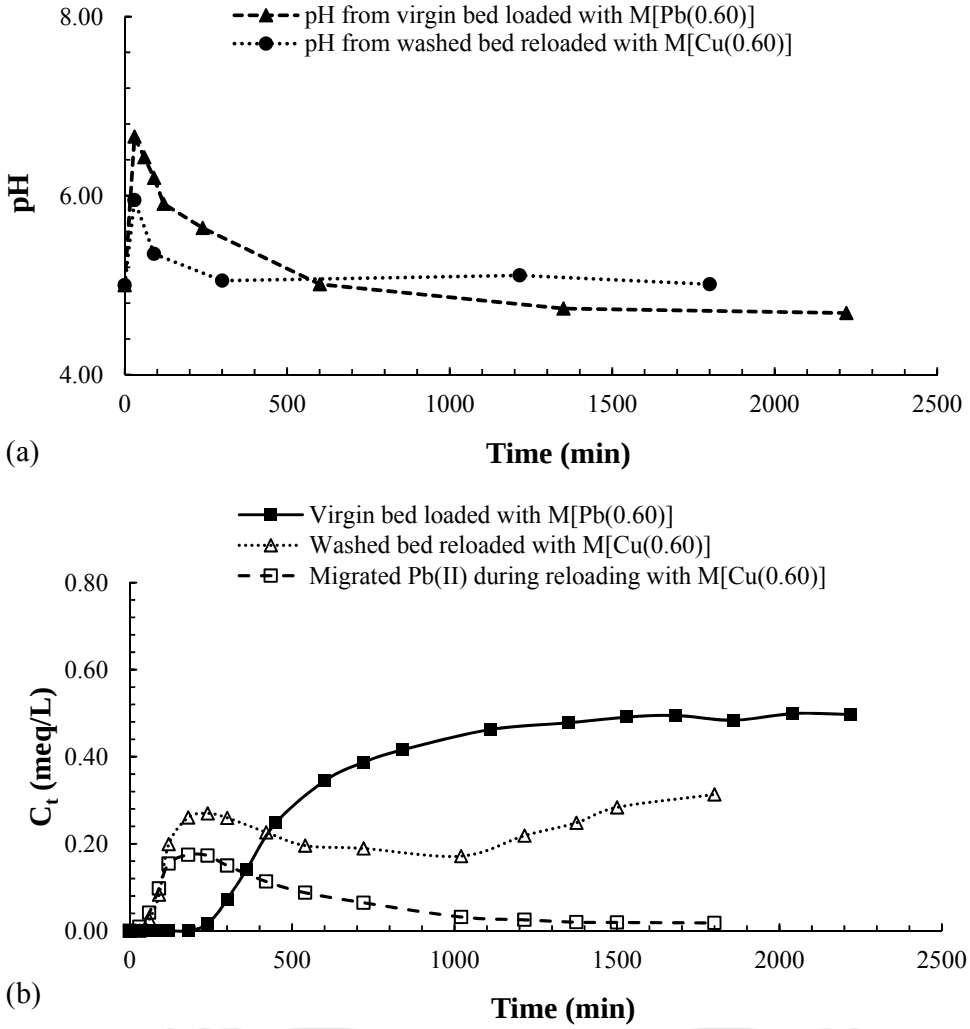

Fig. B.6: Virgin GAA bed loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cu(0.60)] system under uncontrolled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Pb(0.60)] = 0.59±0.01 meq/L, M[Cu(0.60)] = 0.60±0.01 meq/L, Initial adjusted pH = 5.00±0.03, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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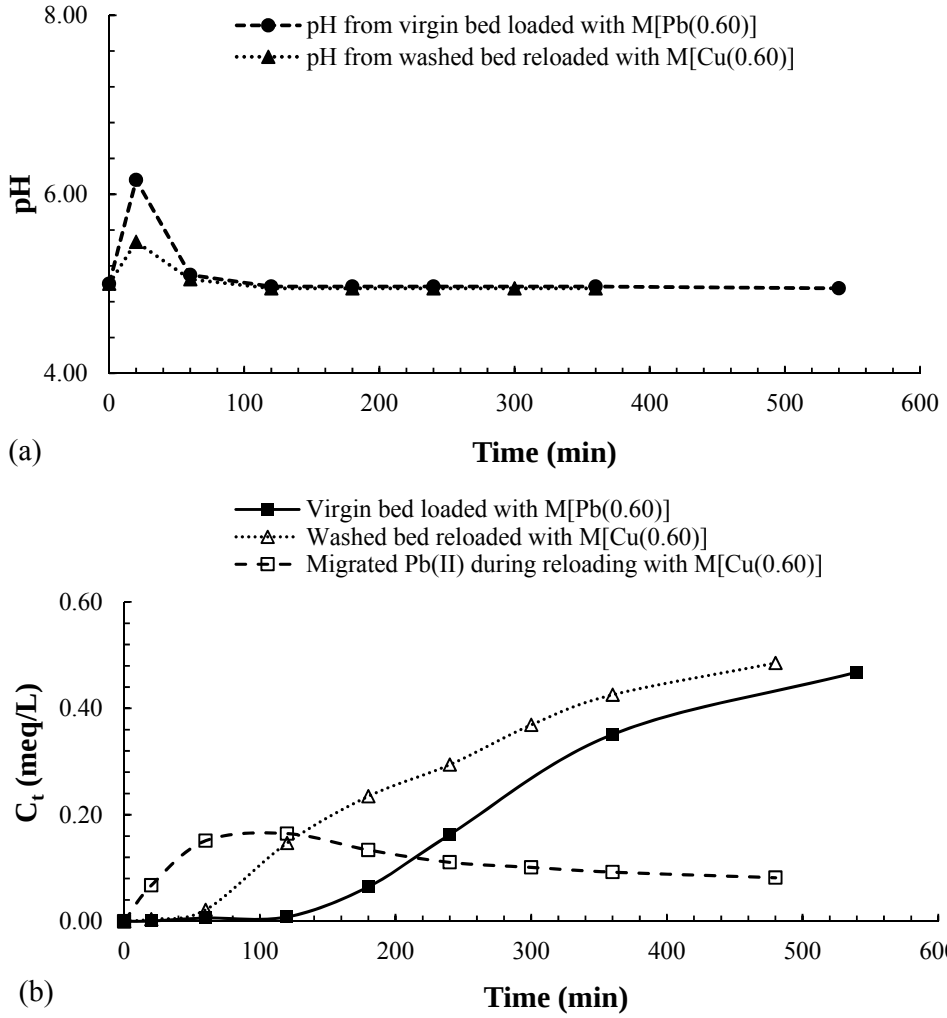

Fig. B.7: Virgin GAA bed loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cu(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Pb(0.60)] = 0.58±0.02 meq/L, M[Cu(0.60)] = 0.60±0.02 meq/L, Buffered pH = 5.00±0.02, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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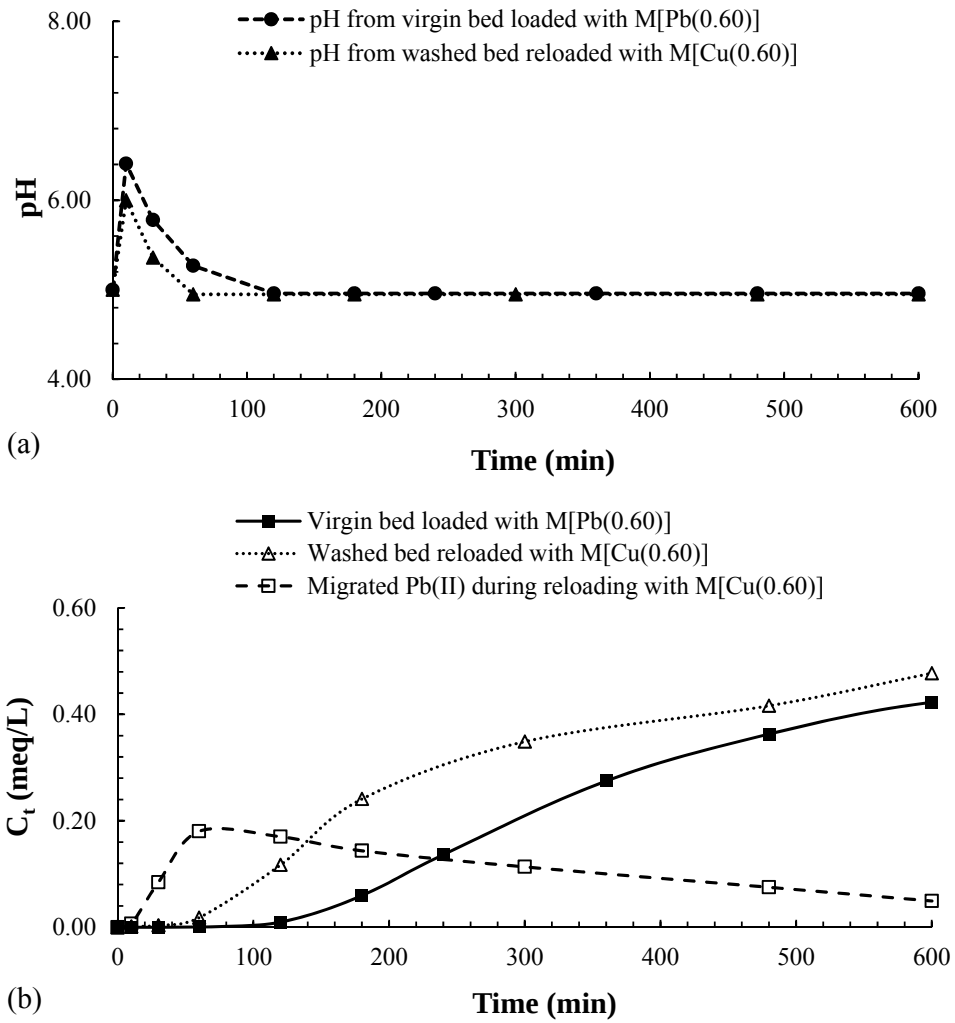

Fig. B.8: Virgin GAA bed loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cu(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Pb(0.60)] = 0.58±0.02 meq/L, M[Cu(0.60)] = 0.60±0.02 meq/L, Buffered pH = 5.00±0.02, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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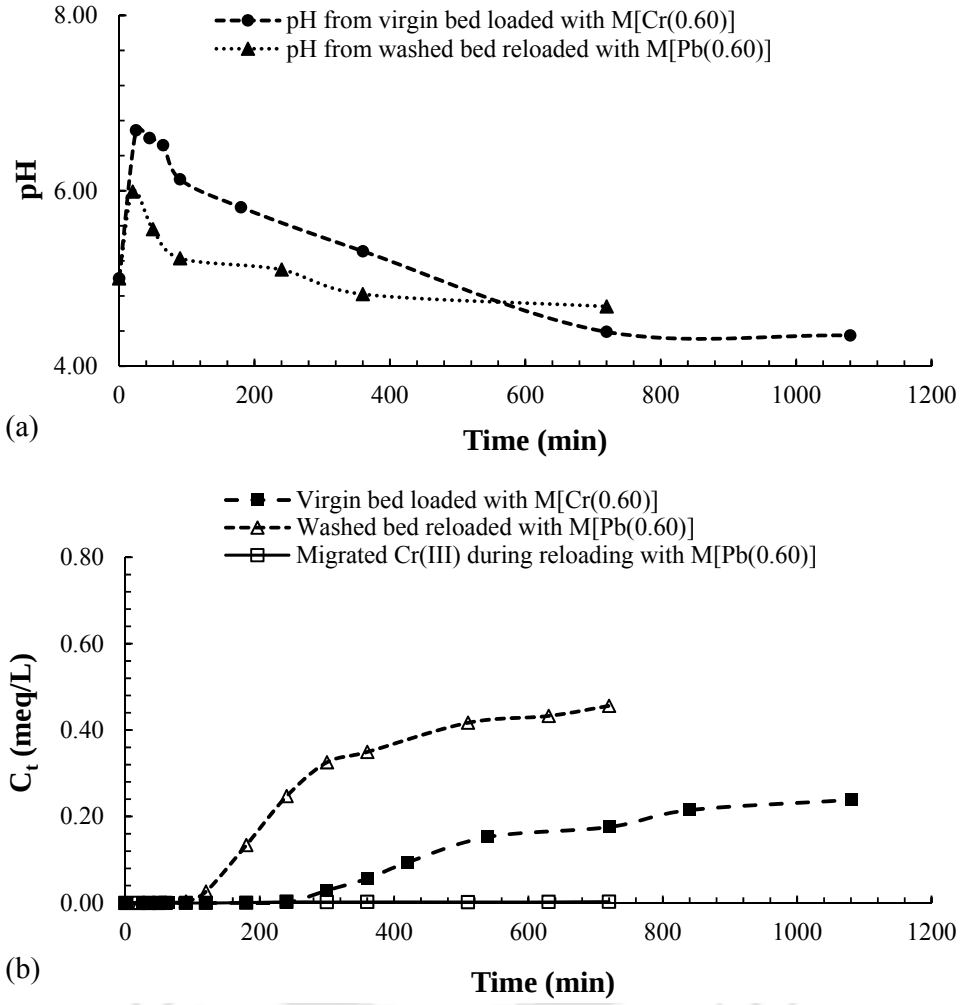

Fig. B.9: Virgin GAA bed loaded with M[Cr(0.60)] system and washed bed reloaded with M[Pb(0.60)] system under uncontrolled pH conditions: (a) pH variation (b) breakthrough curves {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cr(0.60)] = 0.61±0.01 meq/L, M[Pb(0.60)] = 0.59±0.01 meq/L, Initial adjusted pH = 5.00±0.02, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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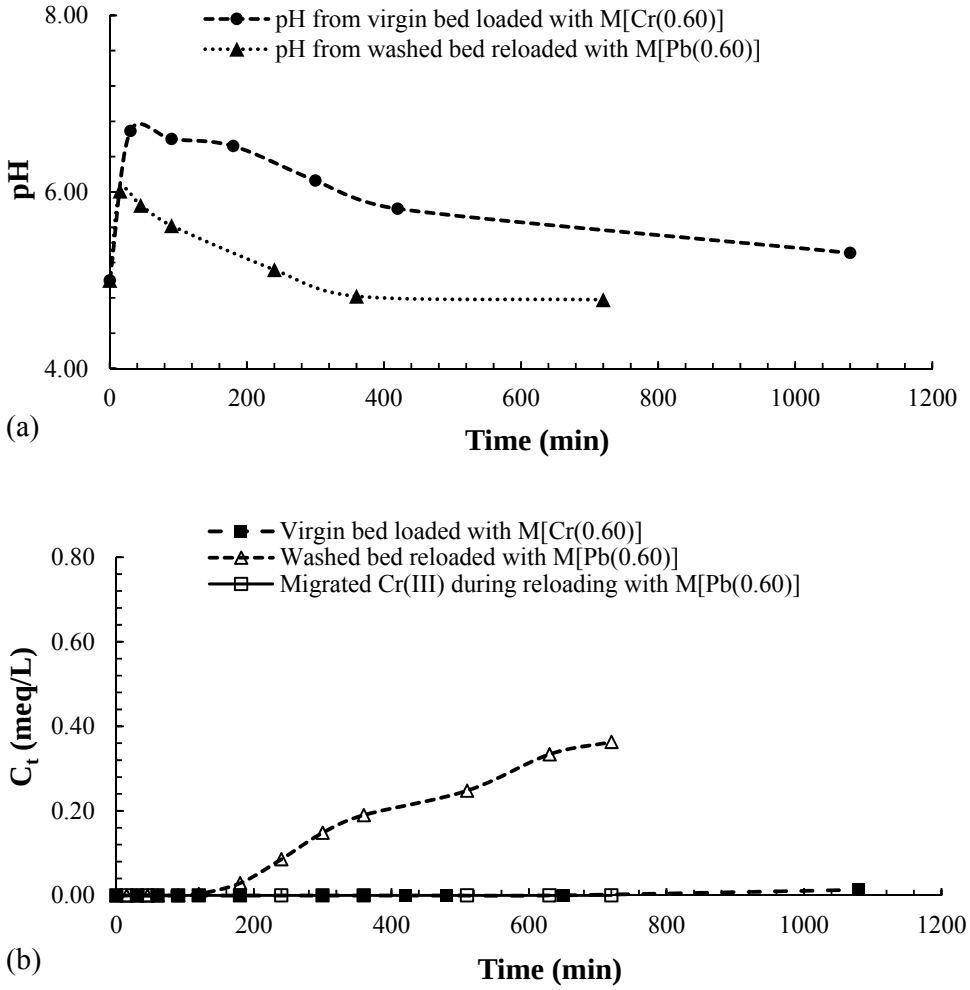

Fig. B.10: Virgin GAA bed loaded with M[Cr(0.60)] system and washed bed reloaded with M[Pb(0.60)] system under uncontrolled pH conditions: (a) pH variation (b) breakthrough curves {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cr(0.60)] = 0.61±0.02 meq/L, M[Pb(0.60)] = 0.60±0.02 meq/L, Initial adjusted pH = 5.00±0.02, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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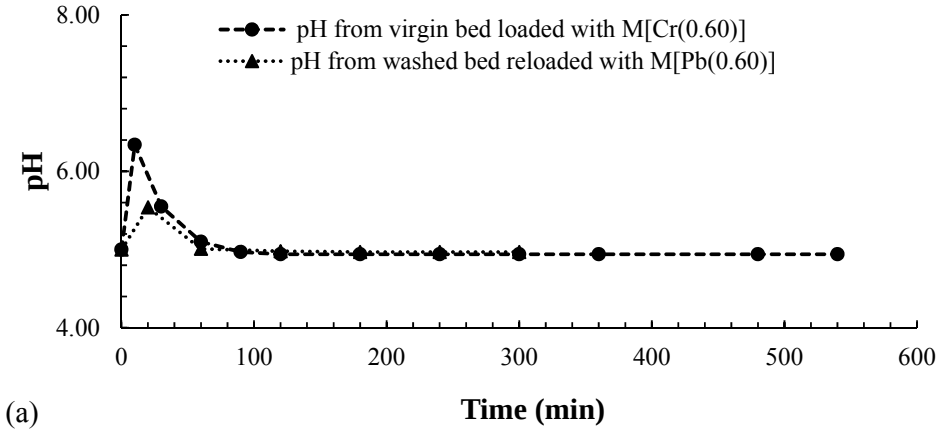
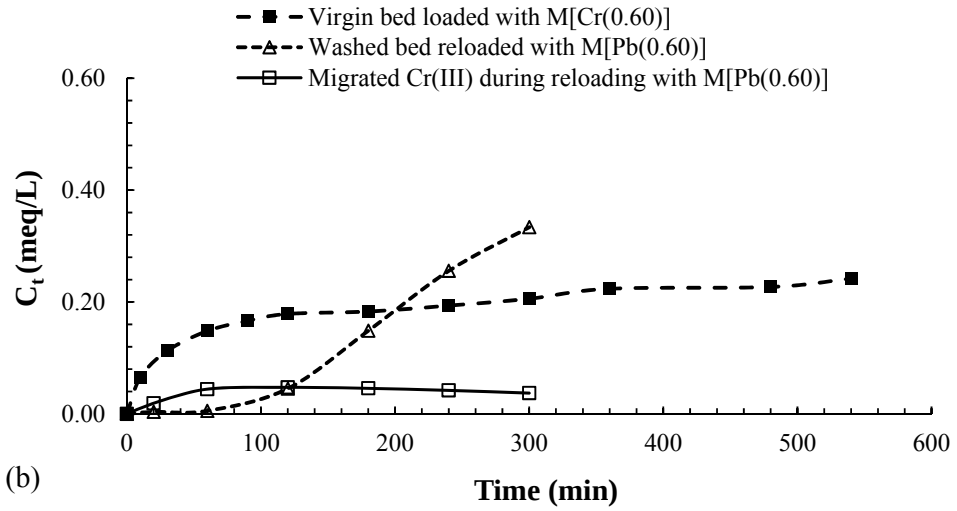


(a)



(b)

Fig. B.11: Virgin GAA bed loaded with M[Cr(0.60)] system and washed bed reloaded with M[Pb(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cr(0.60)] = 0.61±0.01 meq/L, M[Pb(0.60)] = 0.58±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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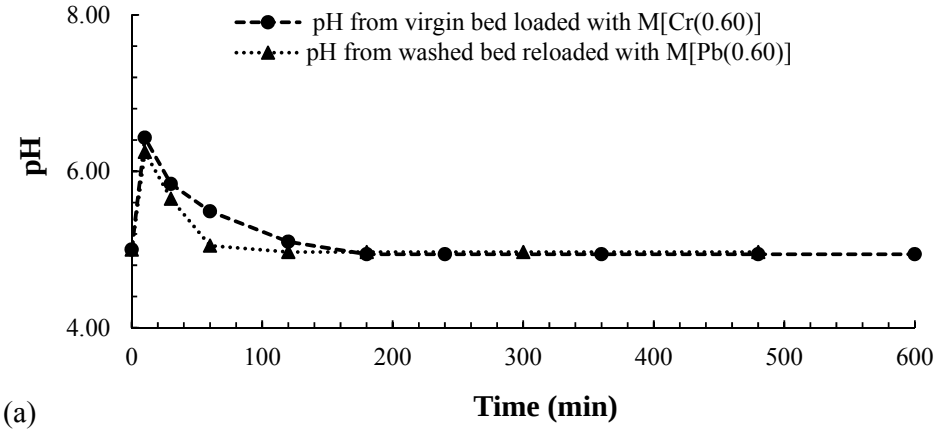
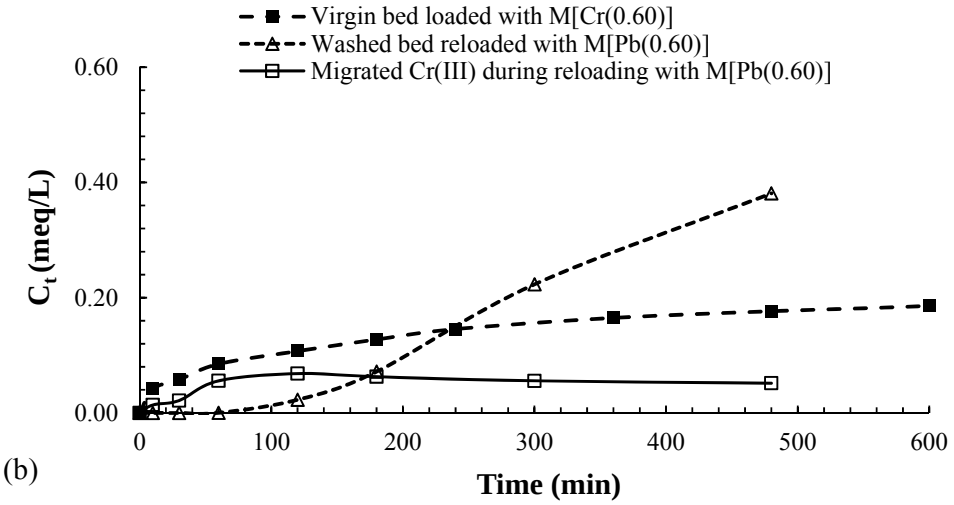


(a)



(b)

Fig. B.12: Virgin GAA bed loaded with M[Cr(0.60)] system and washed bed reloaded with M[Pb(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cr(0.60)] = 0.61±0.01 meq/L, M[Pb(0.60)] = 0.58±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1 °C} (Each data represents an average of two independent experimental values).

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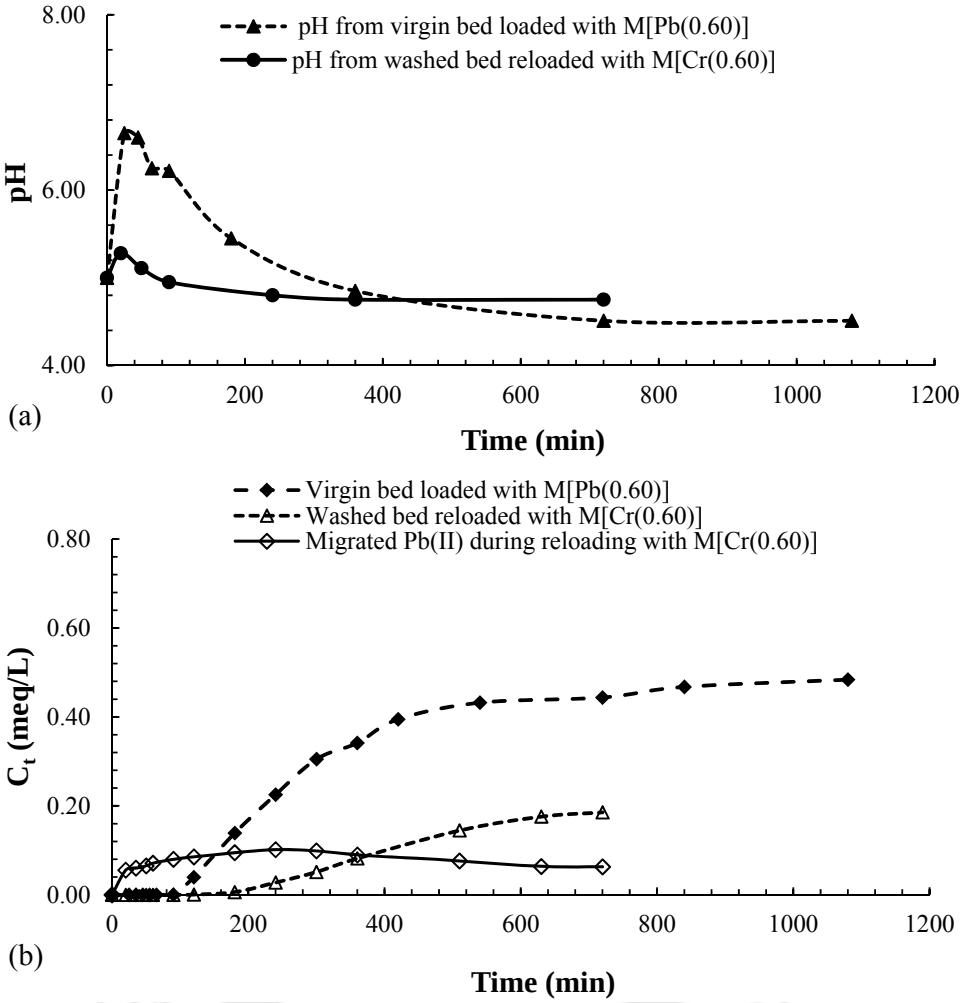

Fig. B.13: Virgin GAA bed loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cr(0.60)] system under uncontrolled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Pb(0.60)] = 0.62±0.02 meq/L, M[Cr(0.60)] = 0.58±0.01 meq/L, Initial adjusted pH = 5.00±0.01, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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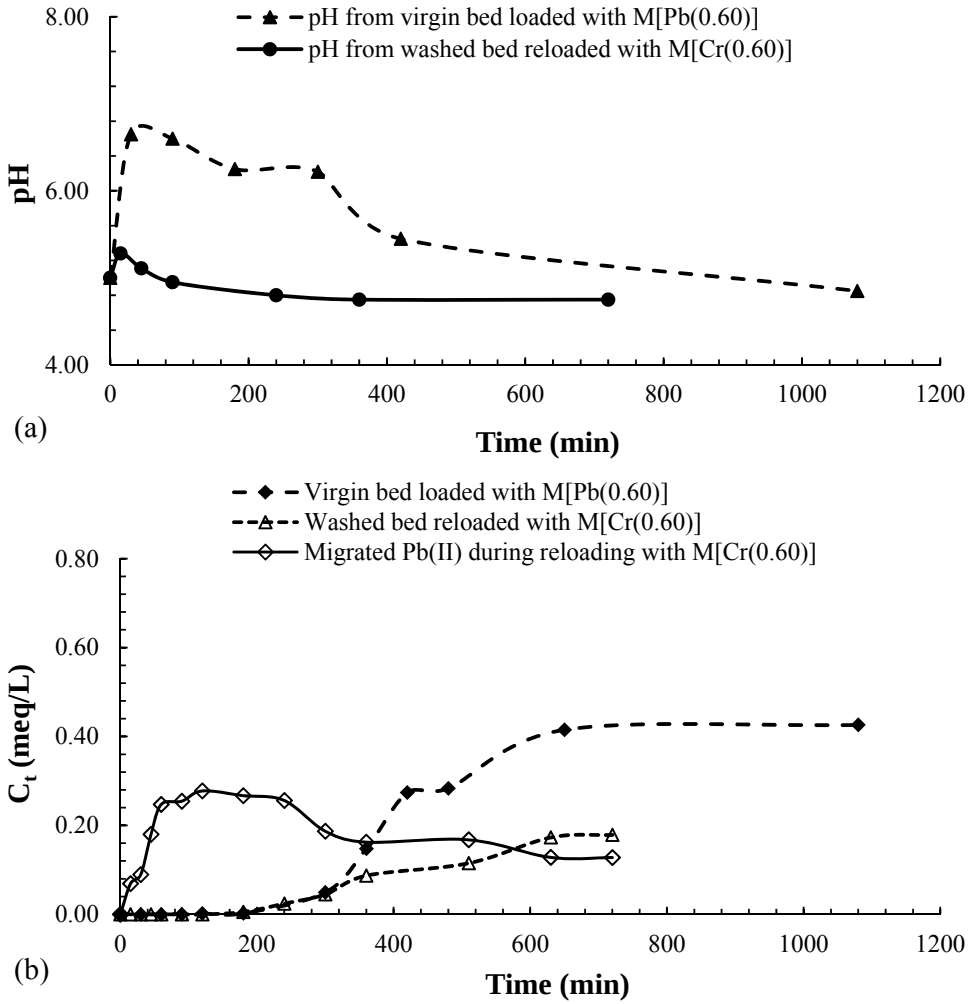

Fig. B.14: Virgin GAA bed loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cr(0.60)] system under uncontrolled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Pb(0.60)] = 0.62±0.02 meq/L, M[Cr(0.60)] = 0.62±0.01 meq/L, Initial adjusted pH = 5.00±0.01, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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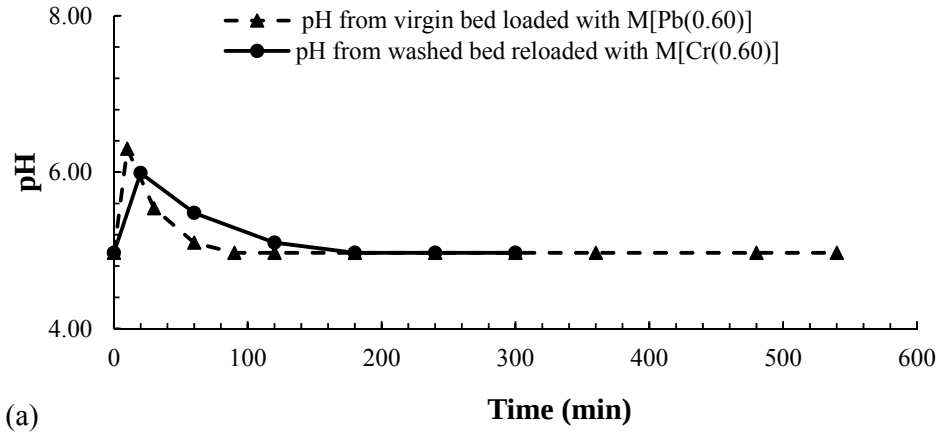
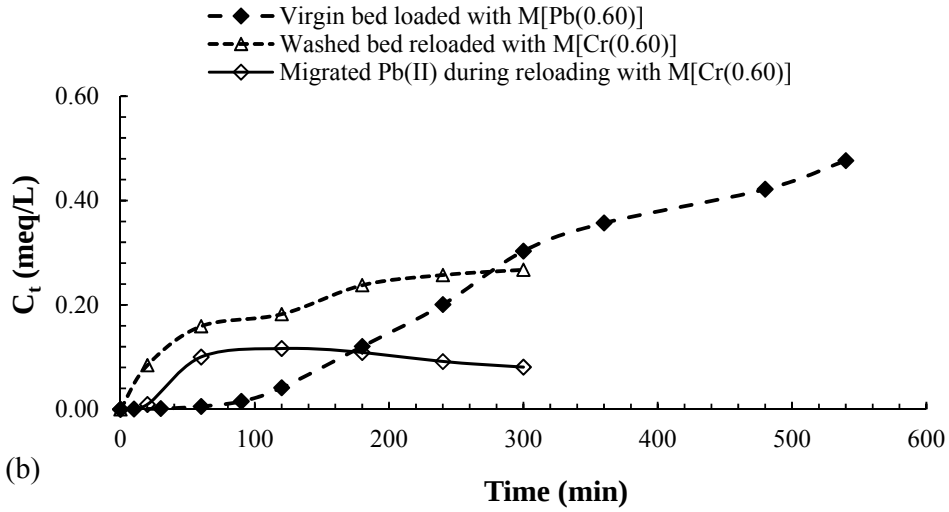


(a)



(b)

Fig. B.15: Virgin GAA bed loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cr(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Pb(0.60)] = 0.58±0.01 meq/L, M[Cr(0.60)] = 0.61±0.01 meq/L, Buffered pH = 5.00±0.01, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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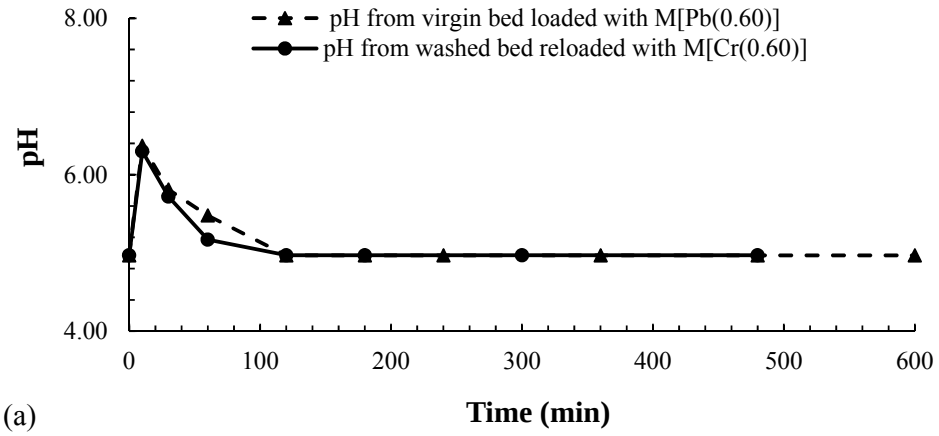
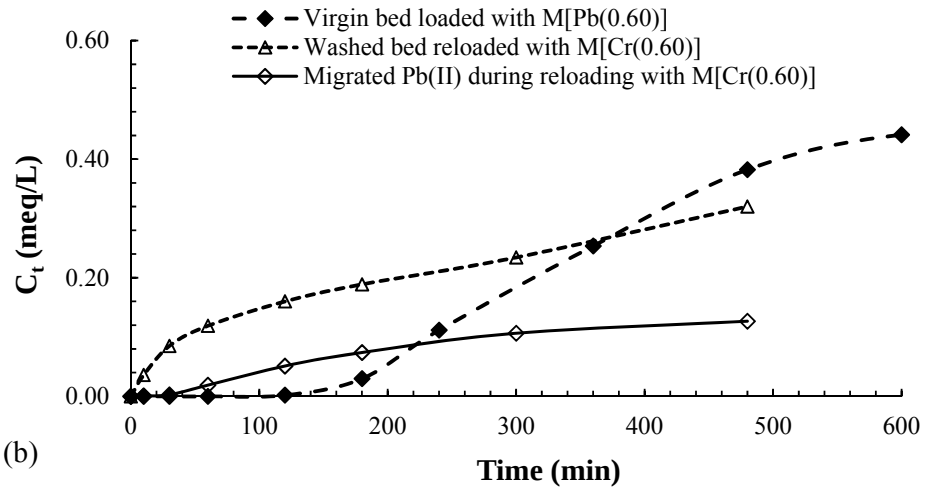


(a)



(b)

Fig. B.16: Virgin GAA bed loaded with M[Pb(0.60)] system and washed bed reloaded with M[Cr(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Pb(0.60)] = 0.58±0.01 meq/L, M[Cr(0.60)] = 0.61±0.01 meq/L, Buffered pH = 5.00±0.01, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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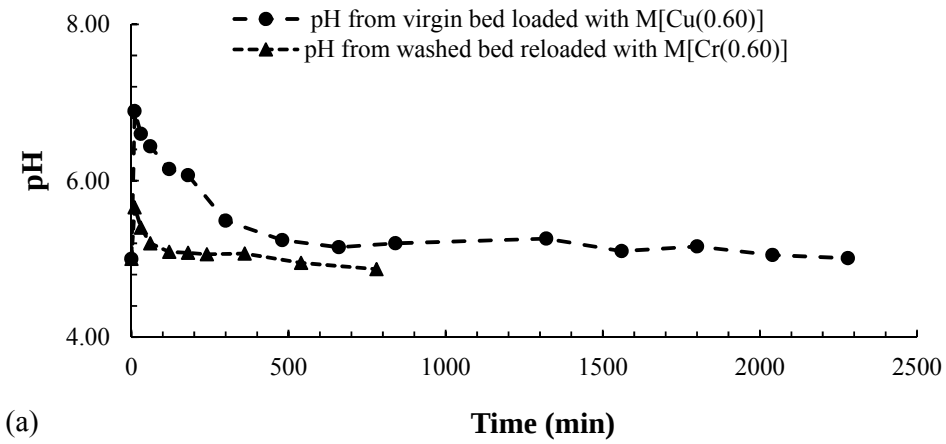
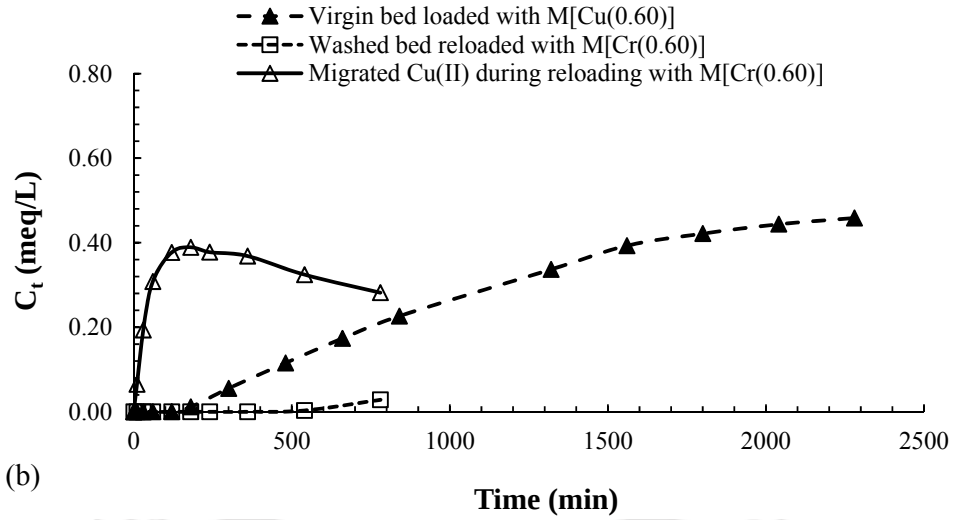


(a)



(b)

Fig. B.17: Virgin GAA bed loaded with M[Cu(0.60)] system and washed bed reloaded with M[Cr(0.60)] system under uncontrolled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cu(0.60)] = 0.58±0.01 meq/L, M[Cr(0.60)] = 0.58±0.01 meq/L, Initial adjusted pH = 5.00±0.02, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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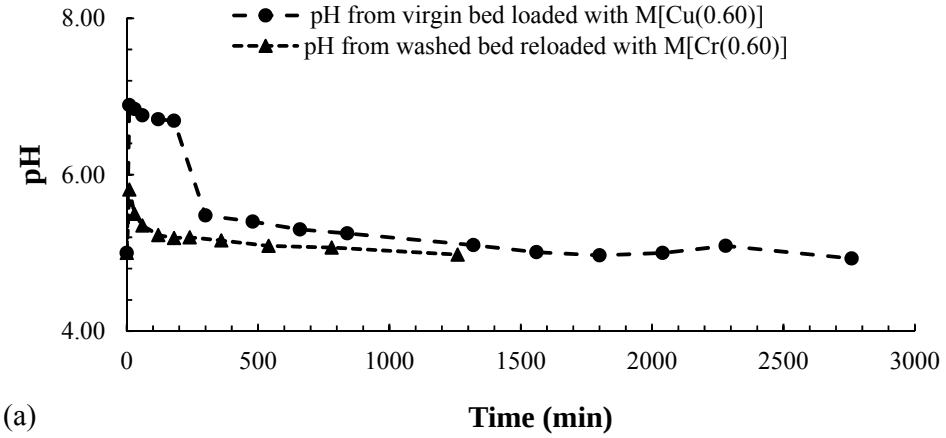

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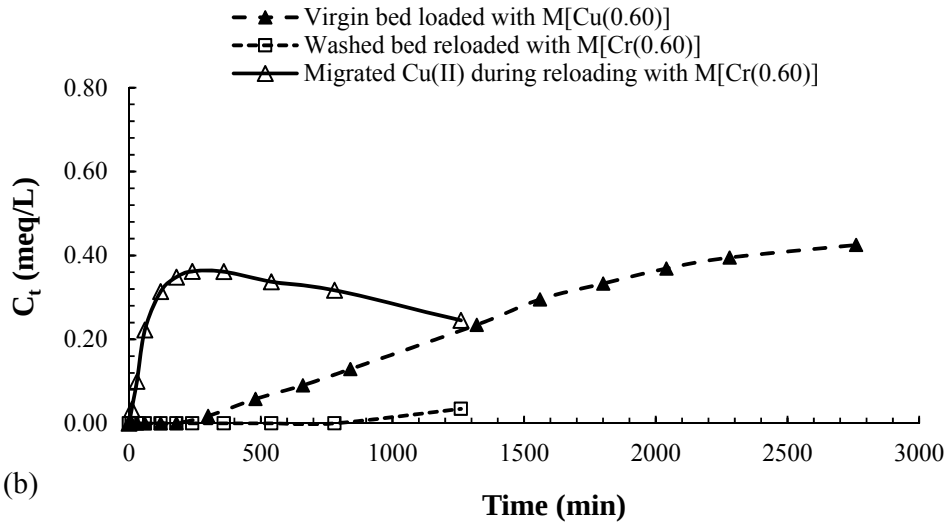

(b)

Fig. B.18: Virgin GAA bed loaded with M[Cu(0.60)] system and washed bed reloaded with M[Cr(0.60)] system under uncontrolled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cu(0.60)] = 0.58±0.01 meq/L, M[Cr(0.60)] = 0.58±0.01 meq/L, Initial adjusted pH = 5.00±0.02, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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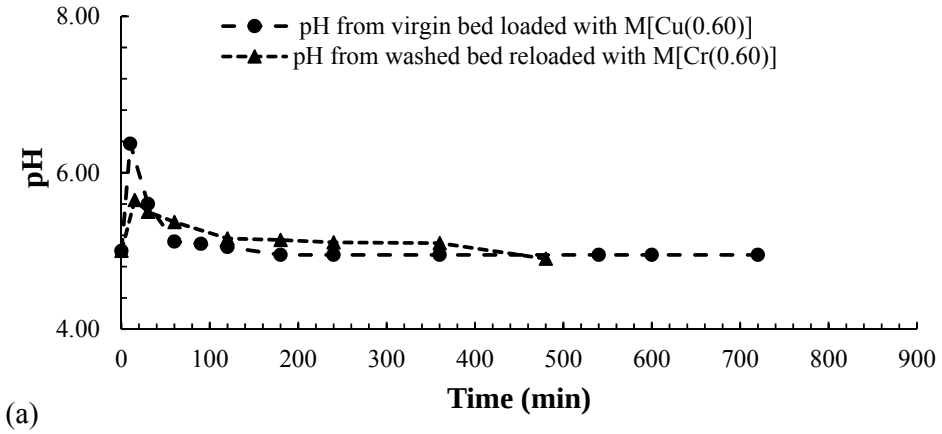
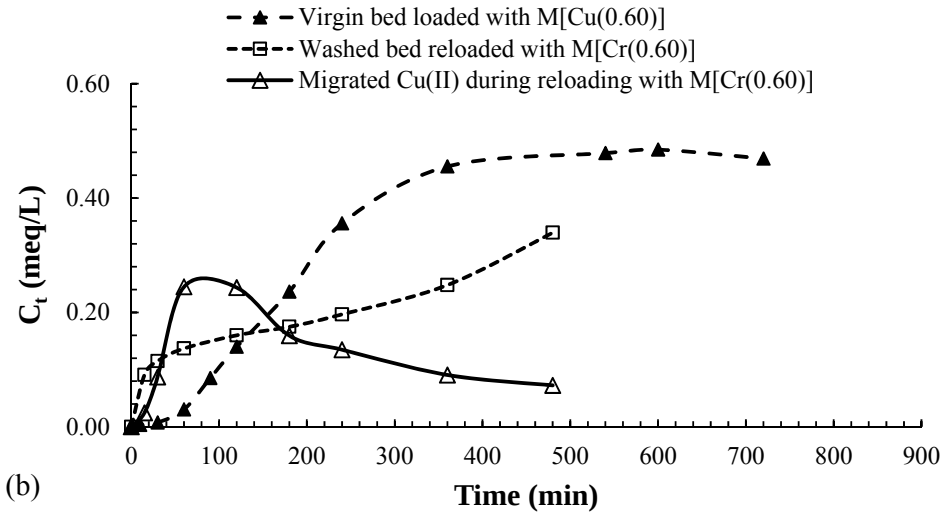


(a)



(b)

Fig. B.19: Virgin GAA bed loaded with M[Cu(0.60)] system and washed bed reloaded with M[Cr(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cu(0.60)] = 0.58±0.01 meq/L, M[Cr(0.60)] = 0.58±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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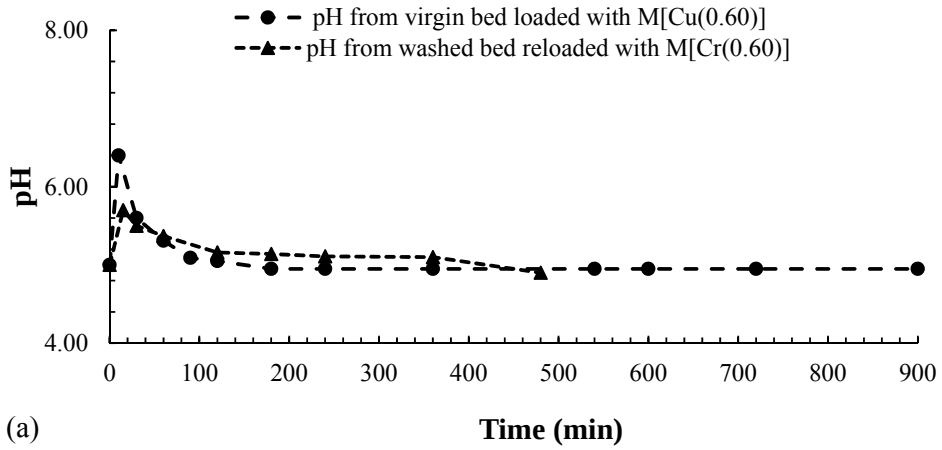
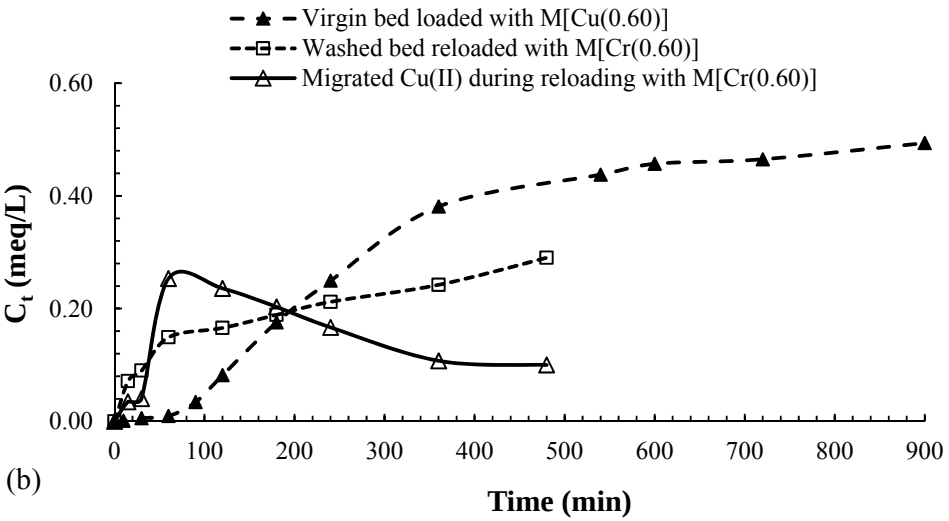


(a)



(b)

Fig. B.20: Virgin GAA bed loaded with M[Cu(0.60)] system and washed bed reloaded with M[Cr(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cu(0.60)] = 0.58±0.01 meq/L, M[Cr(0.60)] = 0.58±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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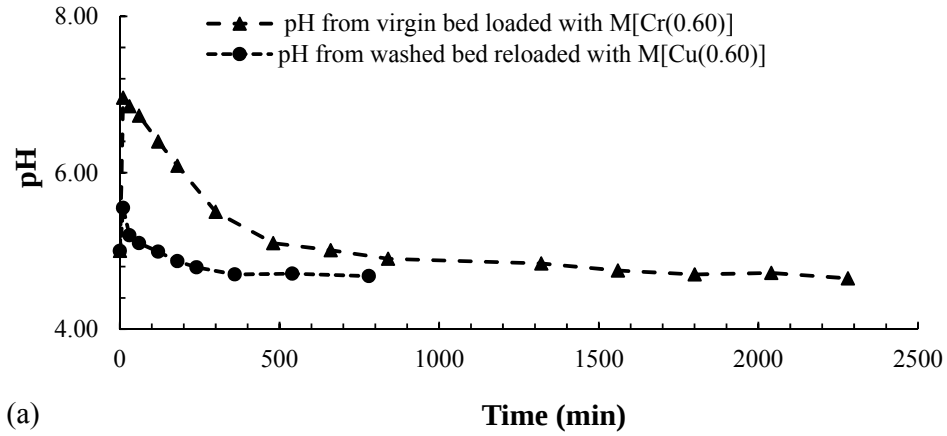
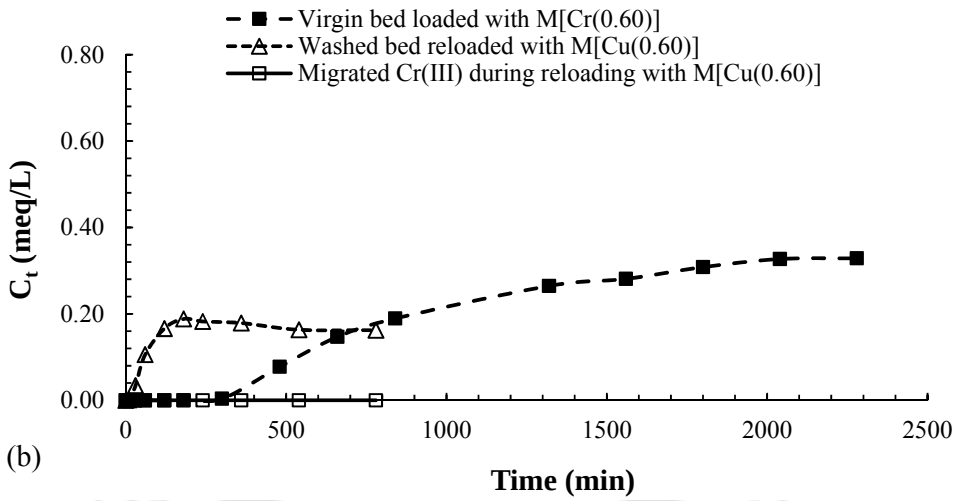


(a)



(b)

Fig. B.21: Virgin GAA bed loaded with M[Cr(0.60)] system and washed bed reloaded with M[Cu(0.60)] system under uncontrolled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cr(0.60)] = 0.58±0.01 meq/L, M[Cu(0.60)] = 0.58±0.01 meq/L, Initial adjusted pH = 5.00±0.03, Temp. = 30±1 °C} (Each data represents an average of two independent experimental values).

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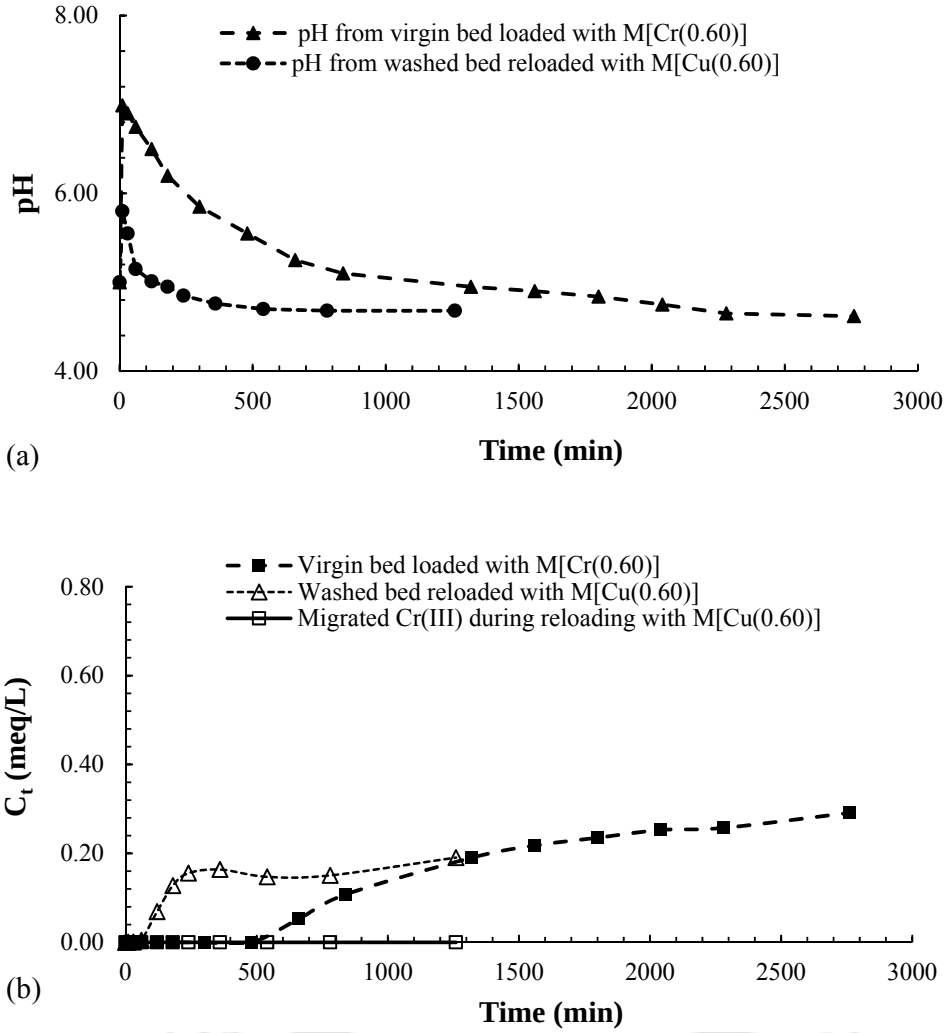

Fig. B.22: Virgin GAA bed loaded with M[Cr(0.60)] system and washed bed reloaded with M[Cu(0.60)] system under uncontrolled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cr(0.60)] = 0.58±0.01 meq/L, M[Cu(0.60)] = 0.58±0.01 meq/L, Initial adjusted pH = 5.00±0.03, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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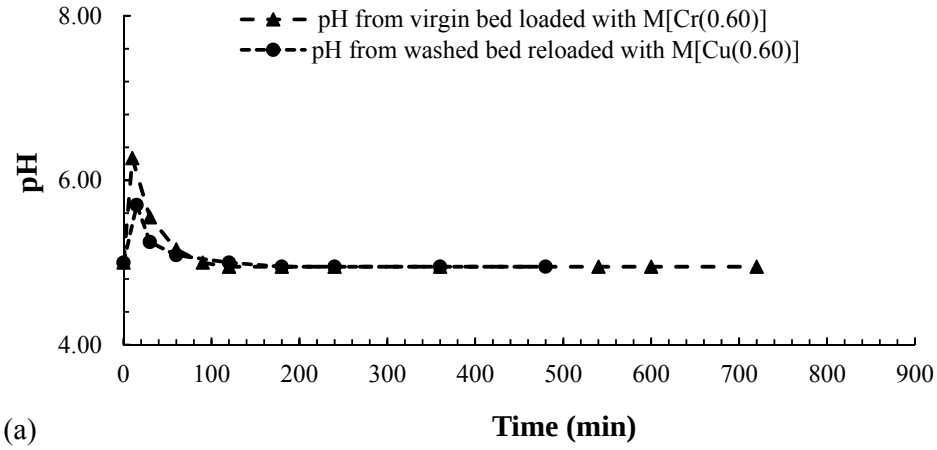
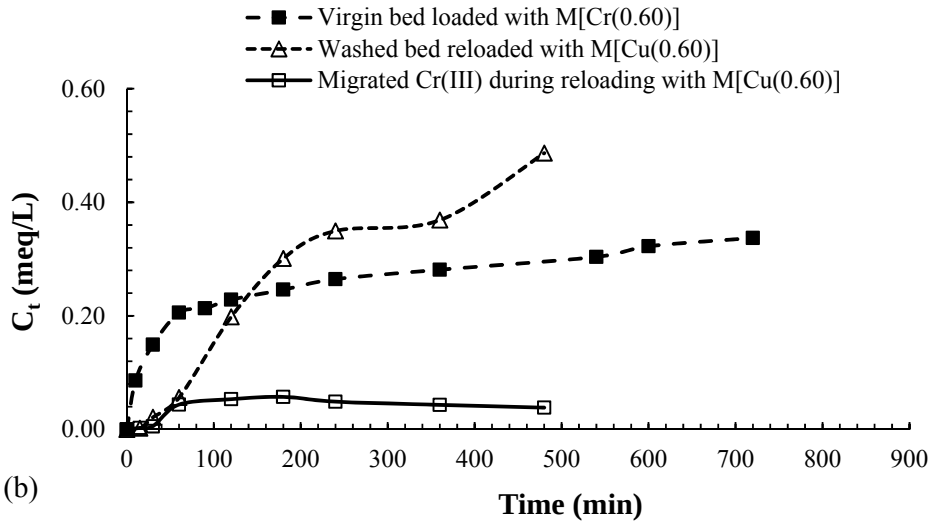


(a)



(b)

Fig. B.23: Virgin GAA bed loaded with M[Cr(0.60)] system and washed bed reloaded with M[Cu(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cr(0.60)] = 0.58±0.01 meq/L, M[Cu(0.60)] = 0.58±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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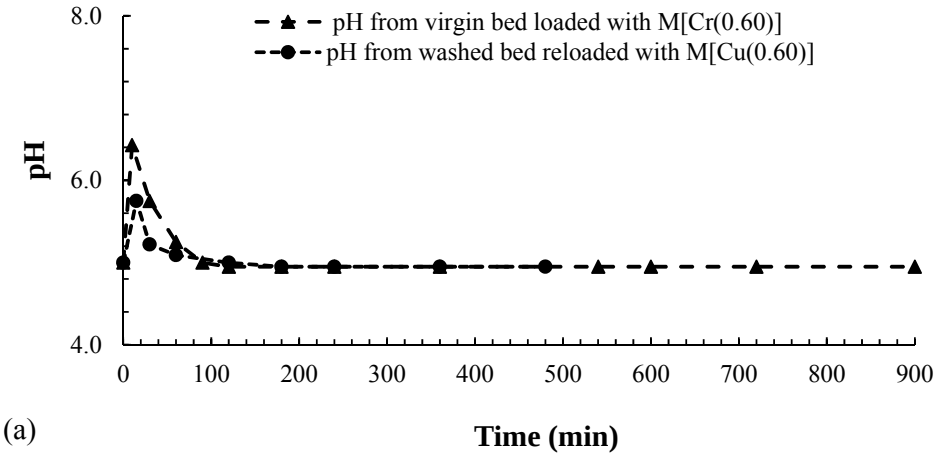

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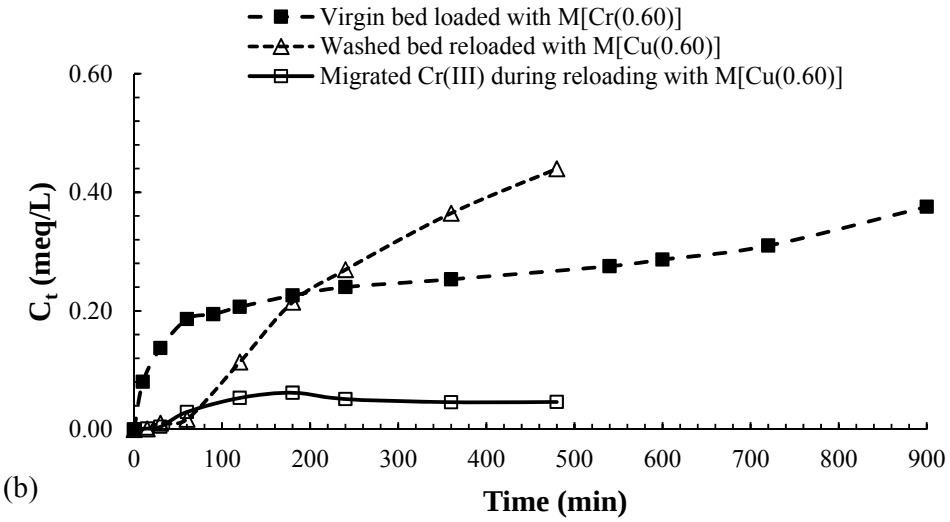

(b)

Fig. B.24: Virgin GAA bed loaded with M[Cr(0.60)] system and washed bed reloaded with M[Cu(0.60)] system under controlled pH conditions: (a) pH variation and (b) breakthrough curves {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in M[Cr(0.60)] = 0.58±0.01 meq/L, M[Cu(0.60)] = 0.58±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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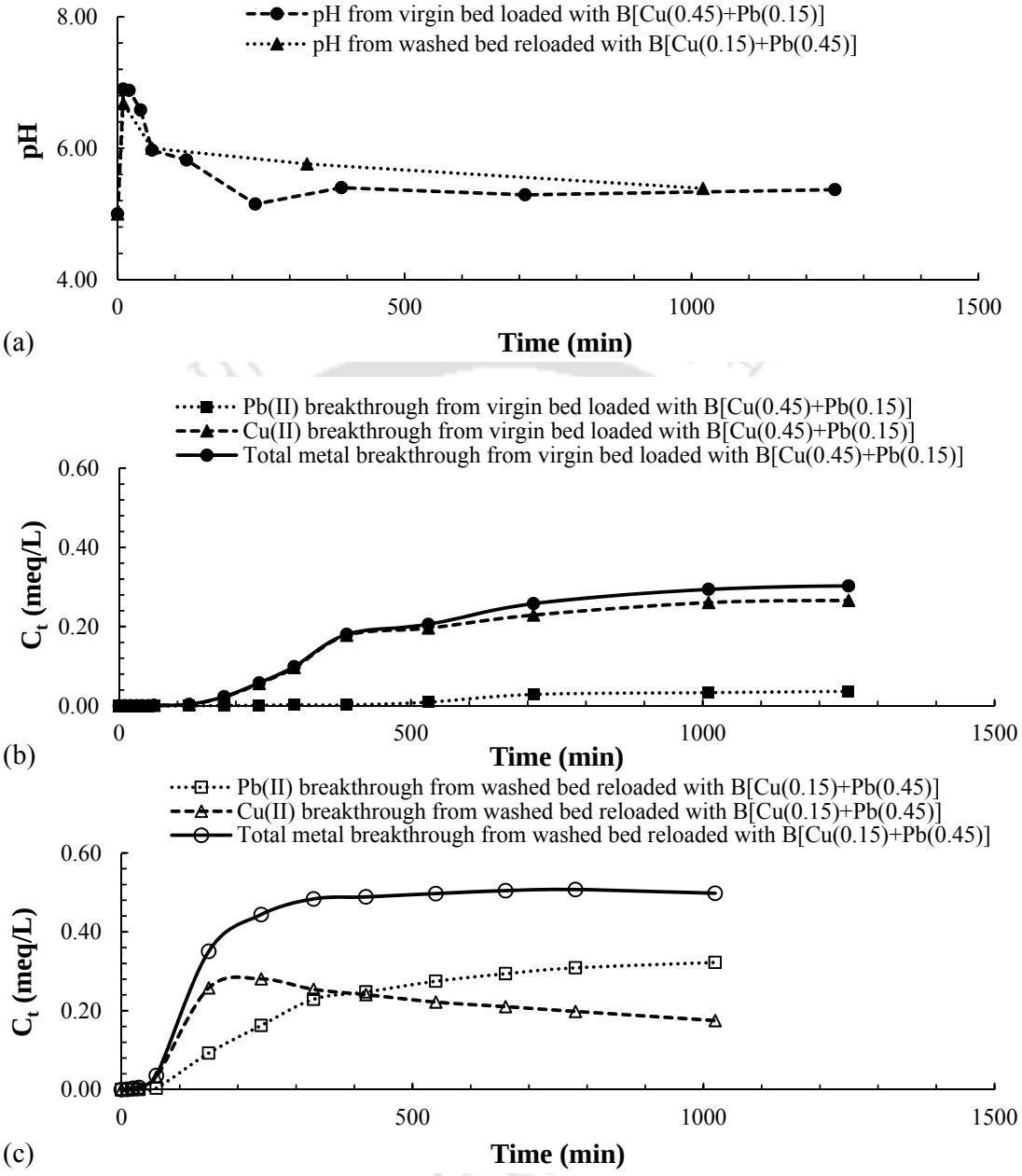

Fig. B.25: Virgin GAA bed loaded with B[Cu(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cu(0.15)+Pb(0.45)] combination under uncontrolled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cu(0.45)+Pb(0.15)] combination: Cu(II) = 0.45±0.01 meq/L + Pb(II) = 0.15±0.01 meq/L and B[Cu(0.15)+Pb(0.45)] combination: Cu(II) = 0.15±0.03 meq/L + Pb(II) = 0.45±0.01 meq/L, Initial adjusted pH = 5.00±0.04, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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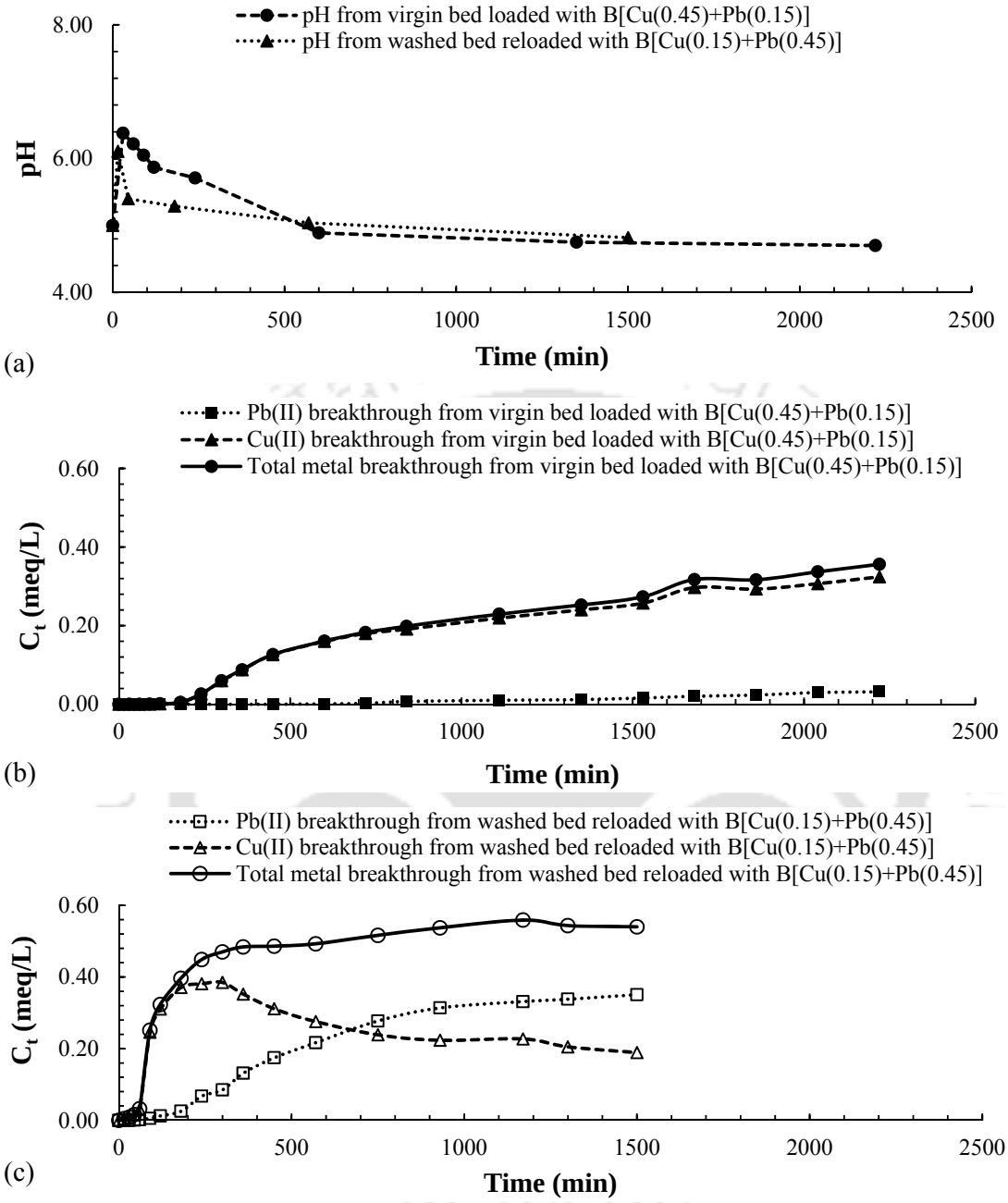

Fig. B.26: Virgin GAA bed loaded with B[Cu(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cu(0.15)+Pb(0.45)] combination under uncontrolled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cu(0.45)+Pb(0.15)] combination: Cu(II) = 0.46±0.01 meq/L + Pb(II) = 0.15±0.01 meq/L and B[Cu(0.15)+Pb(0.45)] combination: Cu(II) = 0.15±0.00 meq/L + Pb(II) = 0.45±0.02 meq/L, Initial adjusted pH = 5.00±0.04, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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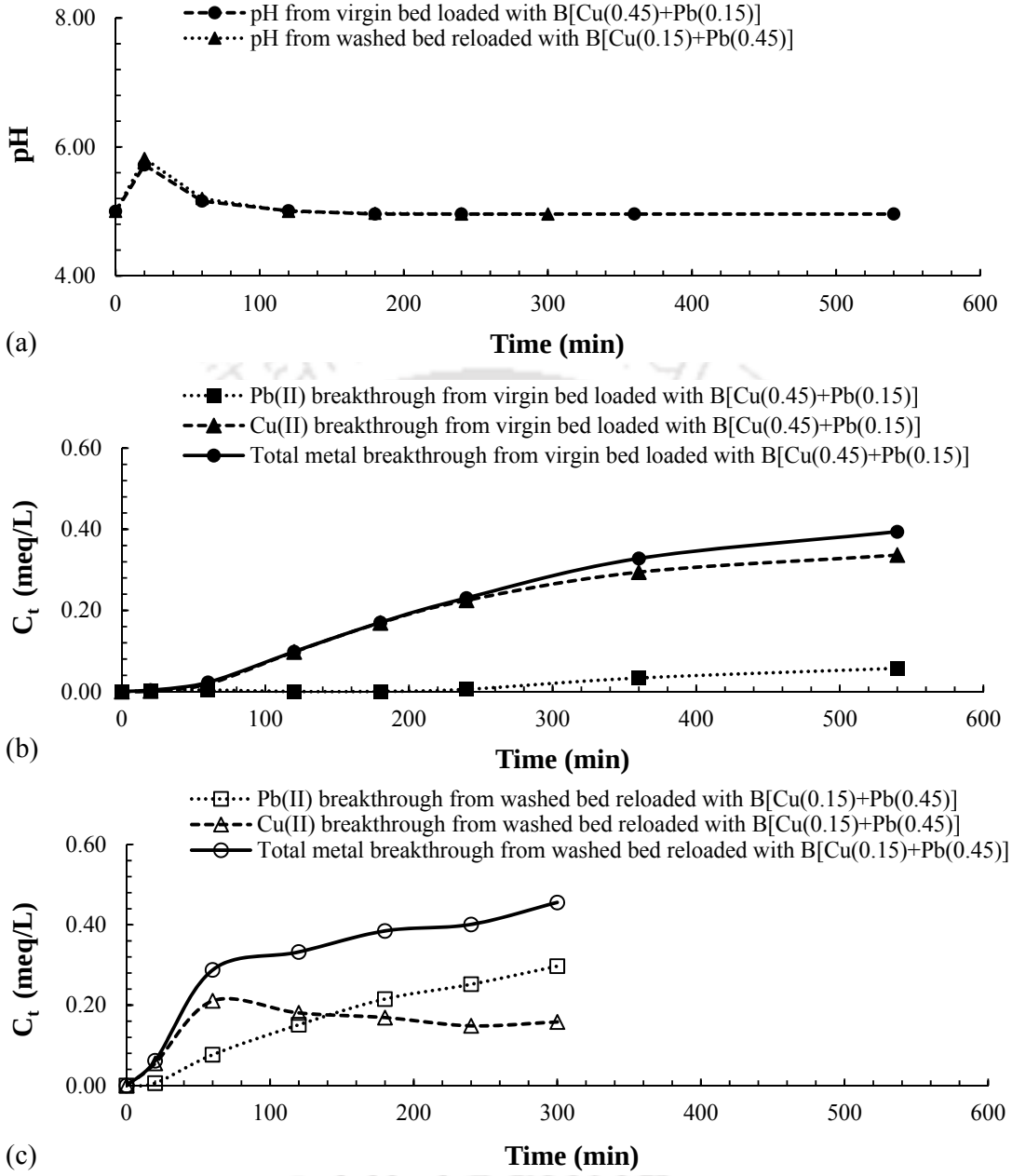

Fig. B.27: Virgin GAA bed loaded with B[Cu(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cu(0.15)+Pb(0.45)] combination under controlled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cu(0.45)+Pb(0.15)] combination: Cu(II) = 0.43±0.01 meq/L + Pb(II) = 0.16±0.01 meq/L and B[Cu(0.15)+Pb(0.45)] combination: Cu(II) = 0.14±0.00 meq/L + Pb(II) = 0.45±0.02 meq/L, Buffered pH = 5.00±0.04, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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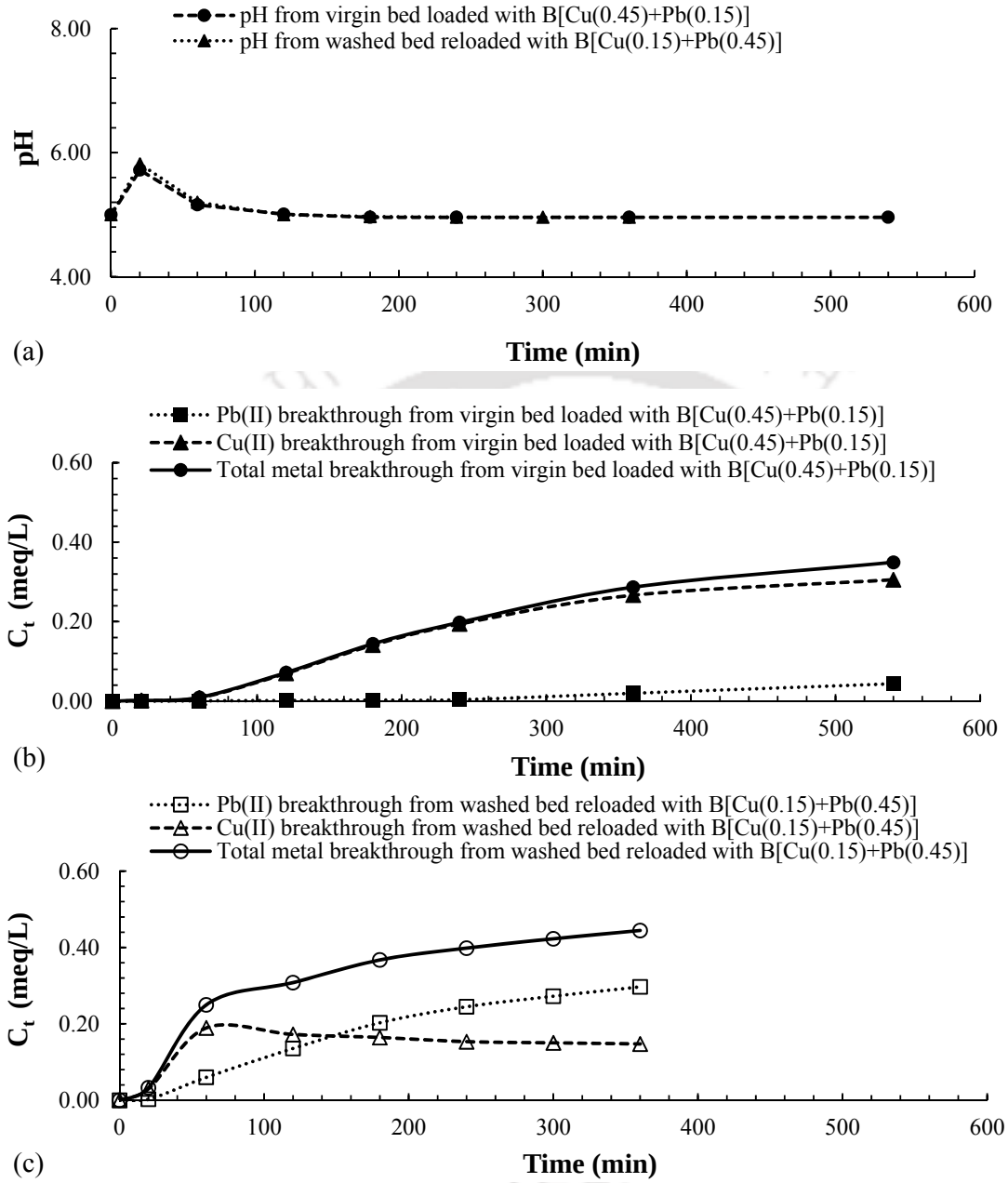

Fig. B.28: Virgin GAA bed loaded with B[Cu(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cu(0.15)+Pb(0.45)] combination under controlled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cu(0.45)+Pb(0.15)] combination: Cu(II) = 0.43±0.01 meq/L + Pb(II) = 0.16±0.01 meq/L and B[Cu(0.15)+Pb(0.45)] combination: Cu(II) = 0.14±0.00 meq/L + Pb(II) = 0.45±0.02 meq/L, Buffered pH = 5.00±0.04, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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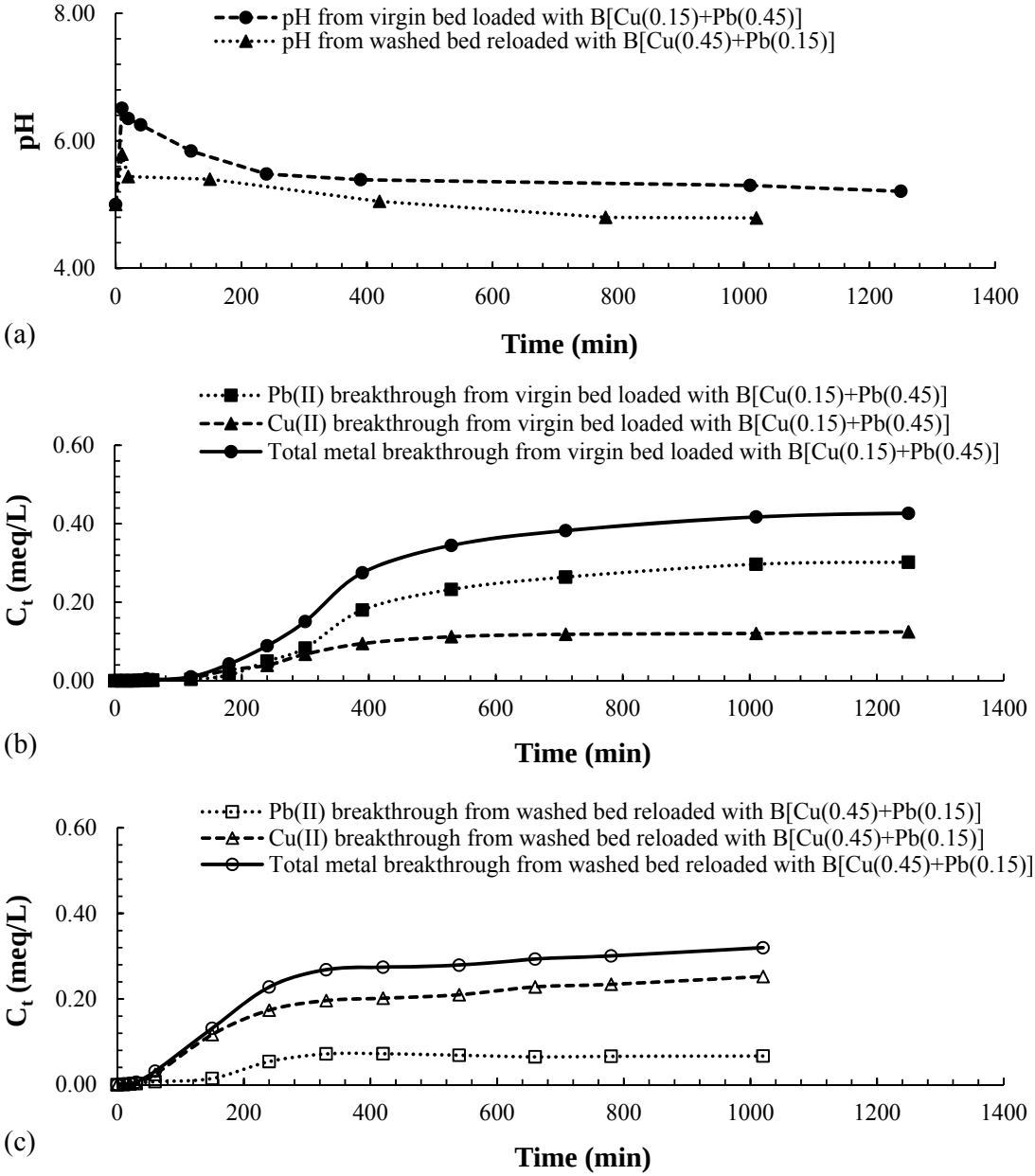

Fig. B.29: Virgin GAA bed loaded with B[Cu(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cu(0.45)+Pb(0.15)] combination under uncontrolled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cu(0.15)+Pb(0.45)] combination: Cu(II) = 0.15±0.01 meq/L + Pb(II) = 0.44±0.02 meq/L and B[Cu(0.45)+Pb(0.15)] combination: Cu(II) = 0.45±0.00 meq/L + Pb(II) = 0.15±0.01 meq/L, Initial adjusted pH = 5.00±0.05, Temp. = 30±1 °C} (Each data represents an average of two independent experimental values).

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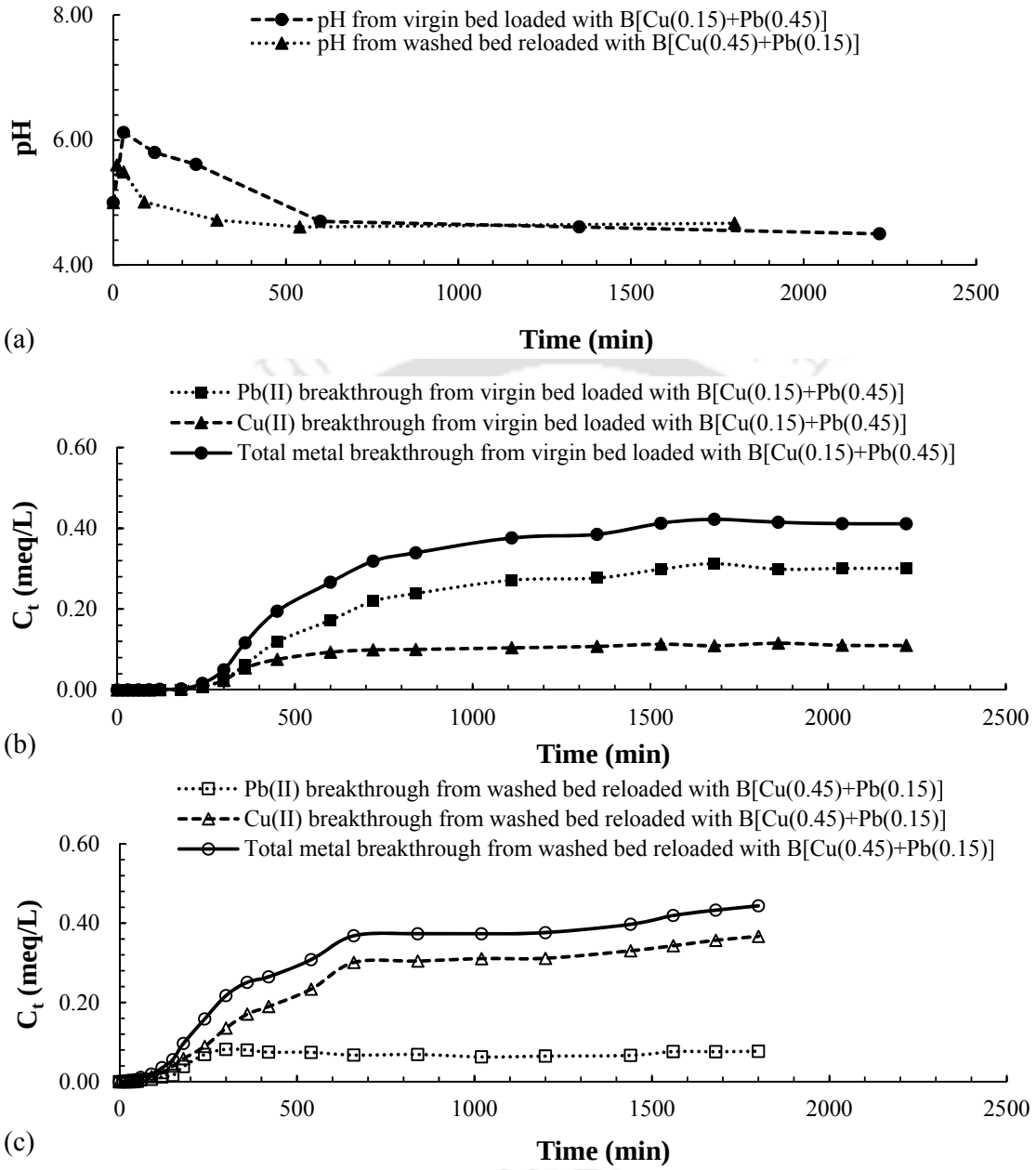

Fig. B.30: Virgin GAA bed loaded with B[Cu(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cu(0.45)+Pb(0.15)] combination under uncontrolled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cu(0.15)+Pb(0.45)] combination: Cu(II) = 0.15±0.01 meq/L + Pb(II) = 0.44±0.02 meq/L and B[Cu(0.45)+Pb(0.15)] combination: Cu(II) = 0.45±0.00 meq/L + Pb(II) = 0.15±0.01 meq/L, Initial adjusted pH = 5.00±0.05, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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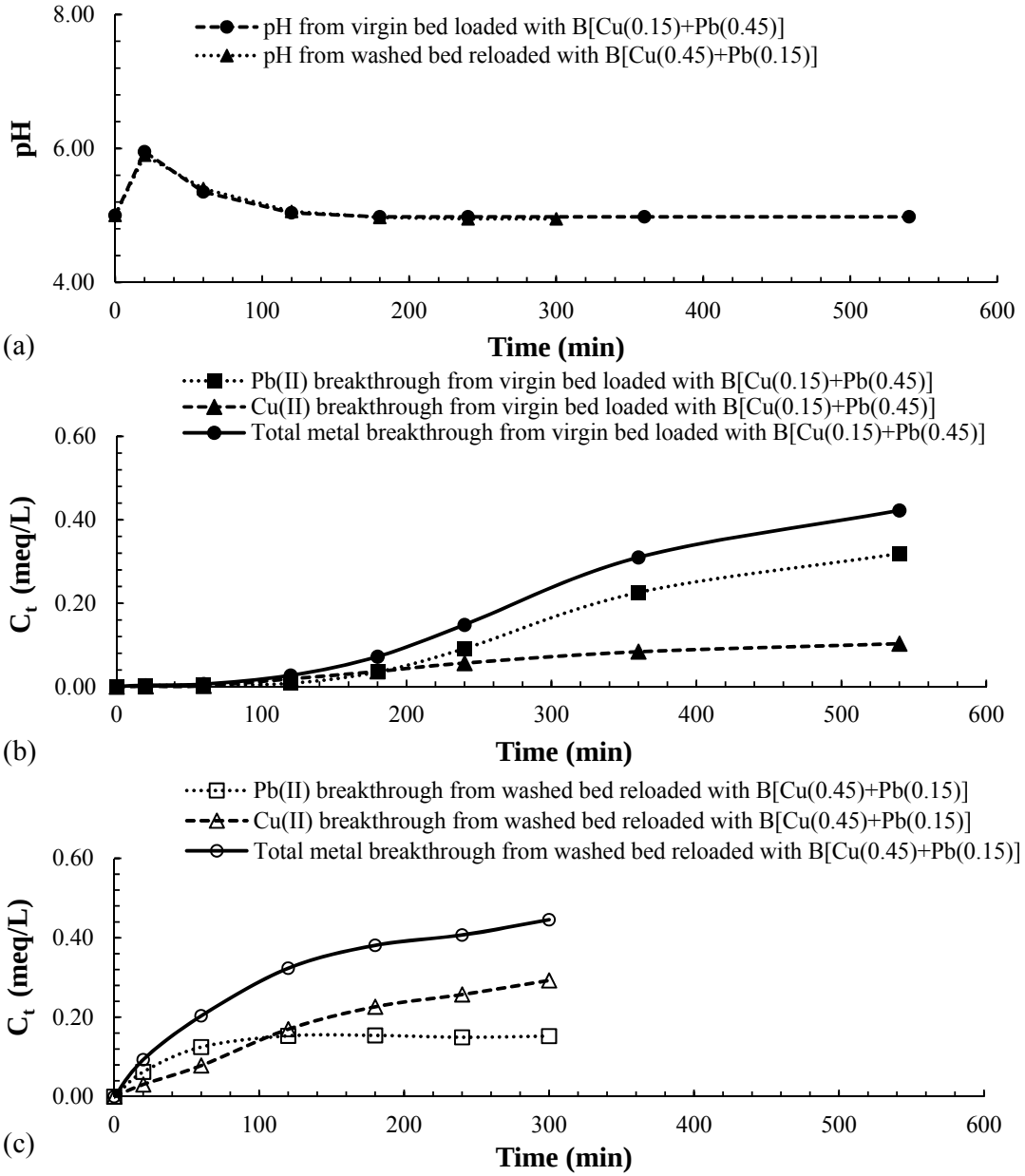

Fig. B.31: Virgin GAA bed loaded with B[Cu(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cu(0.45)+Pb(0.15)] combination under controlled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cu(0.15)+Pb(0.45)] combination: Cu(II) = 0.15±0.01 meq/L + Pb(II) = 0.44±0.02 meq/L and B[Cu(0.45)+Pb(0.15)] combination: Cu(II) = 0.45±0.00 meq/L + Pb(II) = 0.15±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1 °C} (Each data represents an average of two independent experimental values).

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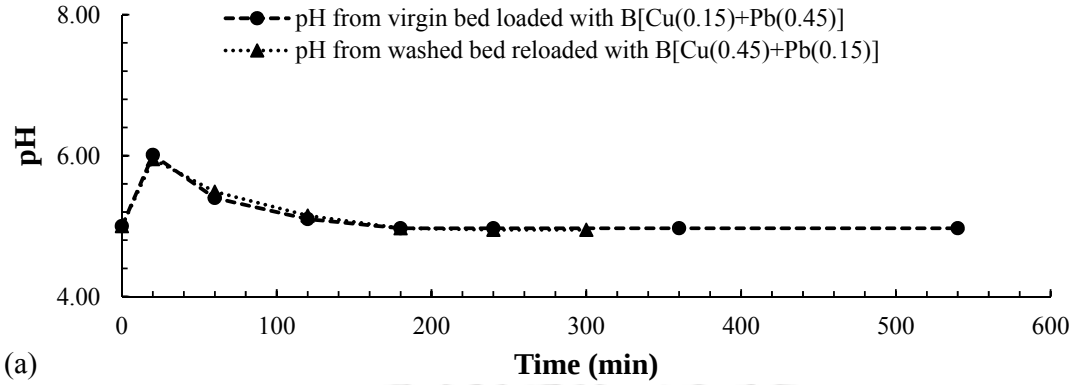
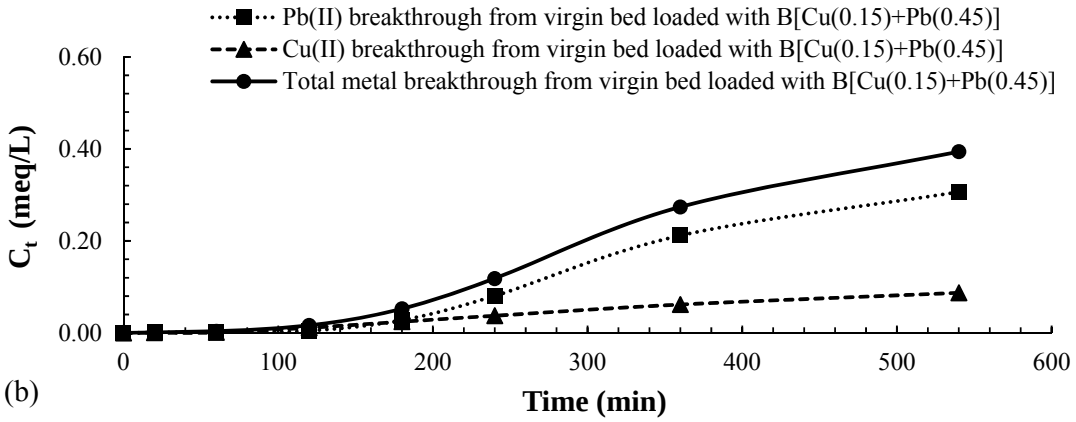
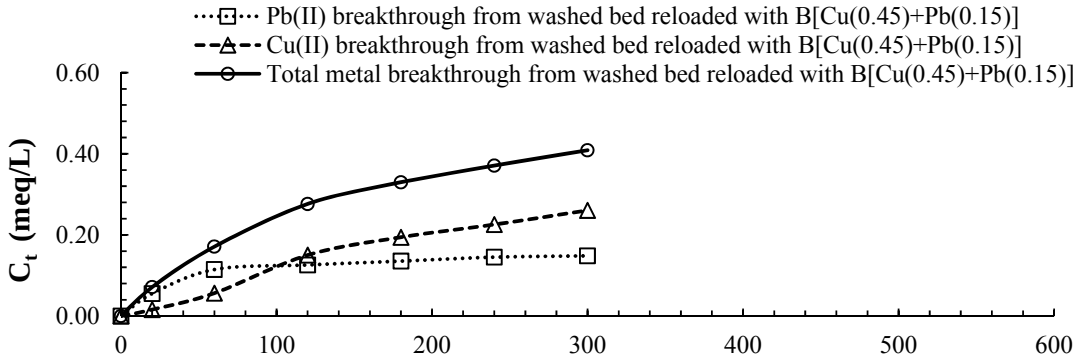


(a)



(b)



(c)

Fig. B.32: Virgin GAA bed loaded with B[Cu(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cu(0.45)+Pb(0.15)] combination under controlled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cu(0.15)+Pb(0.45)] combination: Cu(II) = 0.15±0.01 meq/L + Pb(II) = 0.44±0.02 meq/L and B[Cu(0.45)+Pb(0.15)] combination: Cu(II) = 0.45±0.00 meq/L + Pb(II) = 0.15±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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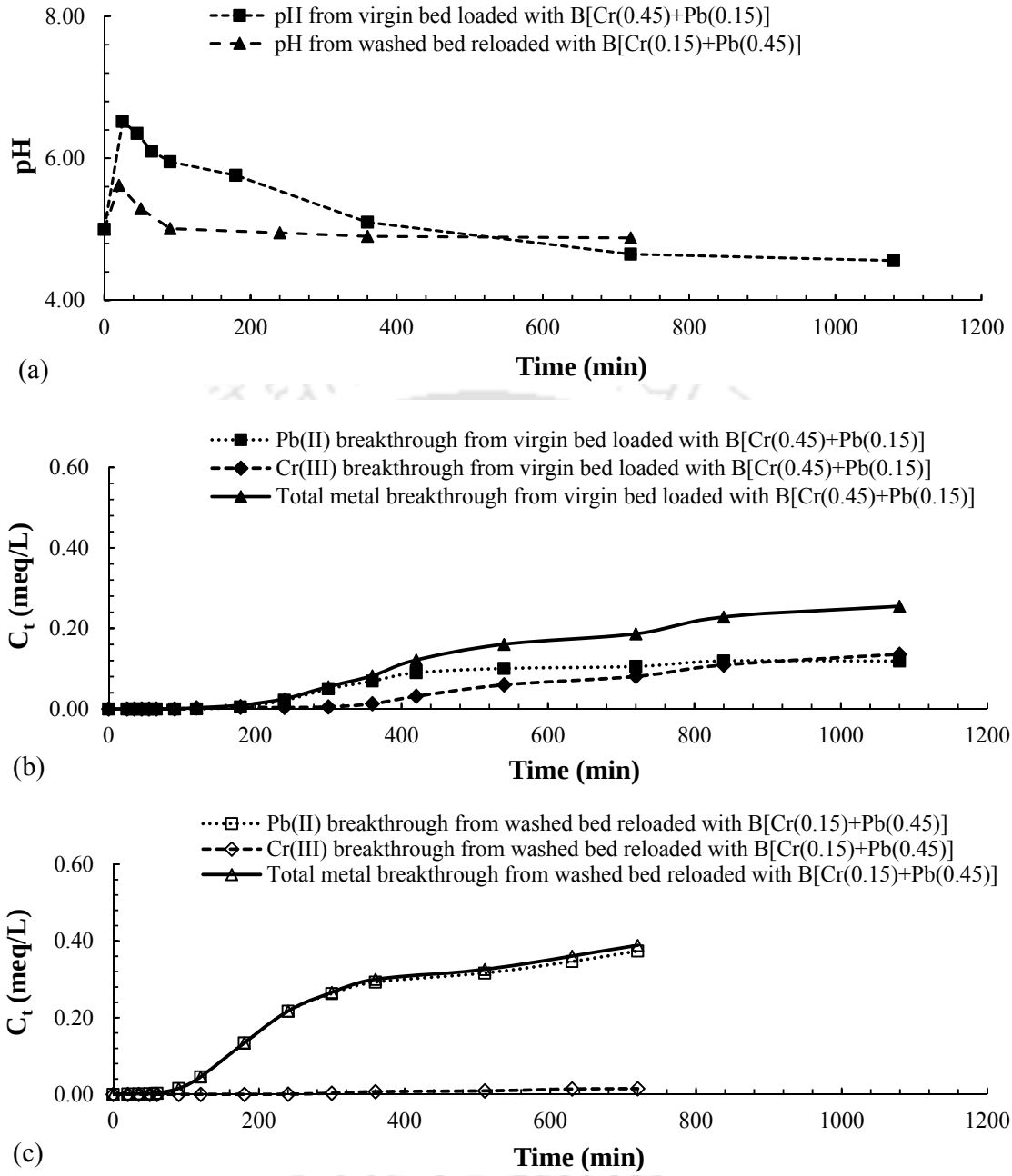

Fig. B.33: Virgin GAA bed loaded with B[Cr(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cr(0.15)+Pb(0.45)] combination under uncontrolled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cr(0.45)+Pb(0.15)] combination: Cr(III) = 0.44±0.01 meq/L + Pb(II) = 0.15±0.02 meq/L and B[Cr(0.15)+Pb(0.45)] combination: Cr(III) = 0.15±0.00 meq/L + Pb(II) = 0.45±0.01 meq/L, Initial adjusted pH = 5.00±0.04, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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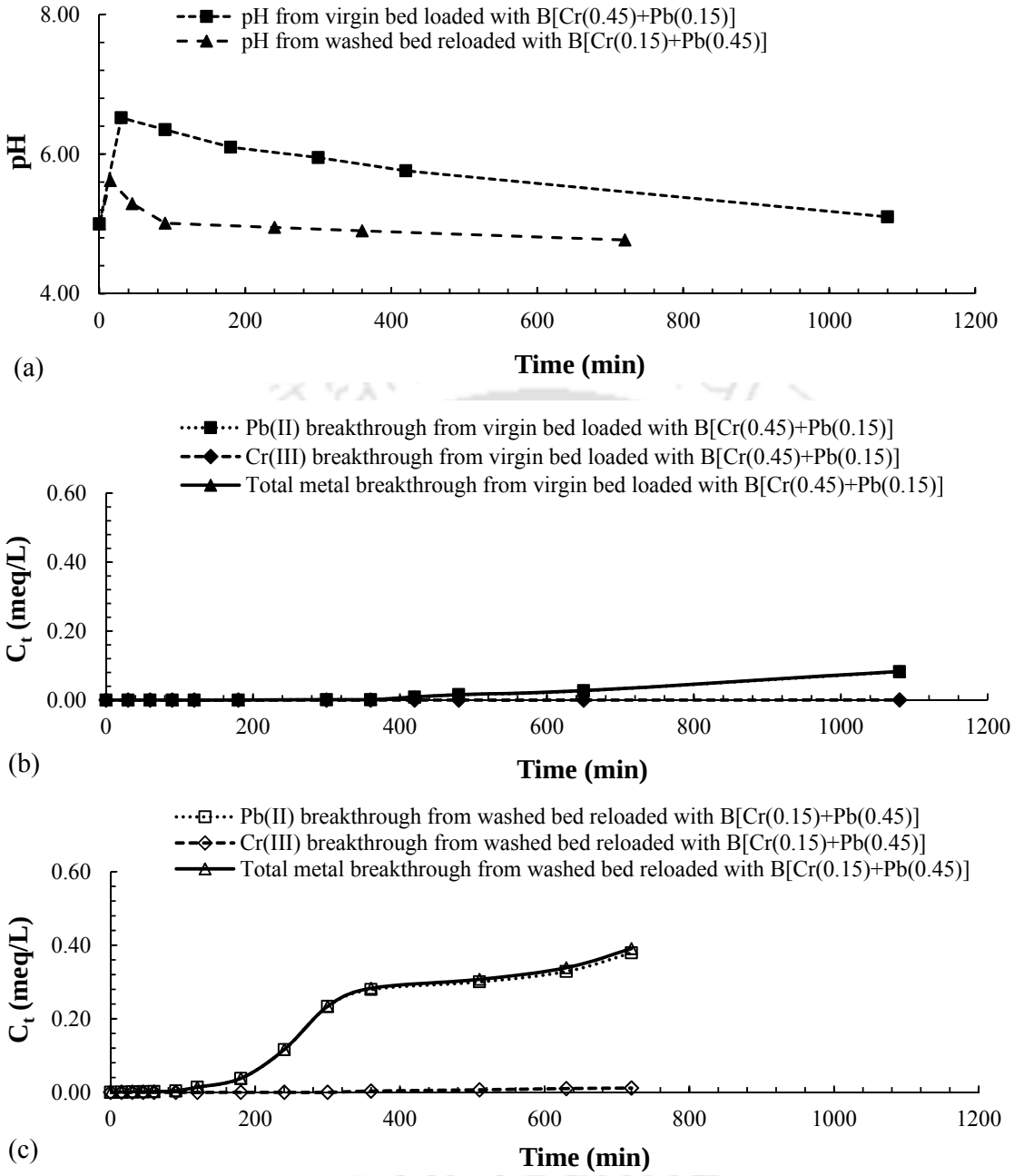

Fig. B.34: Virgin GAA bed loaded with B[Cr(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cr(0.15)+Pb(0.45)] combination under uncontrolled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cr(0.45)+Pb(0.15)] combination: Cr(III) = 0.44±0.01 meq/L + Pb(II) = 0.15±0.02 meq/L and B[Cr(0.15)+Pb(0.45)] combination: Cr(III) = 0.15±0.00 meq/L + Pb(II) = 0.45±0.01 meq/L, Initial adjusted pH = 5.00±0.04, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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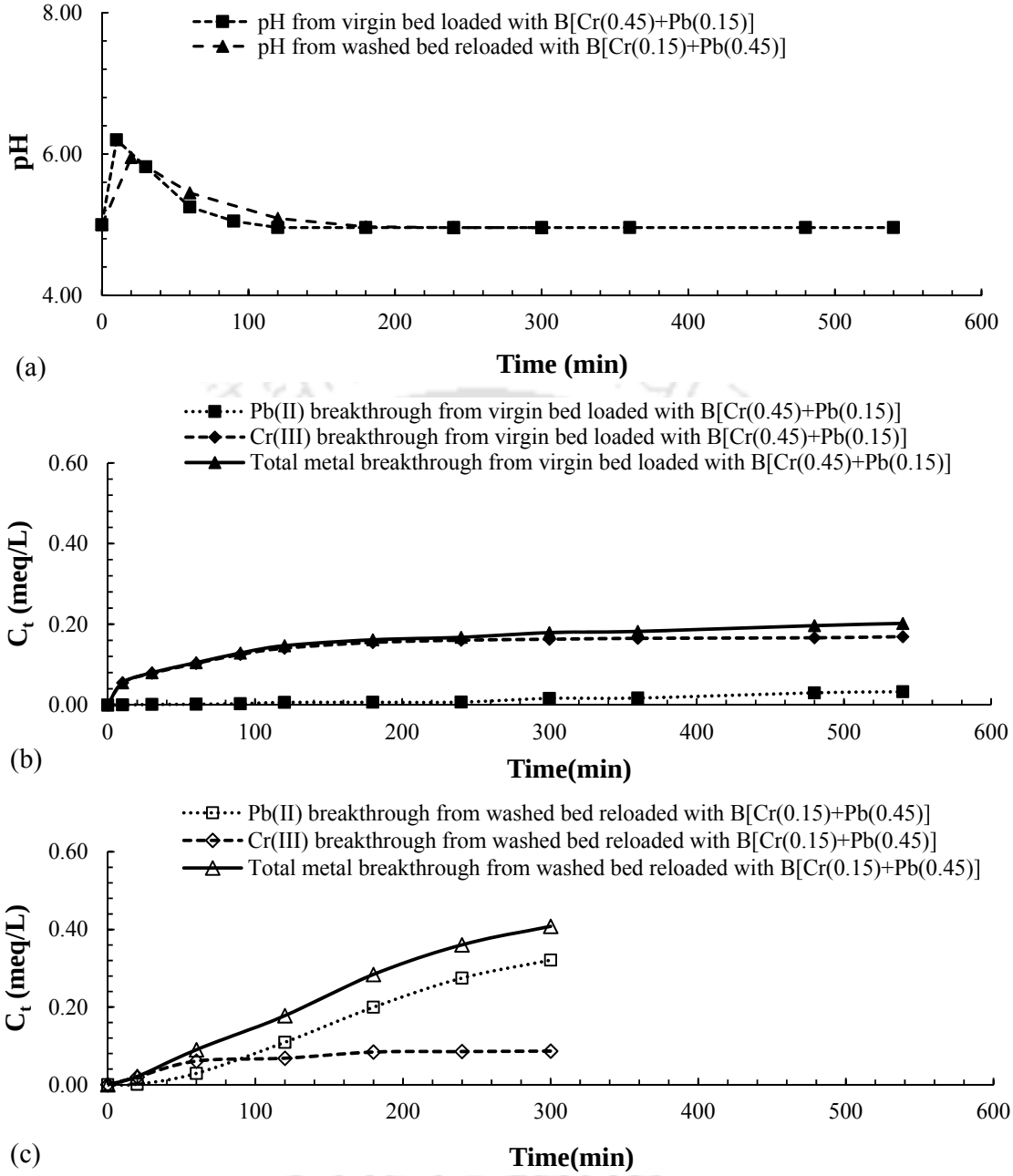

Fig. B.35: Virgin GAA bed loaded with B[Cr(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cr(0.15)+Pb(0.45)] combination under controlled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cr(0.45)+Pb(0.15)] combination: Cr(III) = 0.44±0.01 meq/L + Pb(II) = 0.15±0.02 meq/L and B[Cr(0.15)+Pb(0.45)] combination: Cr(III) = 0.15±0.00 meq/L + Pb(II) = 0.45±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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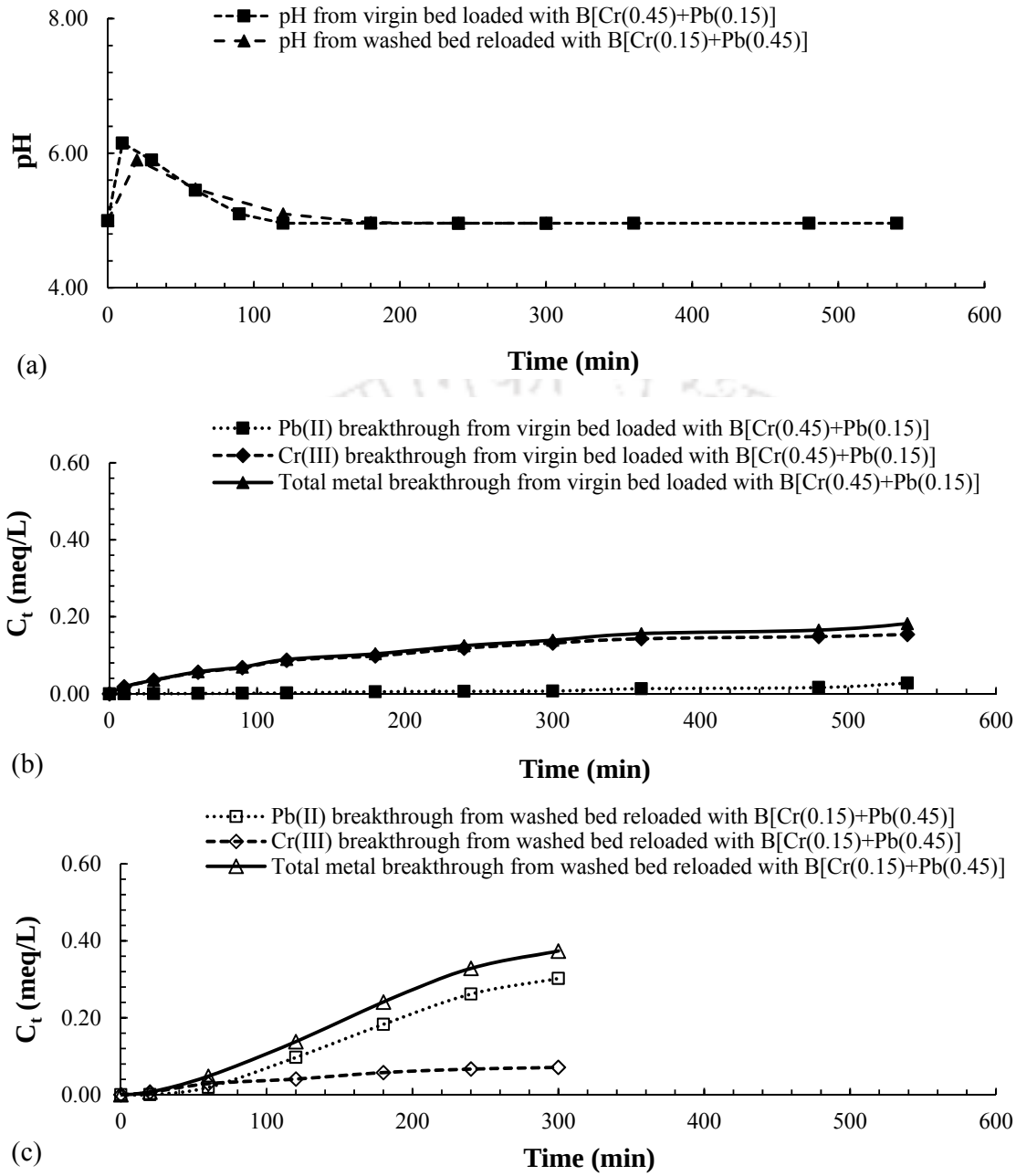

Fig. B.36: Virgin GAA bed loaded with B[Cr(0.45)+Pb(0.15)] combination and washed bed reloaded with B[Cr(0.15)+Pb(0.45)] combination under controlled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cr(0.45)+Pb(0.15)] combination: Cr(III) = 0.44±0.01 meq/L + Pb(II) = 0.15±0.02 meq/L and B[Cr(0.15)+Pb(0.45)] combination: Cr(III) = 0.15±0.00 meq/L + Pb(II) = 0.45±0.01 meq/L, Buffered pH = 5.00±0.03, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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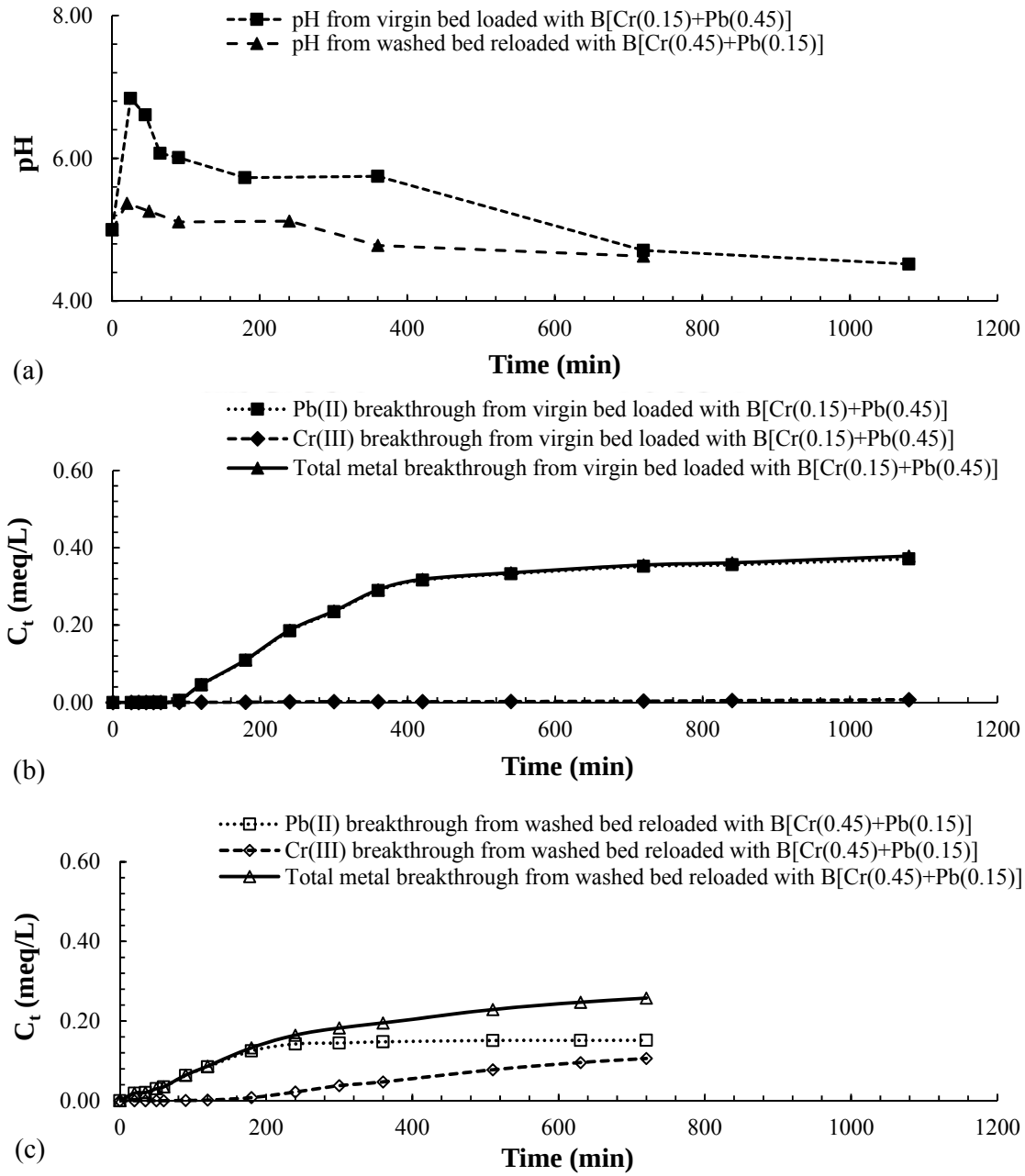

Fig. B.37: Virgin GAA bed loaded with B[Cr(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cr(0.45)+Pb(0.15)] combination under uncontrolled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cr(0.15)+Pb(0.45)] combination: Cr(III) = 0.15±0.01 meq/L + Pb(II) = 0.45±0.02 meq/L and B[Cr(0.45)+Pb(0.15)] combination: Cr(III) = 0.44±0.00 meq/L + Pb(II) = 0.15±0.01 meq/L, Initial adjusted pH = 5.00±0.05, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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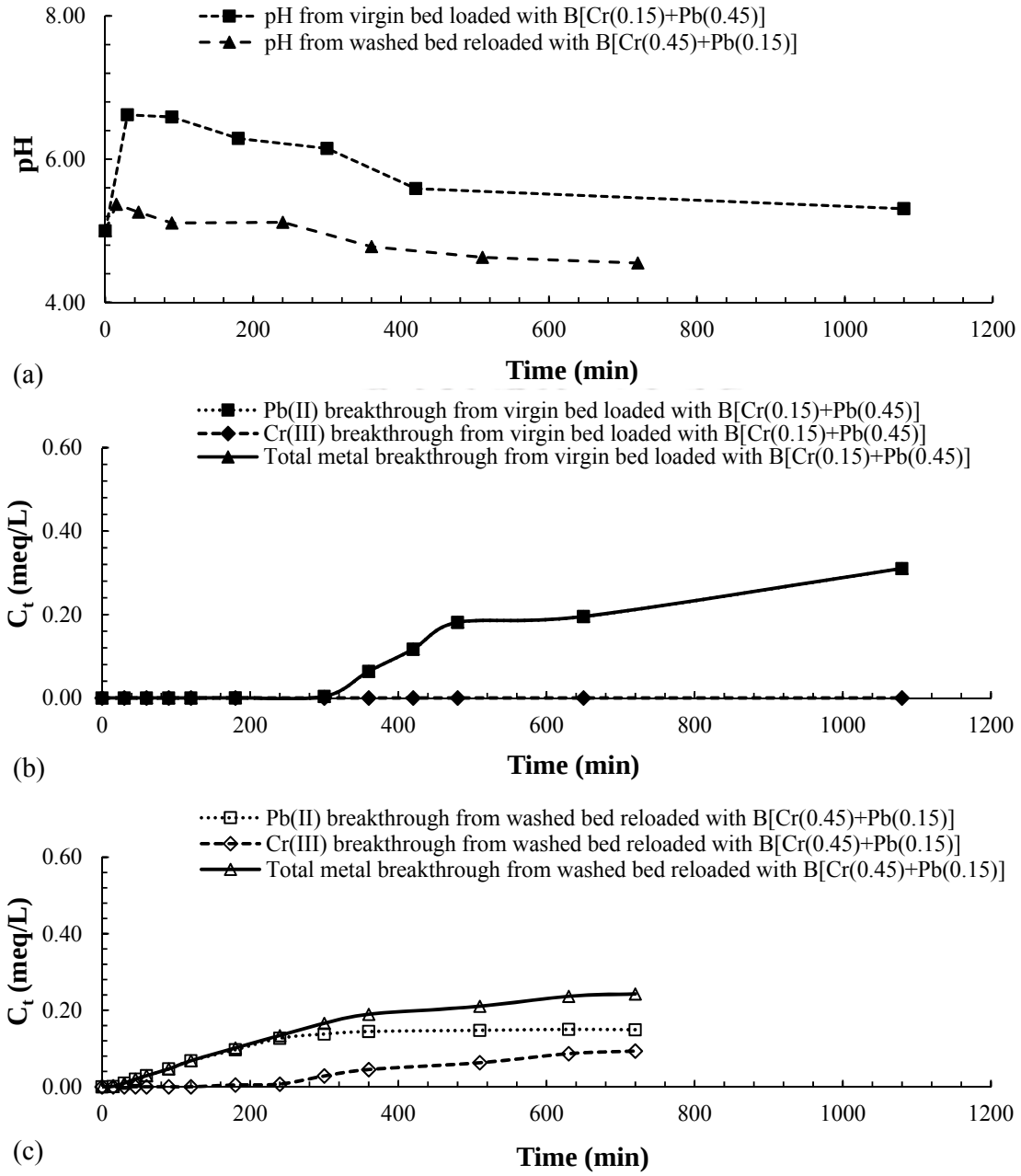

Fig. B.38: Virgin GAA bed loaded with B[Cr(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cr(0.45)+Pb(0.15)] combination under uncontrolled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cr(0.15)+Pb(0.45)] combination: Cr(III) = 0.15±0.01 meq/L + Pb(II) = 0.45±0.02 meq/L and B[Cr(0.45)+Pb(0.15)] combination: Cr(III) = 0.44±0.00 meq/L + Pb(II) = 0.15±0.01 meq/L, Initial adjusted pH = 5.00±0.05, Temp. = 30±1 ºC} (Each data represents an average of two independent experimental values).

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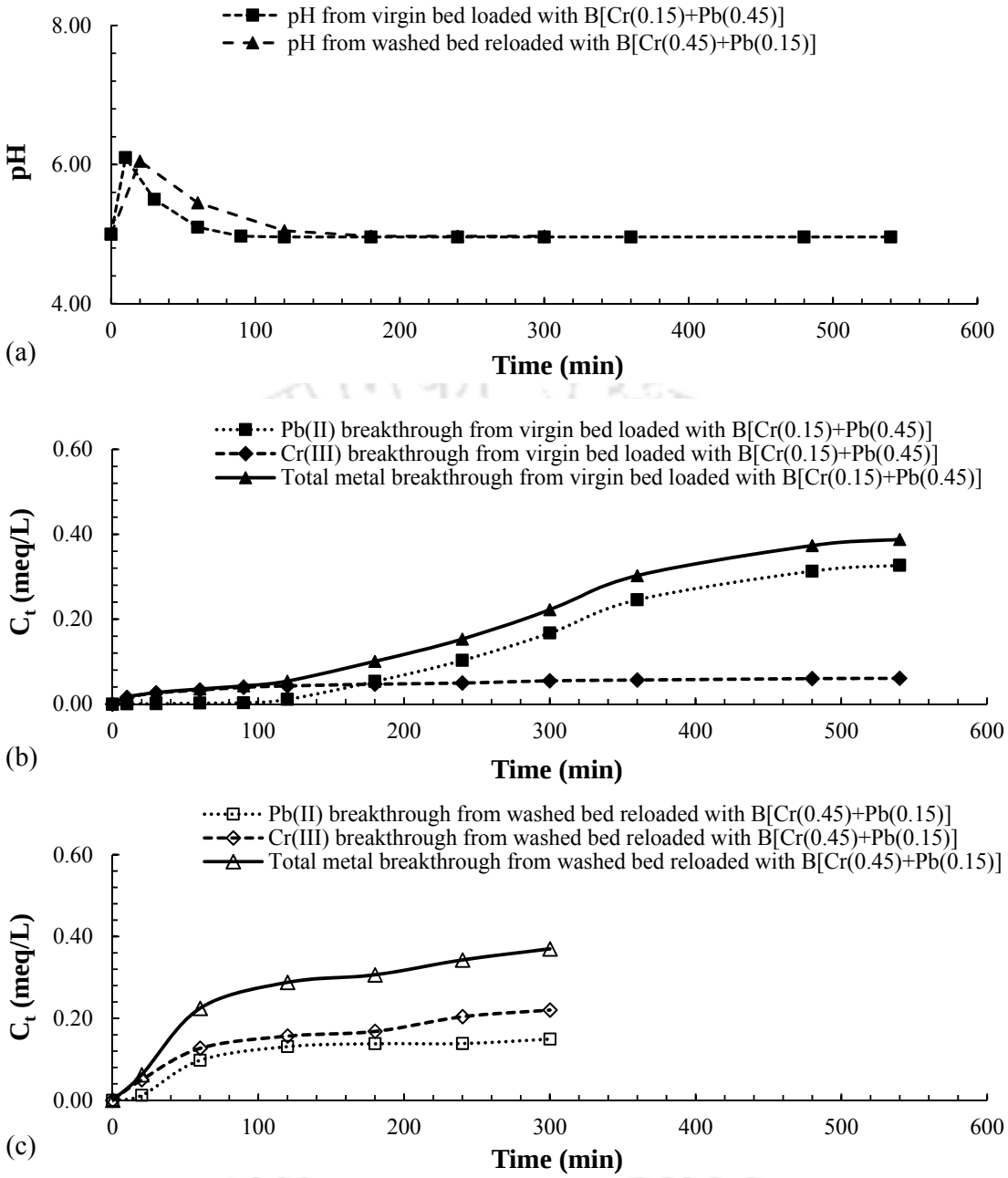

Fig. B.39: Virgin GAA bed loaded with B[Cr(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cr(0.45)+Pb(0.15)] combination under controlled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 4.5 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cr(0.15)+Pb(0.45)] combination: Cr(III) = 0.15±0.01 meq/L + Pb(II) = 0.45±0.02 meq/L and B[Cr(0.45)+Pb(0.15)] combination: Cr(III) = 0.44±0.00 meq/L + Pb(II) = 0.15±0.01 meq/L, Buffered pH = 5.00±0.05, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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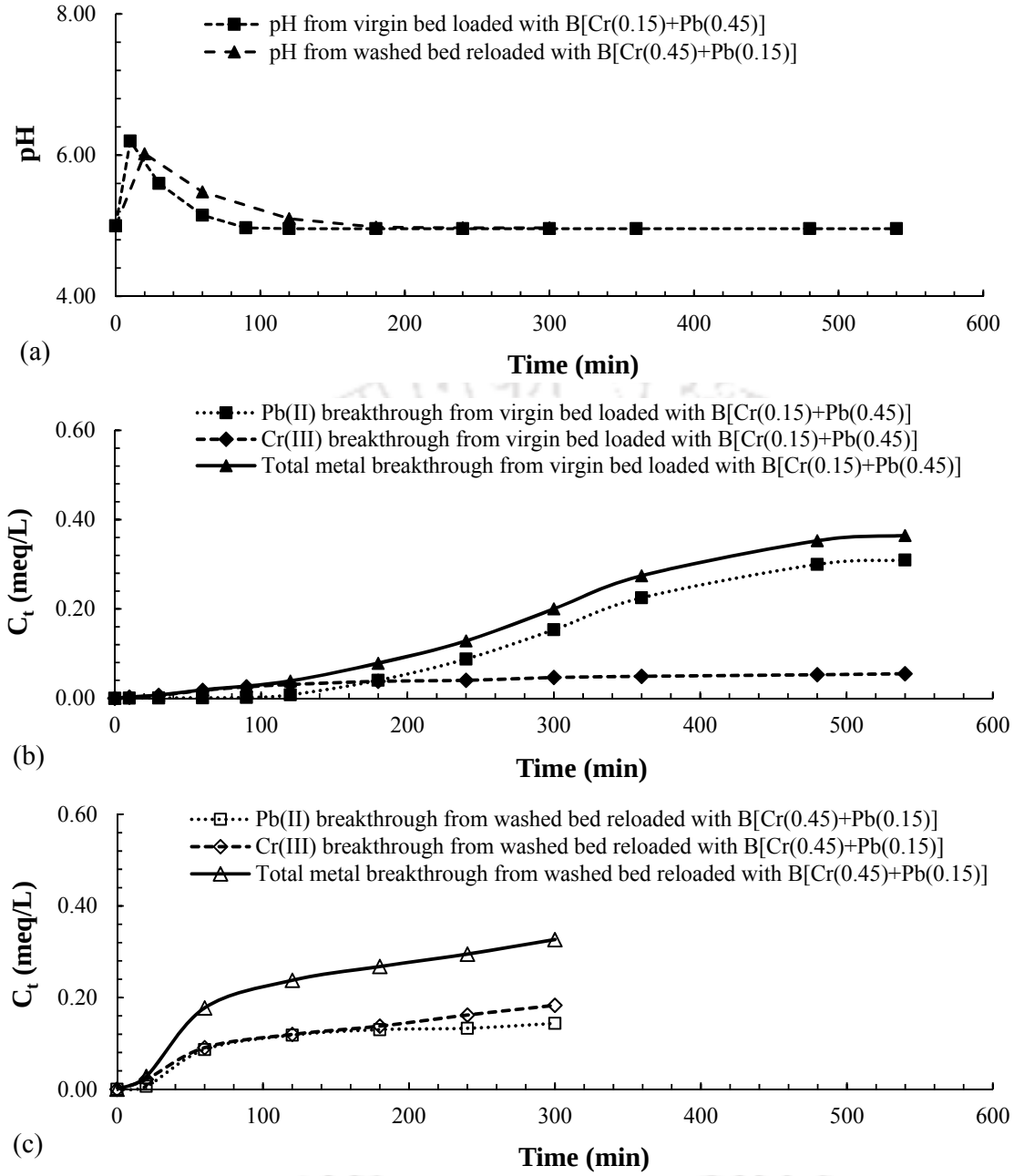

Fig. B.40: Virgin GAA bed loaded with B[Cr(0.15)+Pb(0.45)] combination and washed bed reloaded with B[Cr(0.45)+Pb(0.15)] combination under controlled pH conditions: (a) pH variation, (b) breakthrough curves for virgin bed and (c) breakthrough curves for washed bed {Bed depth = 6.0 cm, Flow rate = 2.0 mL/min, Initial metal conc. in B[Cr(0.15)+Pb(0.45)] combination: Cr(III) = 0.15±0.01 meq/L + Pb(II) = 0.45±0.02 meq/L and B[Cr(0.45)+Pb(0.15)] combination: Cr(III) = 0.44±0.00 meq/L + Pb(II) = 0.15±0.01 meq/L, Buffered pH = 5.00±0.05, Temp. = 30±1 ^{o}C} (Each data represents an average of two independent experimental values).

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