A study on multiple contaminant-soil interaction and its effect on contaminant fate prediction

Thesis
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DOCTOR OF PHILOSOPHY

by

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Dedicated to
My
Beloved Family

(Mom, Dad, Keyur and Julie)

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 and Department of Civil Engineering, Ecole Centrale de Nantes, France.

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 “**A study on multiple contaminant-soil interaction and its effect on contaminant fate prediction**” submitted by Mrs. Poly Buragohain 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 her 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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Chapter 5 **Experimental evaluation of soil-single contaminant interaction**

Abstract

With tremendous urbanization and industrialization enormous amount of waste has been generated, which has significantly affected the quality of geoenvironment and the water resources. Several researchers and practitioners have stressed the importance to circumvent this environmental issue, and to find an appropriate solution to contain these wastes safely. Engineered landfill is an efficient method for meeting this challenge and soils used in these facilities and those below it (natural soil) plays a very vital role. One of the significant chemical properties of a landfill liner material is the contaminant retention capacity which determines the fate of contaminants or pollutants in the geoenvironment. It is necessary to establish the retention property of soils to evaluate its usefulness in waste containment facilities and its potential in minimizing contaminant migration into groundwater. There are several studies that evaluate contaminant retention of soils for single contaminant interaction. In, reality the presence of single contaminants seldom exists. Every contaminant is influenced by multiple ions present in the geoenvironmemt. Therefore, there is a need to evaluate multiple contaminant-soil interaction. There is also a need to further evaluate the retention capacity of locally available soils found abundantly and check its potential use as a cost-effective liner material in waste containment facilities.

The present research work attempted to understand systematically, the multiple contaminant retention behavior of soils. The adequacy of existing mathematical isotherms for quantifying soil-multiple contaminants interaction was evaluated. Effort was made to quantify the influence of multiple contaminants on retention property of different soil type based on existing mathematical isotherm models. Many experimental interaction results were compared in the present study to appraise this objective. Some of the anomalies while using isotherm results for comparing different soil-contaminant retention cases have been brought forth. The contaminant retention results were used to understand the sensitivity of retention parameters on contaminant fate prediction. The influence of different ranges of contaminant concentration on fate prediction was studied. An attempt was made to understand whether there is a possibility of developing a correlation between soil specific parameters such as cation exchange capacity, specific surface area, soil pH with retention parameters.

Keywords: contaminant, retention, single, multiple, isotherm, fate prediction, locally available soils, soil properties, ion chromotograph.

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Nomenclature

α	Dispersion coefficient
θ	Volumetric water content
λ_r	Decay constant representing any attenuation reaction
C_e	Equilibrium concentration in solution
C_f	Flux averaged concentration
C_i	Initial concentration of the soil
C_o	Input concentration of the contaminant solution
C_r	Resident concentration
C_s	mass of the solute sorbed per unit mass of the solid
C_t	Concentration corresponding to time t
D_e	Effective diffusion coefficient
F	Freundlich isotherm
G	Specific gravity
K_d	Linear partition coefficient
K_F	Freundlich partition coefficient
K_L	Partition coefficient for Langmuir isotherm
L	Length of soil mass
La	Langmuir isotherm
Li	Linear isotherm
F	Freundlich isotherm
N	Freundlich fitting parameter
n	Porosity
P	Peclet number
Q_m	Maximum retention capacity
Q_e	Sorbed concentration on soil
R	Goodness of fit
R_F	Freundlich retardation factor
R_{La}	Langmuir retardation factor
R_{Li}	Linear retardation factor
T, Z, C_r, R	Dimensionless parameter
v	Darcy’s velocity or discharge velocity
Vc	Velocity of contaminant

V	Ground water velocity.
v_s	Seepage velocity
x	distance
ρ	Bulk density
ρ_d	Dry density

Abbreviation

ADE	Advection-dispersion equation
BTC	Breakthrough curve
CEC	Cation Exchange Property
CI	Common ions
EDX	Energy dispersive X-ray spectroscopy
EGME	Ethylene Glycol Monoethyl Ether
FAsh	Fly ash
FBent	France Bentonite
FC	Fire Clay
HM	Heavy metals
IBent	Indian bentonite
LL	Liquid limit
LS	Local Soil
OMC	Optimum moisture content
pK	Hydrolysis constant
PL	Plastic limit
RS	Red Soil
SEM	Scanning electron microscope
SSA	Specific Surface Area
USCS	Unified soil classification system
XRD	X-Ray Diffraction

Chapter 1

Introduction

1.1 General The rise in the toxicity level in the geoenvironment due to the enormous generation of waste is currently a significant and challenging concern throughout the world. Heightened awareness of the deleterious effects of pollution to both human life and environment (Zhang et al., 2004; Du et al., 2006) has resulted in an intensive research effort to study the most significant geochemical process (retention and release) affecting the fate, transport and risk of disposed off contaminants in surface as well as subsurface environment (Kent et al., 2000; Davis et al., 2004a; Kohler et al., 2004). This knowledge is mandatory for designing efficient waste containment facilities for municipal and industrial wastes that may be hazardous or non-hazardous (Rowe and Booker 1985; Yong et al., 2001; Chang et al., 2005; Zhang et al., 2005) and also for deciding appropriate remediation scheme for an already contaminated site and ground water (Liu et al., 2004). It is required for performance assessment of shallow and deep nuclear waste disposal sites (Wang et al 2003; Wang and Li 2004; Missana et al. 2008; Rahman et al., 2009). The assessment of groundwater aquifer pollution rate is entirely based on the understanding of contaminant migration and retention mechanism (Rowe 1989; Rowe and Booker 1990; Soller and Berg 1992). The retention property of soil is defined based on the amount of contaminant sorbed on the soil surface during soil-contaminant interaction (Sharma and Reddy, 2004). It is therefore a surface phenomenon and includes processes such as sorption, absorption, precipitation, complexation (Ruthven 1984). Adsorption refers to contaminants (ions and molecules) clinging onto a soil solid surface by means of physical or chemical bonding. Absorption refers to contaminants diffusing into the particle and being adsorbed onto interior surface. On the other hand release or desorption refers to contaminants getting detached from mineral grains and organic matter and entering into the pore fluid when it comes in contact with each other. Retention/release characterization of a soil-contaminant is carried out using laboratory tests or field experiments and quantified with the help of mathematical models known as isotherms (Elkhatib et al., 1990; Hooda and Alloway 1998; Villegas et al., 2003; Villegas et al., 2004; Sharma and Reddy 2004; Serrano et al., 2005).

Predictions of retention properties of soils are not easy due to their highly complex interactions. Numerous research work has demonstrated that the extent of retention is largely dependent on the physico-chemical properties of the adsorbent such as clay content

(Oscarson et al., 1987; Berglof et al., 2002; Tanshuling et al., 2003; Ramakrishna and Philip 2008); residual electric charges (Li et al., 2003), contact time (Cai et al., 2007; Kahle and Stamm 2007), water content (Roy et al., 2000; Ochsner et al., 2006) and ionic strength (Matigold et al., 1979; Kookama and Naidu 1998; Harter and Naidu 2001; Cheng et al., 2006; Sun et al., 2008; Hanna et al. 2008; Li et al., 2008). In addition, temperature, (Chan et al.,1999; Haijun et al.,2008; Prasad et al., 2002; Lu et al., 2009); pH (Moricca et al., 2000; Berglof et al., 2002; Choudhury and Kaif 2003; Villegas et al., 2003; Karahan et al., 2006; Kahle et al., 2007; Kolehi et al., 2007; Cao et al., 2008; Hanna et al., 2008; Nakamaru et al.,2008), presence of organic matter (Agarwal and Singh 1974; Moricca et al., 2000; Wong et al., 2007) and iron oxide (Elliot et al., 1985; Dhillon and Dhillon 1999; Villegas et al., 2004), influence the process of retention. There are different methodologies reported in the literature for determining retention of the soil (Bekesi, and Mcconchie, 2000). It is noted that batch test is one of the established methods for soil-contaminant retention characterization (ASTM D 4606; Taha et al., 2002).

The parameter obtained from retention characterization is termed as distribution coefficient or partition coefficient which is a characteristic parameter for a particular soil and a contaminant. Based on this value several mathematical models use it as input parameter for predicting the fate of contaminant in geoenvironment (Parker and Van Genuchten 1984; Shukla et al., 2002; Selim, 1992). For simplicity, the determination of input retention parameter is mostly based on soil-single contaminant interaction. Several studies have reported different soil-contaminant combinations and the factor influencing it. In reality, soil contaminant interaction always happen in the presence of multiple contaminants. Such multiple contaminant interaction will obviously be different from single-contaminant interaction). There are not many studies that quantify the difference between single and multiple contaminant interaction and its impact on contaminant fate prediction. There is also a need to further evaluate the retention capacity of locally available soils of north-east India and evaluate its potential use as a cost-effective material in waste containment application.

1.2. Motivation for this study

A need for understanding clearly the multiple contaminant retention of soils has motivated this research. It is important to appraise the difference when a modeler uses retention characteristics of a specific contaminant, based on single and multiple contaminant retention laboratory experiments. It is important to understand the validity of using retention isotherms for defining multiple contaminant retention as well. It is of interest to investigate whether such mathematical quantification would help to compare different soil-multiple contaminant interactions. Not many studies are reported in the literature that brings out the influence of multiple contaminant interaction on contaminant fate prediction. There is a need to clearly demonstrate whether simple regressional correlations are possible to predict contaminant retention parameters based on soil specific characteristics.

Chapter 2

Literature Review

2.1 Basic concept

An understanding of the nature of the retention phenomenon is a prerequisite to any attempt to interpret and predict the chemical behaviour of contaminants in soils under different conditions (Singh et al., 2006). The following section deals with a comprehensive literature review on the soil important chemical characteristic such as retention. This retention property is an important and of great significance while dealing with problems related to geoenvironmental applications, especially soil-water-contaminant interaction. Several researchers have proposed different methods for its determination, investigated the factors influencing them and proposed some correlations based on this property. Some of these studies are presented below, followed by the summary and critical appraisal of the reviewed literature.

2.2 Soil Retention Studies

Agarwal and Singh, 1974 have investigated the retention and release of copper by two soils namely black and red soils and checked the variation of organic matter. It has been found that black soils retained more copper than the red soil and the copper so held is not so easily reversible. Further, it was noted that black soil in compared to red soil did not have significant effect because of the presence of organic matter. Destruction of organic matter results in the of a larger amount of adsorbed copper than d by 0.1 N HCl alone indicating that apart of copper held as organo-copper complexes in the original soil is also solubilized.

Matigold et al., 1979 have investigated the effects of ionic strength and ion pair formation on the retention of nickel by Ca^{+2} and Na^{+} saturated Kaolinite. The results demonstrated that increasing ionic strength decreases Ni retention on kaolinite. More Ni was adsorbed on Na-kaolinite than on Ca-kaolinite. Retention of Ni is depressed to a greater degree when SO_4^{-2} is the dominant anion in solution instead of NO_3^-. This difference in retention can be attributed to higher concentrations of adsorbing species (Ni^{+2} and $NiNO_3^{+2}$) present in NO_3 media in comparison to SO_4 media in which only Ni^{+2} was the adsorbing species.

Christensen, 1983 has studied the Cd^{+2} and Pb^{+2} retention at low concentration on two soil (loamy sand, sandy loamy). It was observed that the retention capacities of the soils are found to increase approximately 3 times for each increase in pH of one unit in the pH interval

4 to 7. At low pH value of 4 to 5, the two soil exhibit about the same capacity to sorb trace amounts of Cd^{+2}, while the sandy loam has a slightly larger capacity than the loamy sand at higher pH value (6 to 7). The author has also found that with increase in contact time retention on to the two soils decreases. Ca^{+2} present in the soil solution is found to compete effectively with Cd^{+2} for retention sites in the soil. It was also found that retention of Cd^{+2} on to the soils increases with the increasing in Cd^{+2} concentration.

Oscarson et al., 1987 have studied the interactions of trace levels of cesium with montmorillonite and illitic clays. It was observed that for both the clays, exothermic reactions and pH 5 favored the retention process. Another interesting finding is that though montmorillonite compared to illitic calsy have a significantly greater cation exchange capacity and specific surface area, the illitic clay has a greater retention capacity and affinity for Cs^{+}. This is attributed to selective retention and fixation of cesium on sites large fraction of Cs^{+} on the edge-interlayer region. Potassium present in the suspending medium also has a significant effect on the amount of Cs^{+} sorbed by the clays. The lower the K^{+} concentration, greater the amount of Cs^{+} sorbed by the clays. This is likely due to the competition from K + for the sites responsible for fixing Cs^{+}. Thus, it can be indicated that for the disposal of nuclear fuel waste containing 135Cs, the illitic clay would be a more effective component of the barrier material than the montmorillonitic clay.

Barone et al., 1989 have studied the effect of multiple contaminant migration on diffusion and retention of domestic waste contaminants: Cl^{-}, Na^{+2}, K^{+}, Mg^{+2} and Ca^{+2}, in a natural clayey soil. It is observed that Ca^{+2} and Mg^{+2}, which were originally predominant in clay are heavily desorbed against the preferential retention of migrating Na and K. A comparison of retention and diffusion parameters obtained for Na and K, from multiple contaminant migration studies, are noted to be lower than the values obtained from the single salt model. This has been attributed to the competition for exchange sites when dissolved cations migrate simultaneously. However, the diffusion coefficient of Cl^{-} is noted to be higher than that obtained from the single salt model. It has been demonstrated that diffusion and retention phenomena is significantly influenced by the chemical composition of the source leachate, in addition to the type of the contaminant and the soil itself.

Elkhatib et al., 1991 have studied the lead retention in calcareous soils with different in texture and calcium carbonate content in three different temperature. The lead retention was found to conform to both Freundlich and Langmuir isotherms. In addition, at a given temperature Pb retention follow the order of $CaCO_3$ > clay > sandy. It was also observed that the freundlich retention coefficient Kf for Pb^{+2} increased as temperature increases.

Bundle at el., 1997 have studied the rate of strontium retention and the effects of variable aqueous concentrations of sodium and potassium on strontium distribution coefficients of surficial sediment at the Idaho National Engineering Laboratory, Idaho. Analyses of these data indicate that sodium can successfully compete with strontium for retention sites on the surficial sediment at initial solution concentrations above 300 mg/l. Thus, concentrations of sodium greater than 300 mg/l in wastewater, which have occurred historically, can increase the availability of strontium for transport beneath waste disposal ponds at the INEL relative to groundwater by decreasing strontium retention on the surficial sediment. Concentrations of sodium and potassium less than 300 and 150 mg/l, respectively, have little effect on the availability of strontium for transport. The results of this study should be used with caution when applied to radioactive strontium, which normally is present at concentrations far below the concentration of stable strontium used in this study.

Hooda and Alloway 1998 have studied the Cd^{+2} and Pb^{+2} retention behavior of selected English and Indian soils. They have studied the effects of soil pH, CEC, organic matter, clay and $CaCO_3$ on Cd^{+2} and Pb^{+2} retention. Batch technique and Freundlich isotherms were used in this study. It was observed that the English soils generally retained greater amounts of Cd and Pb compared to the Indian soils. Soil pH, organic matter, clay content, $CaCO_3$ content and CEC were all positively correlated with Freundlich metal retention whereas sand content had negative correlation. The study also showed that application of sewage sludge increased both Cd^{+2} and Pb^{+2} retention by all English soils which is due to the increases in the organic matter content and pH of the soils.

Chan et al., 1999 have investigated in their research the factors affecting resistant of hydrophobic organic contaminants like caustic effect, temperature, and competitive retention from both the reversible and irreversible compartments from natural sediments. It was found from previous work by the authors that the release of hydrophobic organic compounds is biphasic – containing a reversible and an irreversible fractions. The size of the irreversible compartment was finite for a specific chemical-sediment combination, and the release behavior associated with this compartment was independent to chemical and sediment properties. The present study indicated that while various factors and competitive release may affect the from the reversible compartment to a certain extent, these factors cannot affect the from the irreversible compartment in any significant extent. Also, the release from the irreversible compartment was driven by the hydrophobic mechanism.

Li et al., 1999 have investigated the retention behavior of atrazine (2-chloro-4-ethylamino-6-isopropylamino-striazine), a commonly used herbicide for corn, on intact soil columns by incorporating a new two-stage retention mechanism into PESTFADE, a pesticide fate and transport model. The model was tested with soil column experiments under controlled laboratory conditions, by maintaining a steady flow of water, representing 1/50 of the soil's saturated hydraulic conductivity. The findings indicated that when the intraparticle diffusion term and the retention capacity were functions of soil properties and the distribution coefficient was treated as a variable, the two-stage mechanism brought about a much improved simulation of atrazine transport in intact soil columns, as compared with the conventional retention approach. The modified model was more sensitive to certain parameters, such as soil moisture content, bulk soil density, soil tortuosity, retention capacity, and intraparticle diffusion parameters.

Dhillon and Dhillon, 1999 carried out laboratory experiments to investigate the behaviour of retention and release of Selinium in Indian soil samples varying in phsiochemical characteristics and mineralogical composition. It was observed that at the same value of surface coverage, the acidic soils have greater affinity for Se compared to the alkaline soils. Selenium retention data conformed to both Freundlich and Langmuir Isotherms. It was also found that there was significantly good correlation between organic carbon and free iron content of the soils.

Yun-Hwei Shen, 2000 have studied non-ionic surfactants retention to soil and reported the role of soil mineral composition as well as microchemical surface composition. In this study, retention is evaluated by employing scanning electron microscopy (SEM) equipped with energy dispersive X-ray analysis (EDAX). The non-ionic surfactant used in the study is Polyethylene Glyco Mono-p-nonylphenyl Ether (A_9PE_{10}), which is commonly used in detergent, agricultural and cosmetic product. They reported that it is critical to understanding the fate and transport of subsurface contaminants due to the chemical and structural heterogeneities with complex nature of soil. It was noted that the non-ionic surfactant retention capacity decreases with progressively increasing states of soil maturity.

Pacakova et al., 2000 have conducted a study to monitor the equilibrium distribution of lead, cadmium and copper between an aqueous phase modeling natural water and a solid phase modeling natural sediment, under varying conditions. The aqueous phase was analyzed using ETAAS and differential pulse anodic stripping voltammetry (DPASV), whereas XRD and FTIR were used to study the solid phase. Retention isotherms at constant pH were measured. Conditional distribution constants were calculated as functions of the pH, the time of equilibration and the amount of solid material. The results obtained stress the need for standardization of the approaches to the study of water±sediment interactions in order to be able to evaluate and compare the extensive data from field measurements and to predict these interactions.

Morrica et al., 2000 have studied the retention and release characteristics of imazosulfuron (herbicide) on four Italian soils: sandy loam no.1, sandy loam no. 2, sandy clay loam no. 3, and sandy clay no.4 by batch equilibrium method (OCED, 1981). Both the phenomena are well described by Freundlich equation. The effects of organic matter content, clay and pH on distribution coefficient, K_d between the soil and water was also investigated and it was observed that with the decreasing pH, and increasing clay and organic matter content of the soil K_d values increases.

Chang et al., 2001 in their study has attempted to validate the predictions of both linear and nonlinear equilibrium–controlled retention parameters in modeling the copper and cadmium transport in a lateritic silty –clay soil. It was seen that the linear isotherm couldn't be adequately utilized to describe the solute-fate transport at high concentration level. Additionally, it was observed that the non-linear langmuir case has a significantly steeper slope than the experimental results. However, the authors stated that the significant consistence between the theoretical and experimental breakthrough curves by Freundlich non linear retardation factors to the one-dimensional advection-dispersion transport equation with an explicit finite-difference method provided substantial accurate predictions for chemical fate and transport.

Echevarria et al., 2001 have studied the effect of pH on retention of uranium in soils. The authors have also studied the influence of soil type and chemical compositions on uranium retention ratios. From the study it was found that soil pH was linearly correlated with (log SR) showing that increased pH strongly decreased uranium retention onto soils. Whereas there was no effect of clay content or organic matter content on calculated SR.

Lim et al., 2001 have presented in their study the changes in Zn^{+2} retention and speciation in natural clay subjected to various Zn^{+2} loading levels at pH 3.0–7. The speciation data obtained from a sequential extraction technique were analyzed to elucidate Zn^{+2} retention mode in the clay. It was observed that the total Zn^{+2} loading in the soil also governed Zn^{+2} speciation in the clay. It was partly due to the presence of various retention sites with different electrochemical properties on soil minerals or soil solids. These findings imply that, in qualitative terms, in severely contaminated soils, precipitation is the dominant mechanism in metal retention when favorable soil pH exists. In moderately contaminated soils, the sorbed phase is more persistent, and therefore it is less cost-effective to extract the contaminants from the soils. In addition, solid-phase speciation data are both soil- and metal-specific. The Freundlich equation is appropriate for describing the relationship between Zn^{+2} concentrations in the dissolved phase and the amount of Zn^{+2} retention in the exchangeable, carbonate, and residual fractions.

Yong et al., 2001 have evaluated the retention capability of three types of estuarine alluvia for heavy metal (Pb^{+2}, Cu^{+2} and Zn^{+2}) by selective sequential extraction in soil column study obtained from leaching experiments. The breakthrough curves show good retention of heavy metal ions by all soils. SSE indicates qualitively that heavy metals precipitated with carbonates and amorphous materials are higher than heavy metal retention via exchangeable mechanisms.

Li and Li, 2001 have extensively investigated the heavy metal (Cd^{+2}, Cu^{+2}, Pb^{+2}) compatibility on three soils bentonite, forest soil and spruce bark and to check the potential of these soils as a barrier material. Batch retention, leaching cell testing, and selective sequential extractions (SSEs) was carried out. The materials according to retention capacity followed the trend: forest soil > bentonite = spruce bark. The mobility of Cd was 4.5 times higher than that of Pb, and Cu was 2.5 times more mobile than Pb. The leaching cell and SSE results indicate that heavy metals cause significant preferential channeling. The SSE results show that the addition of forest soil and spruce bark to clay barrier mixes promotes heavy-metal fixation.

Elzahabi and Yong, 2001 have investigated the retention characteristics of heavy metal under the influence on pH in an unsaturated illitic soil. To determine the retention coefficient, the authors conducted a series of one dimensional coupled solute and moisture leaching column test with linear retention isotherm. The concentration of heavy metals was obtained from the soil using batch shaker test and acid digestion test. The authors demonstrated that heavy metal retention characteristic is controlled by volumetric water content, soil pH, wetting time and metal concentration. The retention capacity is found to increase with an increase in pH in the presences of carbonate content in soil. It was also noted that the retention coefficient decreased with an increase in degree of saturation as the time of wetting increased.

Prasad et al., 2002 have investigated the low-grade (<15% P2O5) carbonate-substituted rock phosphate (francolite) of Jhabua, Madhya Pradesh (India), as an adsorbent for its possible application in the removal of aqueous lead and zinc from static systems. The effects of temperature on the retention of lead and zinc ions and the applicability of the Langmuir and Freundlich retention models were investigated. The study indicated that the retention of the heavy metal ions was found to follow the order $Pb^{2+} > Zn^{2+}$. Francolite was found to be most effective in removing Pb^{+2}, with a lead removal of 82-99.9% and a maximum LRC (lead removal capacity) of 0.018 (g of Pb)/(g of francolite). The retention process was found to be exothermic, and the Langmuir retention model was found to represent the retention data at different temperatures more suitably.

Berglof et al., 2002 have studied carbendazim retention–release in Vietnamese soils. The retention –release of four Vietnamese soils (AG, CT, ST, and TG) were studied with different pH and organic matter. Batch technique was used for this study. From the study it was found that the retention coefficient Kf and Kd both increased in the order of ST< TG< AG< CT. It was observed that retention of all soil increased with increasing organic carbon (OC) and clay content. The influence of pH on carbendazim retention was studied in the ST and CT soils. The retention of carbendazim by the sandy ST soil increased as the pH decreased, while retention of carbendazim by the CT soil decreased as pH decreased.

Li et al., 2003 have studied the retention and release of pesticides (4, 6-dinitro-o-cresol and dichlobenil) on clay minerals and humic acid complexes by using batch equilibrations and x ray diffraction method (XRD). The authors found that retention and release capacity of 4, 6-dinitro-o-cresol is more than the dichlobenil for both the soils. The authors also observed that for both pesticides, lower charge density clay exhibit greater retention capacity than the higher charge-density clay. It was also observed that clay minerals fractions play an important role in the retention of pesticides.

Choudhury and Kanif, 2003 have carried out a study on the magnesium retention behaviour on three Malaysian Rice soils. Three isotherms freundlich, langmuir and tempkin isotherms were fitted to magnesium adsorbed data. A significant correlation was found between Mg retention and soil pH while there was no correlation between Mg retention and either organic matter or cation exchange capacity. These results indicated that magnesium retention is mainly dependent on soil pH.

Li et al., 2003 have demonstrated the retention and release of pesticides (4,6-dinitro-o-cresol and dichlobenil) on clay minerals such as smectite and humic acid-clay complexes by using batch method and x ray diffraction method. It was found that in both soils, the retention and release was more for 4, 6-dinitro-o-cresol than dichlobenil. The authors observed for both pesticides, lower cation exchange capacity exhibited more retention capacity than higher cation exchange capacity. It was noted that clay fraction was great influenced rather than organic carbon content in the retention of pesticides.

Tanshuling et al., 2003 studied the retention of Zn^{+2} on two clays of different mineralogy namely bentonite and illite by using batch and column test. It was found that batch equilibrium tests overestimates the attenuation capacity of the soil compared to the column test and bentonite shows a higher retention capacity compared to illite.

Kava, 2004 has characterized the retention behavior of acidic phenol and pyridine on two type of clayey soils, bentonite and kaolinite with the help of flow microcalorimetry. It was noted that both clays exhibited different behavior under different pH levels. The author observed phenol retention was more than pyridine retention in bentonite as compared with kaolinite soil. The heat of wetting of bentonite/ kaolinite was found to be more in phenol than in pyridine.

Du et al., 2004 presents an investigation of some factors controlling the retention of potassium (K^+) onto two soils, named Ariake clay and Akaboku soil. The KCl solution and multi-salt solution containing KCl, NaCl and $CaCl_2$ were selected as the synthetic leachates. The results show that with the increase of the solid/solution ratio, the adsorbed amount of K^+ decreased for both soils. This dependence of retention behavior on the solid/solution ratio was found more significant for the Ariake clay. Both soils arrived an equilibrium condition in short time less than the contact time prescribed by the ASTM and US EPA standard batch-type tests. It was observed that both soils adsorbed larger amount of K^+ in the case of KCl solution condition than in the case of multi-salt condition.

Yu et al., 2004 have studied the retention of phenol and chlorophenols on hexadecyltrimethylammonium- and tetramethylammonium-montmorillonite from aqueous solutions. Batch experiments were carried out at 25°C to obtain the retention isotherms of phenol, 2-cholorophenol, 4-chlorophenol and 2, 4-dichlorophenol on HDTMA-M and TMA-M prepared from Wyoming bentonite SWy-2. The isotherms were interpreted principally using the Freundlich model. The reaction orders (n) and Freundlich constants (kF) for the retention of an adsorbate on HDTMA-M and TMA-M remain approximately constant against the variation of adsorbate to adsorbent ratios. The n value for most of the phenolic adsorbates on HDTMA-M is close to unity, indicating Langmuir-type retention but that on TMA-M is variable among different phenolic adsorbates. The degree of retention of phenolic compounds on HDTMA-M is primarily controlled by the hydrophobicity of the adsorbates but those on TMA governed by the complicated combinations of size, shape and hydrophobicities of the adsorbates.

Schultz and Groundl, 2004 have studied the effect of pH on retention behavior of ferrous ion onto two smectite clays viz. SWa-1 and Wyoming montmorillonite. The authors observed that ferrous retention (Fe^+_{aq} = 0.1 mM) to both minerals over pH range 4.0 – 6.75 is relatively constant at 1000l/kg for both minerals. At pH values above 6.75 the amount of ferrous ion sorbed increases dramatically .At pH 8.0, retention reaches 6600 l/kg for SWa-1 and 8000 l/kg for Wyoming montmorillonite.

Villegas et al., 2004 have studied the effect of pH, mineralogy, iron oxides on lead retention onto eutric soil from Francisco I. Madero, Mexico. In this study, batch equilibration experiments were used and analysis was done by Langmuir and Freundlich isotherms. It was observed that as pH is increased retention capacity also increases. Again, presence of minerals such as kaolinite, hallosite, and metahallosite increases the retention of lead due to having permanent charge sites. Iron oxide also has high capacity to absorb lead.

Novoszad et al., 2005 have investigated the retention behavior of pesticide naphthalene (naphthalene, 1-hydroxy-2-naphthoic acid, 1-naphthol, 1, 4-naphthoquinone, 1-naphthylamine) into soil and treated soil (peat, sewage sludge, animal manure, green manure, grassland etc) from a long-term field experiment. It was found that the batch test and linear isotherm was fit for this study. The author demonstrated the pH, soil organic content, pore size, aggregate stability were significantly altered influencing on retention. In this study the retention isotherm on different treatment soils follow an order1-naphthylamine naphthalene1-hydroxy-2-naphthoic acid1-naphthol, 1, 4-naphthoquinone. The soil amended with peat adsorbed more naphthalene than other treatment soil. The author observed that the retention coefficient increase with an increase of soil organic carbon and decrease of pH.

Giesler et al., 2005 have investigated the effect of pH, biocide, dissolved organic content (DOC) and dissolved organic phosphate (DOP) on phosphate retention in Flakastugan (humus soil + less Fe + more Al) and Betsele (humus soil + more Fe + less Al) soils by batch test. It was found that the higher phosphate retention is obtained for the Flakastugan soil as compared with the Betsele soil. The authors observed phosphate retention was pH independent when 0.1 mol dm^{-3} NaCl was used and there was a slight increase of phosphate retention with the addition of biocide (NaN_3). It was noted that DOC gave positive phosphate retention and DOP did not influence phosphate retention.

Yazgan et al., 2005 have investigated the retention of pesticides (imidacloprid, carbofuran) by using batch equilibrium test and centrifugation methods. Freundlich isotherm was used to define pesticide retention. The retention was found to increase with soil organic content (SOC) and the results of batch method was noted to be the higher than that of the centrifugation method. The authors reported that the retention results are influenced by different soil properties such as clay content, organic carbon and cation exchange capacity.

Sheng et al., 2005 have demonstrated the retention characteristic of pesticides (diuron, bromoxynil, ametryne) on soils, wheat char and char-amended soils under different pH conditions. The authors observed that the retention of diuron increased with decreasing pH in soil and wheat-char and an opposite trend in the case of char-amended soil. The bromoxynil and ametryne retention increased with decreasing pH in all three soils. It was noted that soil organic matter was a predominant factor for all retention and retention significant at pH 7.

Ochsner et al., 2006 have demonstrated effect of soil water content on hydraulic pesticide retention (dicamba) to three different soils such as loamy sand, silt loam, silty clay loam. Quantification of retention at low water content was done by considering the unsaturated transient flow method and for higher water content, conventional column method was found to be suitable. The authors observed that the pesticide retention coefficient were nearly same for all three soils at low water content (0.05 kg/kg). At higher water content (0.19-0.24 kg/kg), retention property remained unchanged for loamy sand, but doubled for silt loam and six fold for silty clay loam. The authors call for further investigations to understand the above mentioned observations. The sensitivity of pesticide retention was found to be more for soil with more organic content.

Bhattacharya and Sengupta, 2006 have studied the retention of iron metal (Fe-III) from water in clay soils such as kaolinite (K_1), acid activated kaolinite (K_2), montomorilonite (M_1) and acid activated montomorilonite (M_2). In this study both Langmuir and Freundlich isotherm were used to compute retention isotherms. The authors observed Fe(III) retention gradually increase in the pH range of 1.0 to 4.0 and difficult to determine at pH > 4. The Fe(III) adsorbate in clays increased in the order of $M_2 > M_1 > K_2 > K_1$ adsorbents. It is opined that the kinetics of clay- Fe(III) interactions is very complex and much close to the second order rate kinetics.

Gad and Zaghloul, 2006 have studied the retention and release behaviors of cobalt in three cultivated alluvial soils varing in their clay contents and other soil properties using Electrical Stirred Flow Unit (ESFU). The results indicated retention was influenced by soil characteristics especially pH and clay content in these soils. In addition, movement of Co towards slower retention reactions with increasing period of soil incubation was observed. The kinetic parameters were increased by increasing rate of Co applied and decreased with increasing incubation period. In Co treated soils, kinetic parameters were mainly influenced by soil clay content since k parameter of 1st order kinetic equation were decreased in the order of increasing clay contents of the studied soils after 6 hrs of ESFU working. Apparently, the higher specific surface and the slightly higher pH of the alluvial soil contributed in capacity and rate of Co-.

Shirvani et al., 2006 have studied the retention/release of cadmium (Cd) in aqueous silicate clay minerals (palygorskite, sepiolite). The authors employed batch test and Freundlich isotherm to obtain retention/release of Cd^{+2}. The authors observed distribution coefficient of Cd^{+2} decrease with an increase in Cd^{+2} concentration. The authors suggested further study to determine the causes of Cd retention/release hysteresis in these minerals using chemical, microscopic, and spectroscopic techniques .

Cheng et al., 2006 have investigated the retention behavior of p-chlorophenol on the Reed Wetland soils and the effects of various factors such as pH, ionic strength and soil organic matter on retention behavior. In this study batch equilibration experiments were used and analysis was done by Langmuir and Freundlich isotherms. From the study, it was found that retention capacity increased with lower pH, higher ionic strength and soil OC.

Karahan et al., 2006 have studied the removal of boron from aqueous solution by clays and modified clays (modified by nonylammonium). For this study, the authors have investigated the retention capacities of bentonite, sepiolite, and illilte and the modified clay. The retention characteristics were well fitted by Freundlich, and Dubinin-Radushkevich isotherms. For this study, effect of pH and ionic strength were determined. It was observed that retention increased as the pH of solution increased and after reaching the maximum value it decreased with increasing pH of solution for both clays and modified clays. Retention capacities of the clay samples for boron species increase with the increase in ionic strength. Retention capacity of boron onto clays and modified clays increased in the order of sepiolite, NI, illite, NS, bentonite, and NB.

Nakamaru et al., 2006 have studied the antimony mobility in Japanese soils and the factors affecting antimony retention behavior. The mobility of Sb^{+2} was investigated by radiotracer experiment and batch test was used to find out distribution coefficient. It was observed that K_d values were affected by pH and phosphate concentration. K_d decreased with both increasing pH and phosphate concentration. No effect was observed for nitrate concentration.

Ochsner et al., 2006 have determine the effect of soil water content on retention of a hydrophilic pesticide (dicamba) to three different soils such as loamy sand, silt loam, silty clay loam. For studying retention the authors have found suitable to use unsaturated transient flow method at low water contents and vertical column outflow method at high water contents. From the studies it was found that at low water contents (0.05 kg/kg) retention coefficients were similar for all three soils. At higher water content (0.19-0.24 kg/kg) the retention coefficient remained unchanged for loamy sand, doubled for silt loam and for silty clay loam it was almost six fold. The sensitivity of retention of pesticides to water content increases in the soils with higher organic C content.

Pivato and Raga, 2006 investigated the influence of bentonite on the attenuation of ammonium in leachate passing through a landfill liner by conducting the standardized batch test with pulverized bentonite and a batch test with compacted bentonite. The latter was proposed in order to better simulate the real conditions in a landfill liner. It was demonstrated from the findings that the partition coefficient K_d was higher than the average measured for other natural materials usually utilized as components of landfill liners. They also validated the suitability of the standard batch test with pulverized bentonite as it gave similar results with compacted bentonite. The authors also recommended the use of bentonite in landfill liners as it resulted in the increase of the attenuation of ammonium during leachate passage through the landfill containment systems.

Cai et al., 2007 have investigated the influence of contact period on attrazine retention behavior on Fluvo-aquic soil. Batch experiment was performed in this investigation. .From the investigation it was observed that amount of attrazine sorbed to Fluvo–aquic soi decreased with the increase in contact time.

Kahle and Stamm, 2007 have demonstrated the influence of contact time and pH on sulfonamide (sulphatiazole) retention into two clay minerals (illite, montmorillonite) and iron oxide (ferrihydrate). In this study retention isotherm were found by using batch experiment and linear isotherm model. The authors observed sulphatiazole retention increase with increase of contact time and decrease of pH in both clay soils and retention fluctuating in case of ferrihydrate at the same time and pH conditions.

Koleli et al., 2007 have observed the retention behavior of a pesticide, methamidophos, in a heterogeneous alluvial soil profile by batch method. The objective of this study was to identify the effect of soil components and pH on retention of mehamidophos by different soil layers. It was reported that methamidophos retention increases with increase in solution pH due to the presence of amino group. At low methamidophos concentrations the sub soil minerals exhibited greater retention as compared to the top soil organic matter. This is contradictory to the fact that soil organic may be attributed to the presence of methamidophos.

Golberg et al., 2007 have highlighted the importance of equilibrium geochemical models such as surface complexation model which is an extension of the thermodynamic modeling approach to include the reactions between dissolved species and the functional groups present on mineral surfaces. These models in compared to the conventional empirical adsorbtion approaches have the capability of taking into consideration the effect of variable chemical conditions and to predict the uncertainty in transport parameters resulting from spatial heterogeneity in the physical and chemical characteristics of the system of interest. The researchers also pointed out that though solute transport modelers have lacked the necessary expertise to apply the SCM approach as they were too complex to be applied, it has been demonstrated that the simpler GC modeling approach can be applied to simulations of contaminant transport at the field scale. This linkage also provides a framework for conducting uncertainty analyses based on process level parameters rather than on ranges of *K*d values resulting from lumping together multiple processes which in future will lead us to a better understanding of the SCM modeling approaches.

Wong et al., 2007 had investigated the effects of dissolved organic matter (DOM) from anaerobically digested dewatered sludge on Cd^{+2} and Zn^{+2} retention by three different soil types: calcareous clay loam, calcareous sandy loam and acidic sandy loam. Batch test is performed for these studies. In this study Cd^{+2} and Zn^{+2} retention isotherms in the three soils in the presence or absence of Sludge DOM is well described with Freundlich equation. It was found that the retention capacities and binding affinity of the three soils for Cd^{+2} and Zn^{+2} followed the order: calcareous clay loam > calcareous sandy loam > acidic lateritic sandy loam at the same equilibrium concentration of Cd^{+2} and Zn^{+2}. The Cd and Zn retention decreased with the increase in DOM concentration. At a given DOM concentration, metal retention increases in the following order: Acidic sandy loam<calcareous sandy loam<calcareous clay loam. Moreover Zn^{+2} retention was reduced more significantly than Cd^{+2} retention at the same DOM concentration increment.

Cao et al., 2008 have investigated the retention/release behavior of herbicide prometryne on yellow-brown and bleached-paddy soils under the influence of pH, soil organic matter and non-ionic surfactant (Triton X-100). For the determination of retention/release behavior of prometryne, the standard batch equilibrium method (OCED-2000) and Freundlich-isotherm was found suitable. It was observed that prometryne retention increased with decreasing pH and decreases with surfactant concentration.

Haijun et al., 2008 have demonstrated the influence factors which are effect on Cr(VI) retention by natural clay and amended with granular activated carbon (GAC), bentonite activated carbon(BA) soil. The result employed by using batch test and Langmuir isotherm model. It was observed that the retention isotherm increase with an increase of contact time, temperature and pH with the order of (C+GAC) > (C+BA) > C and opposite to the soil-solid concentration. It was noted that CR (VI) transport required more time for C+GAC and less for C.

Jiang et al., 2008 have studied chromate retention by three variable charge soils. From the study it was found that the retention and release of chromate followed the order: the Hyper-Rhodic Ferralsol > the Rhodic Ferralsol > the Haplic Acrisol. It was also found that the retention and release of both increased with elevation of the equilibrium chromate concentration and decreased with increasing of the soil solution pH. From the study, it was seen that both the specific retention and the electrostatic retention were mainly responsible for the chromate retention by three soils and iron oxides were the dominant adsorbents for chromate.

Li et al., 2008 have studied the retention and release behavior of bisphenol A (BPA) in sols which influences with ionic strength (Ca^{+2}, NH_4^+), heavy metals (Cd^{+2}, Pb^{+2}) and surfactants (cetyltrimethylammonium bromide (CTAB)), cetylpyridine chloride (CPC) . The authors reported soil column test and Freundlich isotherm is quite useful for determining retention /release of BPa in soil. It is noted from this study that an increase in ionic-strength, heavy metal and cationic surfactants increase the retention of BPA soil.

Nakamaru and Uchida, 2008 have investigated distribution coefficient of tin in Japanese agricultural soils and the factors effecting tin retention behavior. The authors observed tin solubility is highly pH dependent and tin-retention coefficient increased with decreasing pH concentration. In the soils, Sn mobility was very low with high K_d values. The results indicated that the major part of the sorbed Sn should be in organic matter or Al/Fe-hydroxide-bound form. The authors recommend further study to understand the Sn retention phenomena in soil.

Sun et al., 2008 have investigated the tetrabromobisphenol A (TBBPA) retention behavior by batch nethod in soils. It was found that non –linear and Freundlich isotherms are suitable for the study. The authors reported the retention capacity of TBBPA increase with increasing ionic strength and decrease with increasing pH. The role of soil organic matter on TBBPA retention has been indicated in this study.

Covelo et al., 2007 have investigated the competitive retention and release of heavy metals (Cd^{+2}, Cr^{+2}, Cu^{+2}, Ni^{+2}, Pb^{+2} and Zn^{+2}) in serpentinitic soils (three ferralic Cambisols and three mollic Leptosols). In this study the results were obtained by using batch experiment and correlated with Langmuir and Freundlich isotherm. It was found the retention and release was more for Cu^{+2} and Pb^{+2} rather than Cd^{+2}, Ni^{+2} and Zn^{+2}. Zinc and cadmium exhibited an increased affinity with the highest organic matter contents and pH. The Ferralic Cambisols possess a higher retention and retention capacity for the metals than the Mollic Leptosols.

Giannakopoulou et al., 2007 have investigated the radioactive cesium (Cs) retention behavior in soils such as sandyloam, loam, clayloam and clay under different pH condition using test. It was observed that at all pH levels the Cs retention followed the sequence sandyloam < loam < clayloam < clay. Clay fraction was found to play a dominant role on Cs retention. It was further noted that Cs retention is low at pH < 7, maximum at pH 8 and then lowering up to pH 10.

Gao et al., 2007 have studied the retention of non-ionised herbicide chlorotoluron (CT) found in ammonium sulfate (AS) and urea (UR) and herbicide atrazine (AT) multi-solutes system in soil by batch experiments. In this study, retention characteristics have been established by using Freundlich isotherm. The authors observed CT retention decreased with increasing of AT concentration. At the same concentration of AT, CT retention increased in AS treatment and decreased in UR treatment.

Koleli et al., 2007 have observed the retention behavior of a pesticide, methamidophos, in a heterogeneous alluvial soil profile by batch method. The objective of this study was to identify the effect of soil components and pH on retention of methamidophos by different soil layers. It was reported that methamidophos retention increases with increase in solution pH due to the presence of amino group. At low methamidophos concentrations the sub soil minerals exhibited greater retention as compared to the top soil organic matter. This is contradictory to the fact that soil organic matter significantly increases the retention capacity of soils. Such a contradiction may be attributed to the presence of methamidophos..

Jia et al., 2007 have studied the retention capacity of soil and zerovalent iron minerals to control the groundwater contamination at Oslo International airport site due to benzotriazole (BTA) and methylbenzotriazole (MeBTA). These chemicals are used as deicing agents during winter season. Batch tests and Freundlich isotherm were used to establish retention of soil and iron minerals. It was noted that zero valent iron exhibited more retention than soil which was due to multi-layer coverage. The study reported that triazoles are highly mobile in the subsurface environment, and zerovalent iron can be an effective medium for groundwater remediation.

Covelo et al., 2007 have investigated the competitive retention and release of heavy metals such as Cd^{+2}, Cr^{+3}, Cu^{+2}, Ni^{+2}, Pb^{+2} and Zn^{+2} by humified organic matter (HOM), Fe and Mn oxides, kaolinite, vermiculite and mica. Batch experiments, Freundlich and Langmuir isotherms were used to study the retention characteristics. The authors have used k_{d100} values for the purpose of comparison, where k_{d100} is the distribution coefficient calculated in retention-release experiments in which the initial retention solution contained 100 mg/l of each metal. It was observed that kaolinite and mica preferentially sorbed and retained chromium; vermiculite retained copper and zinc; HOM and metal oxides retained lead in addition to copper. It was observed that kaolinite did not retain copper. Among all the sorbents, vermiculite and Mn oxide showed maximum retention of heavy metal cations.

Pu et al., 2007 have studied the retention-release behavior of pesticide, pentachlorophenol (PCP), on soil organic matter (SOM) and clay minerals (CM) in order to gain a better understanding of the fate of PCP in soil. The study was conducted with different type of soils such as silty loam, sandy-clay-loam, clayey soils, etc. It was specifically noted that expanding clay minerals are a good sorbent. The silty loam has greater PCP retention than sandy-clay-loam and more PCP sorbed on the bentonite surface than kaolinite. The study further calls for further investigation to understand better the interaction between SOM and clay minerals and their influence on retention.

Lair et al., 2007 have studied the retention of heavy metals (Cu, Zn, Cd) on organic and inorganic bulk soils. It this study the retention data was obtained by using batch OECD guideline 106 (2001) method and Freundlich isotherm. The retention behavior was significantly influenced by pH and soil organic matter (SOM). The retention of heavy metals followed the order of $Cu^{+2} > Zn^{+2} > Cd^{+2}$ with increasing SOM in soils. In this study retention characteristics obtained without additives was more influenced by SOM than soil mineral (SM). The authors suggested physical complexity and heterogeneity of soils complicated the retention behavior.

Pan et al., 2007 have studied the effect of physical forms of soil organic matter on phenanthrene (PHE) retention. It was noted that the retention capacity is more for Dissolved humic acids (DHA) than solid humic acids (SHA). Further, a nonlinear retention behavior was observed for organo-mineral content and a linear retention behavior for organic carbon content,

Lair et al., 2007 have studied the effect of soil organic content and clay mineral on heavy metals (Cu^{+2}, Cd^{+2}, Zn^{+2}) retention on treated soils such as animal manure, green manure, no nitrogen addition, fallow, grassland, from a long term field experiment. It was noted that organic content is more effective sorbent than clay content for metal retention and the retention increased in the order, $Cu^{+2} > Zn^{+2} > Cd^{+2}$. The study shows more retention for grassland and less for soil treated fallow. The author investigated physical structure of soil organic matter and interaction with the soil mineral phase is found to influence the retention capacity of soils.

Chaturvedi et al., 2007 have investigated the retention and leachability of heavy metals (Pb^{+2}, Cu^{+2}, Zn^{+2}, Mn^{+2}) at different pH into zinc mine tailing soil (ZMTS) amended with two soils such as phosphatic clay (PC) and humus rich soil (HS). In this study to determine leachability by using batch as well as column test and to evaluate the amendment feasibility by batch retention experiment. It was noted that Langmuir isotherm was fit to characteristic the retention isotherm.

Kahle and Stamm, 2007 have demonstrated the influence of contact time and pH on sulfonamide (sulfathiazole) retention into two clay minerals (illite, montmorillonite) and an iron oxide (ferrihydrite).In this study retention isotherm found by using batch experiment and linear isotherm model. The authors observed sulfathiazole retention increase with an increase of contact time and decrease of pH in both clay soils and retention fluctuating in case of ferrihydrite at the same time and pH conditions.

Covelo et al., 2007 have studied the competitive retention and release of heavy metals (Cd^{+2}, Cr^{+2}, Cu^{+2}, Ni^{+2}, Zn^{+2} and Pb^{+2}) in acidic soils by using batch method. The influence of soil organic matter, clay mineral and cation exchange capacity are appraised in this study. The retention capacity of all heavy metals depends on the presence of clay minerals.

Appel et al., 2008 have studied the sequential retention of lead (Pb^{+2}) and cadmium (Cd) on different osoil surfaces and the nature of reaction between heavy metals and soils. It was noted that if Pb^{+2} is introduced before Cd^{+2}, there is a decrease in Cd^{+2} retention onto both exchange and high affinity retention sites but not vice-versa. Pb^{+2} was replaced by Cd^{+2} and even less Cd^{+2} was replaced by Pb^{+2} in all soils. Cd^{+2} was more exchangeable when Pb and Cd^{+2} were added to the soils concurrently. The observations may be attributed to the mobility of Cd^{+2} as compared to Pb^{+2}.

Asci et al., 2008 have demonstrated the comparative study for the retention of Cd(II) by different clay soils and the recovery of Cd^{+2} with rhamnolipid biosurfactant by using the batch equilibrium experiments. It was noted that the Cd^{+2} retention isotherm were performed using the Langmuir, Freundlich, Redlich–Peterson,Koble–Corrigan retention models and the Freundlich model showed the best fit. The authors investigated the Cd(II) retention characteristics varied with metal concentration, soil pH and clay mineralogy and the Cd^{+2} recovery affected by pH, amount of Cd^{+2} loaded to the soils, and rhamnolipid concentration. Cd^{+2} recovery efficiencies from the soils using rhamnolipid biosurfactant decreased in the order of soil A > soil B > soil C. This order was the reverse of the Cd^{+2} retention efficiency order on the soils. When 80mM rhamnolipid was used, the recovery efficiencies of Cd^{+2} from the soils A, B, and C was found to be 52.9%, 47.7%, 45.5% of the sorbed Cd^{+2}, respectively. Rhamnolipid retention capacity of the soils in the presence of Cd(II) ions decreased in the order of soil A > soil B > soil C.

Haijun et al., 2008 have demonstrated the influence factors which are effect on Cr(VI) retention by natural clay (C) and amended with granular activated carbon (GAC), bentonite activated (BA) soil. The result employed by using batch test and Langmuir isotherm model. The author observed the retention isotherm increase with an increase of contact time, temperature and pH with an order of C+GAC > C+BA > C and opposite to the soil-solid concentration. It was noted that Cr(VI) transport required more time for C+GAC and less for C.

Liu et al., 2008 have studied the influence of the ratio of clay content to total organic carbon of the herbicide butachlor retention behavior on different soils (silty clay loam, silt loam, clay, loam, silty clay, sandy loam sandy clay loam etc). It was found that the batch equilibrium experiment and Freundlich isotherm was fit to gave better response. The author investigated the retention isotherm influenced with solution concentration, organic content and ratio. It was noted that the herbicide retention increase with solution concentration. The author observed the higher retention capability of herbicide due to the organic content, when ratio less than 60 than the ratio greater than 60 which was highly influenced by clay content.

Jacobsen et al., 2008 have demonstrated the competitive retention and mineralization of pesticides (MCPA, metribuzine, methyltriazine amine, glyphosate) through the vadose zone in different soil horizons (A, B, C) with variation of clay, sand, and silt content. In this study necessary data was obtained by using batch test, MACRO modeling and partial least squares regression process. It was noted that results was influenced by pH and soil organic content. The retention of pesticide increased in the order A > B > C. The influence of organic content is more on MCPA and metribuzine retention as compared to methyltriazine amine and glyphosate retention. The MCPA retention was found to decrease with an increase in pH.

Liu et al., 2008 have studied the retention behavior of aromatic compound (polar and nonpolar) into different clay soils. The authors employed the results by using batch experiment and Freundlich isotherm model. It was noted that all aromatic retention isotherm increases with an increase of sorbed concentration in all soils. The author observed the polar solutes sorbed more than the nonpolar solutes. It was found that the phenanthrene retention isotherm increase with the soils such as bulk, black carbon, humic substances soil. The author monitored the aromatic retention isotherm mechanisms control by soil organic carbon, black carbon content, mineralogy, morphology, soil structure, size fraction and solute molecular structure and it is reported that the solute molecular structure has great influence on retention isotherm. The author suggested further study needed to obtain the role of black carbon content in the polar retention

Ahangar et al., 2008 have investigated the effect of soil organic content-clay mineral interaction and organic matter chemistry on non-ionic herbicides (diuron and phenanthrene) retention before (whole soil) and after hydrofluoric acid treatment (HFT) of soil samples. The study indicates that the phenanthrene retention coefficient was more for HFT soil than whole soils (without treated soil) as compare with diuron retention. In the case phenanthrene retention, the organic matter chemistry has more influence on treated soil and not for whole soils, where as diuron retention got influenced for treated and untreated case. It is also reported in the study that the ratio of phenanthrene retention after HFT to before HFT increase with an increase of clay content.

Nakamaru and Uchida, 2008 have investigated distribution coefficients of tin (Sn) in Japanese agricultural soils and the factors affecting tin retention behavior. The authors observed tin solubility is highly pH dependent and tin-retention coefficient increased with decreasing p^H concentration. In the soils, Sn mobility was very low with high Kd values. The results indicated that the major part of the soil-sorbed Sn should be in organic matter or Al/Fe-hydroxide-bound form. The authors recommend further study to understand the Sn retention phenomena in soil.

Drori et al., 2008 have studied the influence of soil organic content on retention/release of herbicides (phenanthrene, atrazine, chlorotoluron) in two different type of soils (sandy-loam, clay soil) irrigated with freshwater and treated wastewater. Batch method and Freundlich isotherm was used to establish retention characteristics. The retention of herbicides on both the soils was in the order phenanthrene > chlorotoluron > atrazine. The retention was found to increase with SOC in the freshwater than wastewater in case of both soils. The results indicates that clay soils act as a higher sorbent as compared to sandy loam soils.

Ishikawa et al., 2008 have observed the retention behavior of radioactive selenium (Se) on humic acid (HA) under different Se-concentration and solid/liquid ratio. The Freundlich-isotherm was found to give better representation of retention behavior. It was observed from the study that Se retention increased with decreasing solid/liquid ratio. It was further noted that the results are influenced by pH, ionic strength and the physical form of HA.

Yang et al., 2008 have investigated retention of polycyclic aromatic hydrocarbons (PAHs) to carbonaceous materials such as coal, black carbon, char etc in a river floodplain soil. The results showed retention capacity is more for light-fraction sample compare to low rank coals. The retention of Phenanthrene increased due to the presence of carbonaceous materials in all samples. Both the Freundlich-retention model and a combined-partitioning retention model fit for retention data.

Li et al., 2008 have demonstrated the phosphorus (P) changes and P retention characteristic in a calcareous soil under long-term fertilization. The author suggested Langmuir isotherm fit for studying P retention characteristics. It was noted that P retention capacity decrease with decreasing soil pH. The authors implied P retention capacity in the soils increased with inorganic form of P addition and reduced with organic form of P. The author observed long-term fertilization increased with P-organic substances.

Sun et al., 2008 have investigated the tetrabromobisphenol A (TBBPA) retention behavior by batch method in soils. It was found non-linear and Freundlich isotherms are suitable for this study. The authors reported the retention capacity of TBBPA increase with increasing ionic strength and decrease with increasing pH. The role of soil organic matter on TBBPA retention has been indicated in this study.

Sipos et al., 2008 have studied the effect of presence of iron oxide and carbonate on retention of heavy metals (Cu^{+2}, Zn^{+2}, Pb^{+2}) to soil mineral phases. It was found that the sequential extraction test could be successfully completed by the analytical electron microscopy analyses for studying retention. The authors observed that the retention increased in the order of Cu > Pb > Zn in all soils. It was observed that swelling clay have found highest metals sorbed on to it. However, similar results were obtained for Pb retention on iron oxide phases and Cu was sorbed mostly under alkaline condition.

Parekh et al., 2008 have investigated the effect of soil microorganisms (bacteria and fungi), biotic and abiotic microcosms, and temperature, saprotrophic fungi (O. mucida (OM) and T. arantium (TA) on retention and retention capacity of radionuclides (Cs and Sr) within organic soil systems. It was noted that soil microorganisms play an important role in the radionuclide retention and retention process. The retention and retention of Cs was found to be more than Sr. In all experiments, the biotic systems exhibited greater the retention of both radionuclides as compared to abiotic systems. In this study, the retention capacity in biotic systems increased between 10 and 30^0C and lower retention at temperatures above or below the optimum range.

Li et al., 2008 have studied the retention and release behavior of bisphenol A (BPA) in soils which influences with ionic strength (Ca^{+2}, NH_4^+), heavy metals (Cd, Pb) and surfactants (cetyltrimethylammonium bromide (CTAB), cetylpyridine chloride (CPC)). The authors reported soil column test and Freundlich isotherm is quite useful for determining retention/release of BPA in soil. It is noted from this study that an increase in ionic-strength, heavy metal and cationic surfactants increase the retention of BPA in soil.

Covelo et al., 2008 have demonstrated the retention/release behavior of heavy metals (Cd^{+2}, Cr^{+2}, Cu^{+2}, Ni^{+2}, Pb^{+2} and Zn^{+2}) and role of soil organic matter (SOM) in the retention behavior of soil. Two methods such as Fibric Histosol H horizon and organo-mineral fraction (OMF) methods were used to establish the influence SOM on retention/release behavior of heavy metals. It was noted that the Langmuir isotherm is ineffective for Fibric Histosol H horizon method and very much effective for OMF. Pb retention/release increased linearly and others are fluctuating with initial concentration of metals in Fibric Histosol H horizon method the. In the OMF the retention and retention of copper and lead increased almost linearly with their initial concentration in the retention solution.

Hanna et al., 2008 have examined in their investigation whether the use of the surface complexation model (SCM) could correctly describe the migration of zinc and lead in roadside soil under various physicochemical conditions. The and transport of Zn and Pb was studied by means of batch reactors and saturated chromatography columns. Soil batch experiments were conducted to evaluate the effects of pH variation and ionic strength on the metal mobility from soil. It was found that the SCM was able to simulate the mobility of metals from soil by assuming one mononuclear surface reaction between one solution species (Me^{2+}) and one type of site on the surface of soil dominant sorbents.

Cao et al., 2008 have investigated the retention/release behavior of herbicide prometryne on yellow-brown and bleached-paddy soils under the influence of p^H, soil organic matter and non-ionic surfactant (Triton X-100). For the determination of retention/release behavior of prometryne, the standard batch equilibration method (OECD-2000) and Freundlich-isotherm was found suitable. The authors observed the prometryne retention increased with pH and decreases with surfactant concentration.

Ortega et al., 2008 have demonstrated the effectiveness of soil washing, nanofiltration and electrochemical treatment for the recovery of metal ions from a contaminated soil. The leachate reagents used in this study was HCl and H_2SO_4-NaCl mixture with pH value of 2. They observed that both reagents are very effective for soil washing but in some cases acid-base mixture resulted in a very fast removal of pollutants from contaminated soil. For both leachates, nanofiltration membranes and electrochemical treatment methods also exhibited high ions retention rate. However, the authors concluded that to get more information further electro-coagulation process is needed.

Shafiq et al., 2008 evaluated the boron retention in five different textured calcareous soils of Punjab. The retention data were fitted to Freundlich and Langmuir retention models. It was found that Freundlich model showed better fit of retention data than Langmuir model. These encouraging results suggested that for a particular soil, B retention isotherm needs to be constructed for site-specific B fertilizer application. High clay contents ranging from 70 to 320 g per kg and more $CaCO_3$ (35 to 128 g/kg) increased the amount of adsorbed boron in these soils. On an average, maximum retention was observed in Bhalwal soil (108.4 mg/kg) followed by Sultanpur (83.50 mg/kg), Shahpur (63.40 mg), Pindorian (52 mg) and Shahdara soils (47 mg/kg).

Natale et al., 2008 have performed experimental and modeling analysis of As (V) ions retention on granular activated carbon by batch method to understand the effects of arsenic concentration, pH, temperature and salinity on equilibrium retention capacity. It has been shown that at high temperature, neutral pH condition and low salinity levels the retention capacity is more. They also reported that the arsenic retention capacity on granular activated carbon decreases with an increase in NaCl concentration in aqueous solution and with decreasing competitive ions (OH^- and Cl^-). Authors observed the retention and retention capacity of heavy metals increased in the order Pb > Cu > Cr > Cd > Ni > Zn. The retention of Pb and Cu are affected by soil organic content.

Ramakrishna and Philip, 2008 have studied the retention and release characteristics of pesticides lindane, carbofuran and methyl parathion on various Indian soils collected from agricultural fields of Tamilnadu, India. The work was carried out on these soils having various concentration of organic matter, clay minerals and humic substances. The assessment of retention capacity by batch kinetic and equilibrium experiments showed that Lindane exhibited maximum rate of retention followed by methyl parathion and carbofuran. It was found that retention rate constants were highest for compost soils whereas it was the least for sandy soils. It was also reported that organic matter and clay content played a significant role in pesticide adorption. Further, they also stated that nature of organic matter influenced the pesticide retention.

Lu et al., 2009 have demonstrated in their study the effect of soil solids concentration and temperature in batch tests on the retention of Cr (VI) onto landfill liner-soil materials. It was found that the soils specimen retention to Cr (VI) is characterized by a Langmuir isotherm model. The values of the isotherm parameters (qm, b) and soil solids concentrations have a log-log linear relationship at low soil solids concentrations. The values of measured isotherm parameters decreased strongly as soil solids concentration increased, and finally stabilized when the soil solids concentrations were over the critical values. The values of measured isotherm parameters (qm, b) increased linearly with increasing temperature. It was concluded that the values for isotherm parameters measured using batch tests under low soil solids concentration will not properly simulate the field situation, and retardation factors of clay landfill liners systems will be overestimated.

Zu et al., 2009 have evaluated the distribution coefficient (Kd) and retardation factor (Rd) of stronchium in fine-particle media from a VLLW disposal site. The results indicated that Kd values of strontium under different initial concentrations ranged between 20 and 110. The Kd value of Sr from the batch tests was found to be higher than these from the column experiments.

Zhang et al., 2012 studied the competitive retention and release of Pb^{+2} than Cu^{+2} ions in soils of three sites in North China using single and binary metal solutions with 0.01 $molsL^{-1}$ $CaCl_2$ as background electrolyte. The desorption isotherms of $Pb^{+2}$and Cu^{+2} were similar to the adsorption isotherms, which can be fitted well by Freundlich equation (R^2 >0.96). The soil in the three sites had greater retention capacities for Pb^{+2} than Cu^{+2} which was affected strongly by the soil characteristics. In the binary metal solution containing 1:1 molar ratio of Pb^{+2} and Cu^{+2} the total amount $Pb^{+2}$and Cu^{+2} adsorption was affected by the simultaneous presence of the two metal ions, indicating the existence of adsorption competition between the two metal ions. Fourier transform infrared (FT-IR) spectroscopy was used to investigate the interaction between soil and metal ions, and the results revealed that the carboxyl and hydroxyl groups in the soil were the main binding sites of metal ions.

Ghasemi-Fasaei et al., 2012 investigated the retention isotherms studies on two soils (an acidic and a basic soil) for single and binary systems of Ni^{+2} and Cd^{+2}. The adsorption data for metals were analyzed by Langmuir and the Freundlich isotherms. It was observed Freundlich model fitted better than the Langmuir model. The quantity of monolayer adsorption capacity, Q_m, derived from the Langmuir model in basic soil was higher than acidic soil. In both soils the amount of Q_m for Cd^{+2} under competitive condition with Ni^{+2} was lower than noncompetitive condition. Decrease in adsorption capacity of Cd under competitive condition was attributed to the occupation of some adsorption sites by Ni . Changes in the Q_m values of Ni under different treatments was negligible. Bonding energy coefficient, K_L, for Ni was higher in basic soil in comparison with acidic soil. In both soils the amount of K_L for Ni under competitive condition with Cd was higher than non-competitive condition. The quantity of K_F value of Ni was higher in basic soil as compared to acidic soil. Similar trend was observed for Cd. In both acidic and basic soils, the quantity of K_F value for Ni^{+2} was higher than Cd, demonstrating higher sorption capacity of the studied soils for Ni^{+2} in comparison with Cd.

Selim and Zhang, 2013 did a review study and presented equilibrium and kinetic models for competitive heavy metal sorption and transport in soils. The study demonstrated that equilibrium Freundlich approaches can be extended to account for competitive sorption of cations and anions with the incorporation of competition coefficients associated with each reaction. and equilibrium Langmuir and kinetic second-order models can be extended to simulate the competitive sorption and transport in soils. The study pointed out major drawback of the empirically based Freundlich and Langmuir approaches which was attributed because of their associated parameters are specific for each soil.

2.3. Affinity trends according to properties of metal

Table 2.1 shows the trends of heavy metals based on literature review on the properties related to electrostatic interactions (physical retention and/or ionic bonding), covalent bonding, complexation and redox, and other trends observed in experimental results through literature survey. The trends are helpful in understanding the behavior of these metals.

Table 2.1 Relative affinity table of heavy metals according to soil properties (Holmberg 2006)

Property	Trends	Rationale	Authors cited
A. Properties related to electrostatic interactions (physical retention and/or ionic bonding)			
Charge and hydrated radius, hydrated ion size	Pb > Ni > Cd > Cu > Zn	Ions with the higher charge and the smaller hydrated radius have higher affinity; greater polarization facilitates electrostatic ion exchange	(Helfferich, 1962; Sparks, 1995; Xiao and Thomas, 2004)
Ionic Potential (Charge-to-radius ratio)	Ni > Cu > Zn > Cd > Pb	Effect on ionic bonding-the strongest bond should be formed by the metal with the greatest	(Ong and Swanson, 1966; McBride, 1994)

		charge-to-radius ratio. Removal of metals from solution is sequential according to the ionic potential.	
B. Properties related to covalent bonding, complexation and redox			
Electronegativity (Pauling)	Cu > Ni > Pb > Cd > Zn	The more electronegative metals should form the strongest covalent bonds with O atoms on any particular mineral surface.	(McBride, 1994; McKay and Porter, 1997; Brown, T.L. *et al.*, 2000)
Standard reduction potential	Cu > Pb > Ni > Cd > Zn	The trend corresponds closely with electronegativity in explaining the relative complexing strength of Cu compared to those of Cd and Zn.	(McKay and Porter, 1997; Brown, T.L. *et al.*, 2000)
Irving-Williams order of complexing strength (metal ion radius & electron onfiguration)	Cu > Ni, Zn	Divalent metals of smaller radius generally from the stronger complex with organic ligands. But for transition metals, it is a factor of both radius and electron configuration.	(Sposito, 1989; McBride, 1994)
Intrinsic binding constants	Cu > Pb > Ni ~ Zn > Cd	Related to pH metallic speciation, the numbers are a good indicator of the relative extent of complexing to be expected between the individual metals and natural dissolved organic matter. Also accounts for electrostatic attraction/repulsion, and takes account of non-specific binding due to counterion accumulation.	(Tipping and Hurley, 1992; Drever, 1997)

C. Other trends observed in experimental results			
Metal ion-exchange	Pb > Cu > Zn		(Chen et al., 1990)
Retention of metals	$Pb^{2+} > Cu^{2+} > Zn^{2+}$		(Pakarinen et al., 1981)
Affinity for peat	$Cu^{2+} > Zn^{2+} > Ni^{2+}$		(Maslennikov and Kiselva, 1989; Chistova *et al.*, 1990)
Retention efficiency	Cu > Pb > Zn		(Kalmykova et al., 2006a)
Retention capacity	Pb > Cu > Ni > Cd > Zn		(Kalmykova et al., 2006b)

2.3. Summary of this review

The reviewed literature highlights that retention (retention and release) characteristic is very important in defining the physical, chemical and physiochemical properties of the soil in terms of its reactivity, contaminant retention mechanism etc. Several laboratory methods have been adopted to measure retention in soils by using different chemical procedures. Retention is found to depend on various factors and in general it is noted that determining retention by the soil is a complex procedure and suitable mostly for fine-grained soils. Some of the important factors influencing retention are summarized below:

1. Soil water content or soil moisture content: It was noted that the retention capacity (pesticide) increases with increase in soil water content (Roy et al., 2000; Bergloof et al., 2003; Ochsner et al., 2006).
2. Soil particle size: It was studied the particle size distributions have an important role on retention behavior of soil. The size of aggregates was shown to be a significant factor that influences retention in this way. There is an increase of soil retention with decreasing particle size (Oscarson et al., 1987; Echevarria 2001; Berglof 2002; Li et al., 2003; Tanshuling et al., 2003; Ersahin et al., 2006; Ramakrishna and Philip 2008).
3. Degree of saturation or volumetric water content: The retention capacity (heavy metal) increases with increase in the degree of saturation (Elzahabi et al., 2001).

4. Contact time and Temperature: It was found that to evaluate retention isotherm, it was very effective the effect of contact time and temperature. Most studies observed retention increases with an increase of contact time and temperature. (Cui et al., 2007; Kahle and Stamm 2007; Huijan et al., 2008; Hai et al., 2008; Kahle et al., 2008).
5. Clay mineralogy: Clay mineralogy potentially contributes to the retention in soils (Oscarson et al., 1987; Chiou et al., 2000; King et al., 2002; Berglof 2002; Li et al., 2003). The retention capacity is increasing with swelling behavior of clay mineral (Chi et al., 1999).
6. Soil organic content: Presence of organic matter in soil increases retention (Dhillon and Dhillon 1999; Morrica et al., 2000; Sheng et al., 2001; Haberhauer et al., 2001; Ochner et al., 2006; Lair et al., 2007; Wong et al., 2007; Ramakrishna and Philip 2008; Cao et al., 2008)
7. Soil pH solution: There are contradictory findings on the role of solution pH on retention behavior of soil sample. In one of the study by Koleli et al., 2007 indicated an increase in retention with increasing pH. It was also found that pesticide retention decreases with an increase in pH (Haberhauer et al., 2001; Sheng et al., 2005).
8. Specific surface area (SSA): The specific surface area of the soil plays a vital role in determining reactivity of the soil (Hepper et al., 2005). The retention behavior of soil increases with an increase in SSA of soils and vice-versa (Ersahin et al., 2006).
9. Cation exchange capacity (CEC): Retention of soil increases with an increase in cation exchange capacity of soils (Bekesi and Mcconchie, 2000).
10. Ionic strength: It was demonstrated that the retention of soil increases with an increase in ionic strength (Matigold et al., 1979; Cheng et al., 2006; Karahan et al., 2006; Cao et al., 2008; Hanna et al., 2008; Sun et al., 2008).

2.4 Critical Appraisal

The critical appraisal of the a reviewed literature clearly highlights that for accurate assessment of environmental risk and fate prediction in the geoenvironment, there is still a need for a systematic investigation and understanding of the contaminant retention mechanism, especially when several ions co-exist. It is noted from the numerous research work that emphasis has been given for evaluating the sorption and the factor affecting its mechanism. Most of the studies conducted were pertained to single contaminants interaction, whereas the waste containment facilities would be seldom present with single contaminants. The contaminant retention or interaction with soil would largely be influenced by the presence of multiple contaminant species. There is a need for a systematic comparison and quantification of multiple contaminant interaction in different type of soils. Not many studies have been done to understand the impact of multiple contaminant-soil interaction on contaminant fate prediction. It is also of interest to study whether the empirical mathematical models (sorption isotherm) are successful to define multiple contaminant-soil interaction. It was noted that not much work has been carried out to quantify the retention characteristics of locally available soils of north-east India. To address a few of the research gaps discussed above, the following scope was formulated for the present research work.

2.5. Scope of the work

The following scope of the study has been defined based on the critical appraisal presented above:

1. Determination of retention properties of seven different soil of varying index properties by employing 24 hour batch method.
2. To determine the retention capacity of all seven soils for common ions Na^+, K^+, NH_4^+, Ca^{+2} and heavy metals Cu^{+2}, Ni^{+2}, Zn^{+2} and Pb^{+2}.
3. To investigate the influence of multiple ions on soil-contaminant retention and quantify the variation in retention characteristics between single and multiple contaminant solution.
4. To evaluate the suitability of isotherms for the soil-contaminant (single and multiple contaminant solution) interaction considered in this study. To appraise any anomalies while using these isotherms for comparing multiple contaminant retention in soils.
5. To explore the possibility of developing correlation between soil specific parameters such as specific surface area, cation exchange capacity, soil pH and sorption isotherm parameters.

Chapter 3

Theoretical Background

3.1 General

This chapter discusses about the theoretical aspects related to the contaminant retention in soils. The various factors influencing this property, methodologies adopted in determining soil-contaminant retention and the mathematical representation of retention behavior is presented. Finally, the chapter discuss on the advection - dispersion equation used for understanding the fate of contaminants.

3.2 Soil retention theory

In general, the retention of soil is the process by which chemicals or contaminants are attached to the surface of soil particles by surface forces. There are two types of retention; physical and chemical. The physical retention is a low heat sorption process, in which there is no chemical reaction and no electron transfer. The forces involved in physical retention are the weak van-der-waals force. The chemical retention is due to the result of chemical reaction between the sorbent and the sorbate (Thompson 2012; Sitea 2001; Sparks 1999). In general, v retention of soil depends on physio-chemical properties of soils and the nature of contaminant. The natural fine-grained soils have negative surface charges, (Sposito 1999) which is a key parameter for the retention of positively charged cations.

3.3 Factors influencing retention of the soil

Important factors which influence the retention of a soil is discussed below:

1. Cation exchange capacity (CEC): Retention of soil increases with an increase in cation exchange capacity of soils (Bekesi and Mcconchie., 2000).
2. Ionic strength: It was demonstrated that the retention of soil increases with an increase in ionic strength (Sun et al., 2008).
3. Specific surface area (SSA): The specific surface area of the soil plays a vital role in determining reactivity of the soil (Hepper et al., 2005; Torres et al., 2007). The retention behavior of soil increases with an increase in SSA of soils and vice-versa (Ersahin et al., 2006).

4. Soil pH solution: There are contradictory findings on the role of solution pH on retention behavior of soil sample. Koleli et al., 2007 indicated an increase in retention with increasing pH. It was also found that pesticide retention decreases with an increase in pH (Haberhauer et al., 2001; Sheng et al., 2005).It may be noted that solution pH also influences surface charge of soils.
5. Contact time and Temperature: Most studies observed retention increases with an increase of contact time and temperature. (Hai et al., 2008; Kahle et al., 2008) an optimal contact time for different sorbing materials.
6. Clay mineralogy: Clay mineralogy potentially contributes to the retention in soils (Chiou et al., 2000; King et al., 2002). The retention capacity increases with swelling of clay mineral like montmorillonite (Chi et al., 1999).
7. Soil organic content: Presence of organic matter in soil increases retention (Sheng et al., 2001; Haberhauer et al., 2001; Lair et al., 2007)
8. Soil particle size: There is an increase of soil retention with decreasing particle size (Ersahin et al., 2006).
9. Degree of saturation or volumetric water content: The retention capacity (heavy metal) increases with increase in the degree of saturation (Elzahabi et al., 2001).

3.4 Retention isotherm of soil

Retention (sorption) isotherms are used to quantify the retention (or release) of a substance from the aqueous media to a solid-surface at a constant temperature and pH (Foo and Hameed 2010). These isotherms provide a convenient visual demonstration of ion retention or release and a means of assessing surface retention capacity (Harter 1991). The most obvious use of isotherm is to compare the relative amounts of adsorbate the soil can retain or release under given condition. The retention isotherm is defined as the relationship between the contaminant retained on the soil (Q_e in mg/kg) and the soil pore water concentration (C_e in mg/L) at equilibrium. There are different types of retention isotherm, linear isotherm and non-linear isotherms such as Langmuir and Freundlich isotherm, Redlich-Peterson isotherm, Koble–Corrigan retention models. It is reported that the linear and non-linear isotherms are useful in various studies to predict retention coefficient. Following are the common isotherms used for retention studies of soils.

3.4.1 Linear isotherm

In linear isotherm, Q_e is directly proportional to the C_e at equilibrium condition and at a constant temperature. It is commonly used isotherm in contaminant migration analysis because of its simplicity. This is valid at a low contaminant concentration ranges only. The linear isotherm is expressed mathematically and given by Eq. 3.1

$$Q_e = KC_e \tag{3.1}$$

where K_d is known as distribution or partitioning coefficient and its unit is L/kg.

3.4.2 Langmuir isotherm

The Langmuir retention isotherm is the non-linear relationship between Q_e and C_e on a set of distinct localized monolayer retention sites. This isotherm is developed based on the concept that a solid surface posses a finite number of retention sites. This model is based on some basic assumptions; 1) There is no interaction between molecule adsorbed on neighboring sites. 2) All sites are energetically equivalent. 3) Each sites can hold one adsorbed molecule. 4) Molecules are adsorbed at a fixed number of well defined localized sites. 5) The surface is covered with a monolayer only. 6) The retention reaction is reversible. The Langmuir retention isotherm equation is given by Eq. 3.2

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{3.2}$$

where K_L is the retention constant related to the binding energy (L/mg) and Q is the maximum contaminant adsorbed by solid (mg/kg). The Langmuir isotherm was developed to represent this site limitation, and it describes retention better under some conditions, particularly as the solid becomes saturated and solute molecules have trouble finding retention sites.

3.4.3 Freundlich isotherm

The Freundlich isotherm equation is empirical in nature. It may be obtained from Langmuir's monolayer retention theory by assuming that due to surface heterogeneity retention free energy decreases with increasing surface coverage. It is more often used to address precipitation reactions as well. The limitation of this isotherm is that it cannot be used to provide direct information on retention capacity and retention energy. This retention isotherm is very suitable for higher concentration. In the range of low concentration the Freundlich model acts similar to Langmuir isotherm. The Freundlich retention isotherm is expressed by Eq. 3.3

$$Q_e = K_F C_e^{N} \tag{3.3}$$

where K_F and N are constant. One limitation with this isotherm, however, is its failure to consider that there may be a limited amount of retention sites on the surface of the solid and the lack of further sites may prevent retention under conditions in which equilibrium is reached.

3.5 Shapes of Isotherm

The isotherm shapes provide information on the strength by which the sorbate is held to the soil and an indication of bonding mechanism. A general classification of adsorption as reflected by different features of the adsorption isotherm, such as the initial slope, the presence or absence of a plateau, or the presence of a maximum, was proposed by Giles et al. (1960). There are four different shapes of isotherm commonly observed such as - C (constant partitioning) isotherms, S, L (Langmuir) and H (high affinity).

3.5.1. The C type isotherm

The curve is a line of zero-origin and the ratio between the concentration of the compound remaining in solution and adsorbed on the solid is the same at any concentration (Fig.3.1a). This ratio is usually named ‘‘partition coefficient’’: K_d or K_p (L/Kg). This isotherm is often used for a narrow range of concentration or very low concentrations such as observed for trace pollutants. The use of this isotherm based on its simplicity could lead to erroneous conclusions. For example, if the solid has a limited quantity of retention sites, the isotherm could be nonlinear because of a possible saturation plateau.

3.5.2. The L type isotherm

The ratio between the concentration of the compound remaining in solution and adsorbed on the solid decreases when the solute concentration increases, providing a concave curve (Fig.3.1b). It suggests a progressive saturation of the solid. There are two sub-groups: (i) the curve reaches a strict asymptotic plateau (the solid has a limited sorption capacity), and (ii) the curve does not reach any plateau (the solid does not show clearly a limited sorption capacity). However, it often appears practically difficult to know if an isotherm belongs to the first or to the second sub-group.

3.5.3. The H type isotherm

This is only a particular case of the ‘‘L’’ isotherm, where the initial slope is very high (Fig.3.1c). This indicates that the compound exhibits sometimes such a high affinity for the solid that the initial slope cannot be distinguished from infinity, even if it does not make sense from a thermodynamic point of view (Toth, 1995).

3.5.4. The S type isotherm

The curve is sigmoidal and thus has got a point of inflection (Fig. 3.1d). This type of isotherm is always the result of at least two opposite mechanisms. Non-polar organic compounds are a typical case: they have a low affinity with clays. However, as soon as a clay surface is covered by these compounds, other organic molecules are adsorbed more easily (e.g. Karimi-Lotfabad et al., 1996; Pignatello, 2000). This phenomenon is called ‘‘cooperative adsorption’’ (Hinz, 2001) and is also observed for surfactants (Smith and Galan, 1995; Groisman et al., 2004). The presence of a soluble ligand can also provide a sigmoidal isotherm for metallic species. At low metal concentrations, the adsorption is limited by the presence of the ligand. The ligand must be saturated and then the adsorption occurs normally (Sposito, 1984, p. 116). The point of inflection illustrates the concentration for which the adsorption overcomes the complexation.

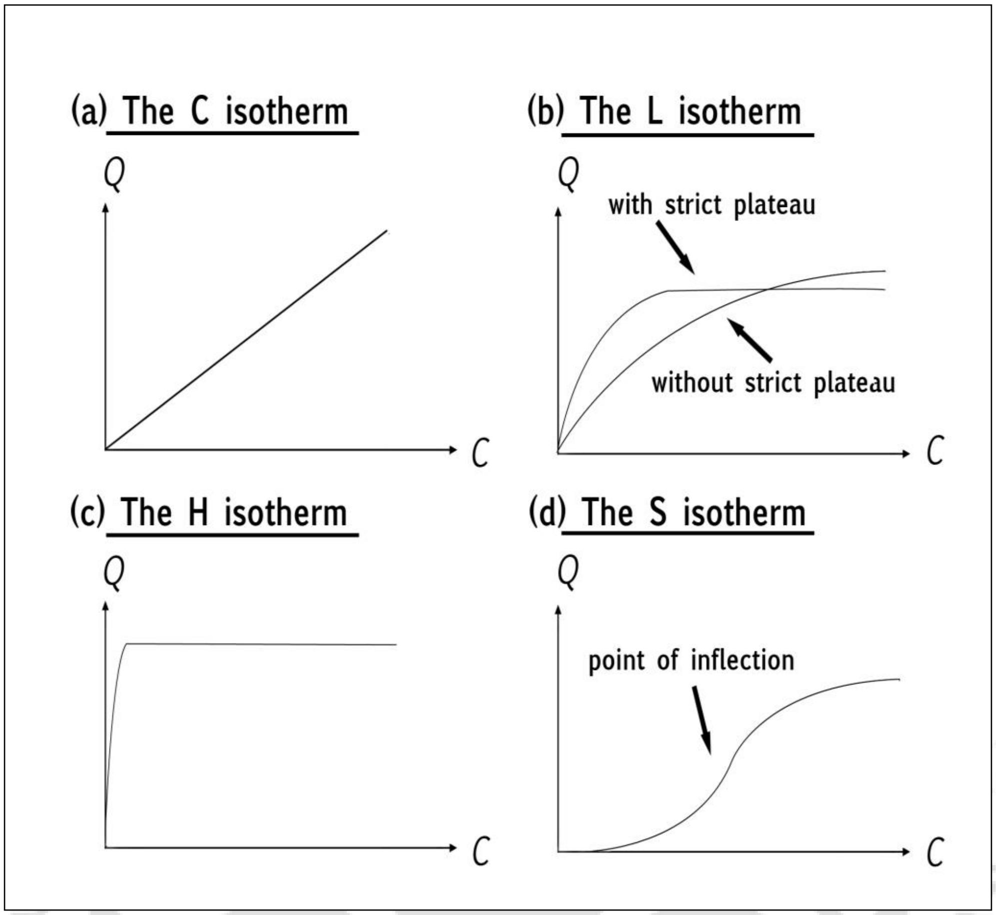


Fig 3.1 The four main types of isotherms (after Giles et al., 1974)

3.6 Instrument used for contaminant analysis - Ion Chromatography

Ion chromatography is a form of liquid chromatography that uses ion-exchange resins to separate atomic or molecular ions based on their interaction with the resin. Its greatest utility is for analysis of anions (such as fluoride, chloride, nitrite, nitrate, and sulfate) for which there are no other rapid analytical methods. It is also commonly used for cations and biochemical species such as amino acids and proteins. Most ion exchange separations are done with pumps and metal columns using conductivity detectors. The column packing for ion chromatography consists of ion-exchange resins bonded to inert polymeric particles (typically 10 μm diameter). For cation separation the cation-exchange resin is usually a sulfonic or carboxylic acid, and for anion separation the anion-exchange resin is usually a quaternary ammonium group.

For example, retention of a metal cation on a cation-exchange resin occurs by the following reaction:

$$-SO^{3-}\ H^{+}(s) + M^{x+(}aq) \text{ ® } -SO^{3-}\ M^{x+}(s) + H^{+}(aq)$$

Where M^{x+} is a cation of charge x, (s) indicates the solid or stationary phase, and (aq)indicates the aqueous or mobile phase. The equilibrium constant for this reaction is:

$$K_{eq} = \frac{[-SO^{3-}\ M^{x+}]_s [H^{+}]_{aq}}{[-SO^{3-}\ H^{+}]_s [M^{x+}]_{aq}}$$

Different cations have different values of equilibrium constant, Keq and are therefore retained on the column for different lengths of time. The time at which a given cation elutes from the column can be controlled by adjusting the pH ($[H^{+}]_{aq}$). Ions in solution are detected by measuring the conductivity of the solution. In ion chromatography, the mobile phase contains ions that create a background conductivity. This problem is reduced by selectively removing the mobile phase ions after the analytical column and before the detector. This is done by converting the mobile phase ions to a neutral form or removing them with an eluent suppressor, which consists of an ion-exchange column or membrane. For cation analysis, the mobile phase is often HCl or HNO_3, which can be neutralized by an eluent suppressor that supplies OH^-. The Cl^- or NO^{3-} is either retained or removed by the suppressor column or membrane. The same principle holds for anion analysis. The mobile phase is often NaOH or $NaHCO_3$, and the eluent suppressor supplies H^+ to neutralize the anion and retain or remove the Na. Any ionic substance that produces a detector response and has a retention time coinciding with that of an analyte, or near enough to cause peak overlap, may interfere with the determination. Most samples require dilution for determination of major ions by ion chromatography, which can introduce additional errors.

3.7 Advection-dispersion equation (ADE) and role of isotherms

When contaminant present in the pore solution migrates through the subsurface, it is subjected to transformation, retardation and attenuation due to different chemical, geochemical and biochemical reactions. The one dimensional contaminant migration equation for a contaminant along with these reactions can be expressed mathematically by a partial differential equation as stated below (Bear 1972; Freeze and Cherry 1979)

$$R\frac{\partial C_t}{\partial t} = D_h \frac{\partial^2 C_t}{\partial x^2} - \frac{v}{\theta}\frac{\partial C_t}{\partial x} - \lambda_r C_t - \frac{\lambda_r C_s \rho}{\theta} \qquad (3.4)$$

where R is the retardation factor representing soil-contaminant interaction, θ is the volumetric water content, C_t is the concentration corresponding to time t, D_h is the hydrodynamic dispersion coefficient ($=\alpha.v_s+D_e$), α is the dispersion coefficient, v_s is the seepage velocity, D_e is the effective diffusion coefficient, x is the distance, v is Darcy's velocity or discharge velocity, λ_r is the decay constant representing any attenuation reaction and C_s is the mass of the solute sorbed per unit mass of the solid (in mg/kg). For a fully saturated soil, θ is equal to the porosity n. The details of these parameters are well established and discussed in the literature (Freeze and Cherry 1979; Shukla et al., 2002).

In the present study, emphasis will be given to the variation in the value of R due to different isotherms and multiple contaminants-soil interaction. For the sake of convenience, all other parameters will be kept constant for all the analysis. The solution of partial differential equation 3.5 is obtained corresponding to different boundary conditions using the program CXTFIT (Toride et al., 1999).

3.8 Retardation factor for different isotherms

3.8.1 Linear isotherm

This isotherm represented by Eq. 3.1 is simple isotherm which assumes linear partitioning of contaminants and is mostly applicable for low concentration of contaminants. Also, it assumes unlimited number of available retention sites. However, this is not true in real practice as there will be only finite number of retention sites. For inorganic contaminants, it is ideal to use this isotherm up to those concentrations that follows linear trend. In general, R is represented by Eq. 3.5

$$R = 1 + \frac{\rho}{\theta}\left(\frac{\partial Q_e}{\partial C_e}\right) \qquad (3.5)$$

where ρ is the bulk density of the transport medium and θ is equal to the porosity n.

The value of retardation factor corresponding to linear retention isotherm, R_{Li}, is given by Eq. 3.6

$$R_{Li} = 1 + \frac{\rho K_d}{\theta} \qquad (3.6)$$

where K_d is the linear partition coefficient (in L/Kg),

3.8.2 Freundlich isotherm

This isotherm represented by Eq. 3.3 is a more general non-linear equilibrium retention isotherm. Similar to linear isotherm, this isotherm also assumes infinite retention sites and hence the maximum limit is not achieved. Care should be taken not to extrapolate this isotherm beyond the limits of experimentally derived data. The value of retardation factor R_F corresponding to Freundlich isotherm is given by Eq.3.7

$$R_F = 1 + \frac{\rho}{\theta}\left[N K_F C_e^{\,N-1}\right] \qquad (3.7)$$

where ρ is the bulk density of the transport medium and K_F is the Freundlich partition coefficient (in L/Kg), N is the Freundlich constant, θ is the porosity, Ce is the equilibrium concentration, when N=1, R_F reduces to R_{Li}.

3.8.3 Langmuir isotherm

This isotherm represented by Eq.3.4 is a more realistic non-linear isotherm, which accounts for limited number of retention sites. Therefore, Q_e versus C_e plot reaches a maximum value, represented by the term Q_m in Eq. 3.4, represents the maximum retention capacity of the sorbent (mg/kg) and K_L (l/kg) represents the strength with which the contaminant is bound to the sorbent. Langmuir isotherm takes into account the decrease in partition coefficient when the retention sites are partially saturated with contaminants. The value of retardation factor R_{La} corresponding to Langmuir retention isotherm is given by Eq. 3.8

$$R_{La} = 1 + \frac{\rho}{\theta}\left[\frac{K_L Qm}{(1 + K_L C_e)^2}\right] \qquad (3.8)$$

3.9 Description on modelling and boundary conditions of the soil column

The program CXTFIT (Toride et al., 1999) is used in this study to model different conditions of advection-dispersion and further analyzing the role of isotherms on fate of contaminant in the geoenvironment. The program can be used to estimate parameters corresponding to steady one-dimensional flow by fitting the parameters to observed laboratory or field data obtained from solute migration experiments. It can also be used to predict contaminant distributions versus time and/or space for a given set of model parameters.

In the present study, deterministic equilibrium ADE has been used, in which degradation and production of the contaminants is not taken into account. Also, the differential equation is presented in terms of non-dimensionless parameters listed in Table 3.1. Based on this, Eq. 3.4 is reduced to Eq. 3.9

$$R\frac{\partial C_r}{\partial t} = \frac{1}{P}\frac{\partial^2 C_r}{\partial Z^2} - \frac{\partial C_r}{\partial Z} \tag{3.9}$$

Table 3.1 Dimensionless parameter for equilibrium ADE

Parameter	T	Z	P	C_r	R
Expression	vt/L	x/L	vL/D	C_t/C_o	Isotherm based

In the table, L = length of the soil column; x = any distance; P = Peclet number; Co = initial concentration of solution. t is the time; v is the seepage velocity. The analytical solution of Eq.3.10 corresponding to the following initial and boundary conditions are given in CXTFIT program (Toride et al., 1999).

Initial condition:

$$C_r\,(Z, 0) = C_i\,(Z) \tag{3.10}$$

where C_i (Z) is the initial concentration of the soil which is a function of Z.

Boundary condition at inlet:

$$C_r\,(0, T) = C_o\,(T) \tag{3.11}$$

where C_o (T) is the input concentration of the contaminant solution soil which is a function of T.

The outlet boundary condition for a semi-infinite system is given by:

$$\frac{\partial C_r}{\partial Z}(\infty, T) = 0 \tag{3.12}$$

However, the same condition has been used for soil of limited extent (length L) and hence,

$$\frac{\partial C_r}{\partial Z}(1,T)=0 \tag{3.13}$$

This condition is based on the assumption that concentration is macroscopically continuous at the outlet and that no dispersion occurs outside the soil. Also, the solution for infinite outlet conditions can be applied to the finite region (0<x<L) by assuming that upstream solute concentrations are not influenced by outlet boundary (Parker and van Genuchten 1984). For contaminant transport column studies where solute BTCs are obtained based on effluent samples, flux-averaged concentrations (C_f) are used instead of resident concentration (C_r). For CDE, C_f is determined from C_r based on the transformation given by Eq. 3.14.

$$C_f = C_r - \frac{1}{P}\frac{\partial C_r}{\partial Z} \tag{3.14}$$

The above discussed solution of Eq. 3.4 and the initial, boundary conditions have been used to model the fate of contaminants corresponding to different isotherm results obtained from this study.

4.1 General

Seven soil samples were collected from local sources as well as procured commercially whole details and designation are listed in Table 4.1. It is expected that the soils cover a wide range of physico-chemical characteristics that would help to understand the influence of soil type on the determination of retention characteristic. The soils were subjected to different physical, chemical, mineralogical and geotechnical characterization, as discussed in the following section.

Table 4.1 Details of soils used in the present study

Sl. No.	Designation	Soil	Remarks
1	IBent	Plastic soils	Commercially available expansive soil from India
2	FBent		Commercially available expansive soil from France
3	Kao		Commercially available Kaolinite from France
4	RS		Locally available red hilly soil from NE India
5	LS		Locally available soil collected from paddy fields of NE India
6	FC		Commercially available fire clay
7	FAsh	Non Plastic	Fly ash from thermal power plant

4.2 Mineralogical characterization of soil

4.2.1 X-ray diffraction (XRD) analysis

This method is very useful and simple to determine the soil mineralogy. The mineralogical composition of the soil was determined by conducting the X-ray diffraction (Bruker AXS D8 model, Canada) analysis by using a graphite monochromatic and Cu-Kα radiation. The soil sample was scanned for 2θ ranging from 5° to 80° and the presence of minerals confirmed with the help of a database software. The X-ray diffraction pattern for all the soils are depicted in Figs. 4.1 to 4.7. The details of minerals present in the soils are listed in table 4.2

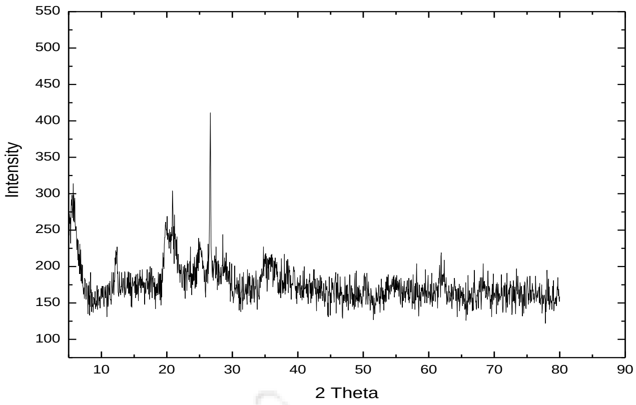


Fig. 4.1 X-ray diffraction pattern of IBent

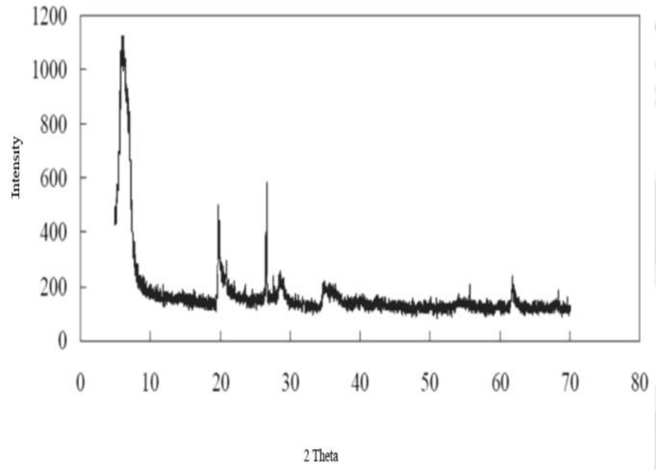


Fig. 4.2 X-ray diffraction pattern of FBent

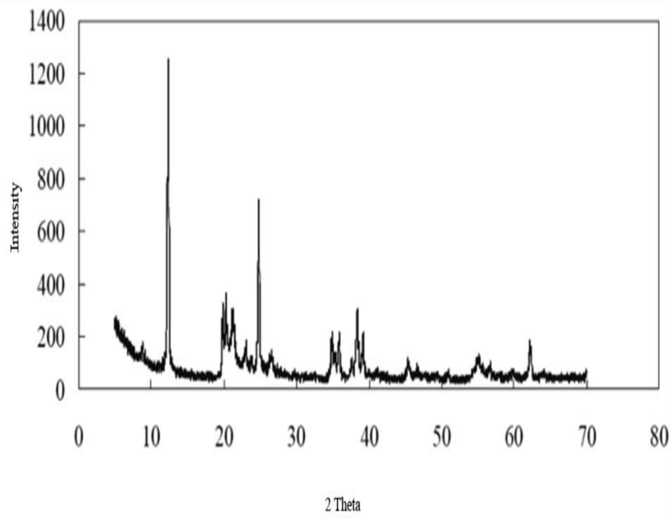


Fig. 4.3 X-ray diffraction pattern of Kao

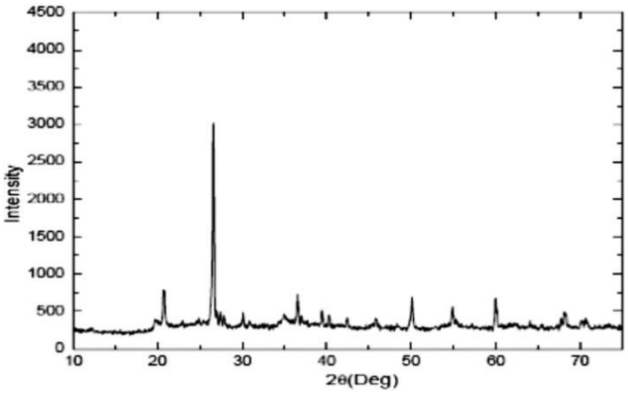


Fig. 4.4 X-ray diffraction pattern of RS

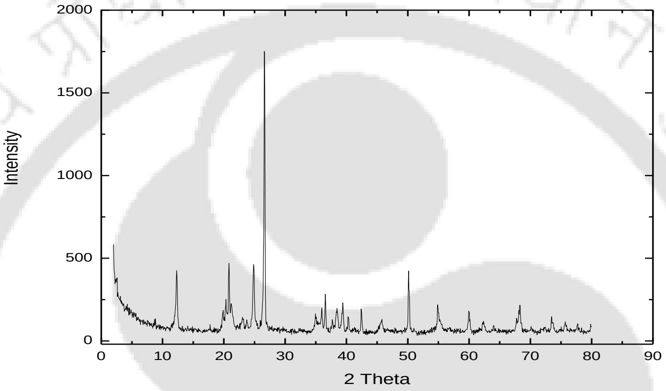


Fig. 4.5 X-ray diffraction pattern of FC

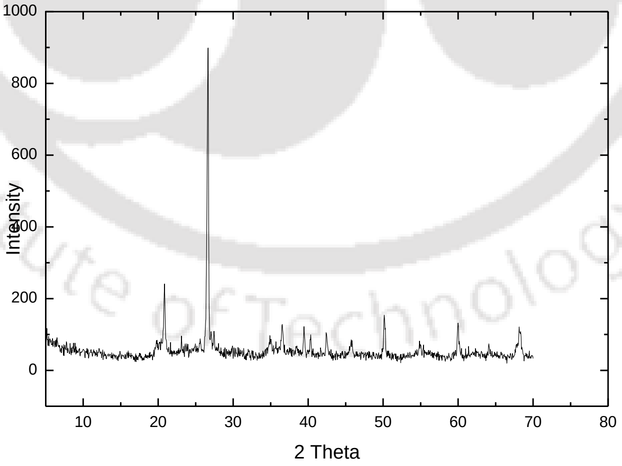


Fig. 4.6 X-ray diffraction pattern of LS

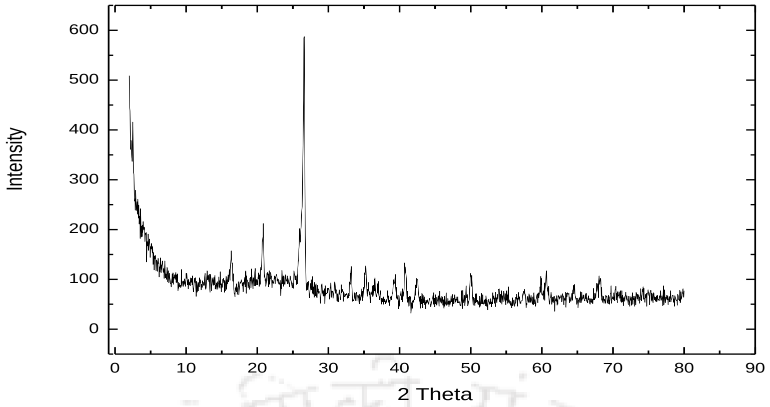


Fig. 4.7 X-ray diffraction pattern of FAsh

Table 4.2 Minerals present in the soil

Designation	**Sample minerals**
IBent	Quartz, Illite, aluminium oxide, montmorillonite, Kaolinite
FBent	montmorillonite, quartz, feldspath, calcite, mica
Kao	kaolinite, mica ,quartz
RS	quartz, magnetite
LS	quartz, kaolinite
FC	quartz, calcium oxide, kaolinite
FAsh	Quartz ,calcium oxide, magnesium

4.3 Chemical characterization of soil

4.3.1 Scanning electron microscope (SEM) and Energy dispersive X-ray spectroscopy (EDX)

The morphological and the chemical characterization of sample was carried out by scanning electron microscopy (SEM) by using a variable pressure digital scanning electron microscope (model LEO 1430VP) with EDX for elemental analysis. For SEM characterization, the sample was first cleaned and completely dried, surface oils/ dirt were removed, if any, with the help of solvents such as methanol and acetone and then blown with compressed gas. The sample was then taken on the sample holders and was analyzed by the instrument at five different target locations. As the target location was fixed, the x-ray beam hits the target location, and during this process there is transfer of electrons from the outer most shell of the atom of the sample specimen (generally the transfer of energy takes from the k shell). There is a change in energy level of atom, which is recorded in the form of different peaks. There may be different peaks for the same element depending on the energy state of the atom and amount of release of energy during the process. Fig. 4.8 to 4.13 represent the EDX pattern for all the soils. The elemental composition obtained by using EDX is summarized in table 4.2.

The SEM images of different magnification obtained for the soils are depicted in Figs. 4.13 to 4.20 respectively. The image of IBent and FBent indicates the presence of cavities and also abundant pores which are distributed on the surface. It can be noted that Kao appears to be crystalline and plate like, RS exhibits angular shape with porous structure, FC appears to be a mixture of angular, rod like and cylindrical formation, LS appears to be angular in structure, whereas the FAsh appears to be spherical in shape.

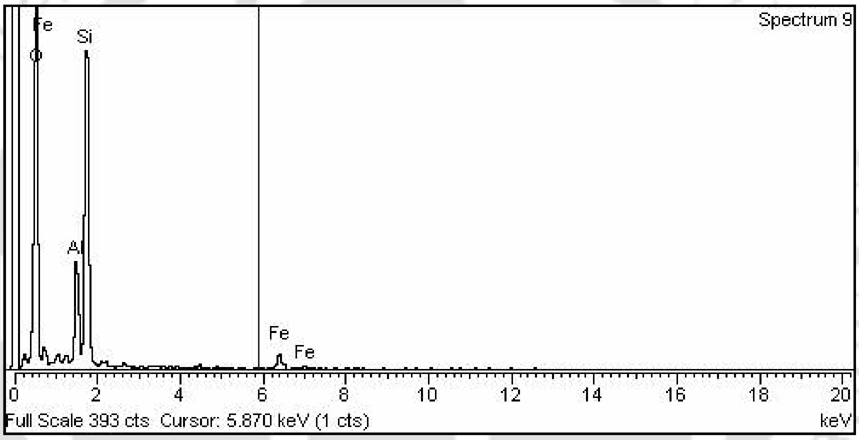


Fig.4.8 EDX pattern for IBent

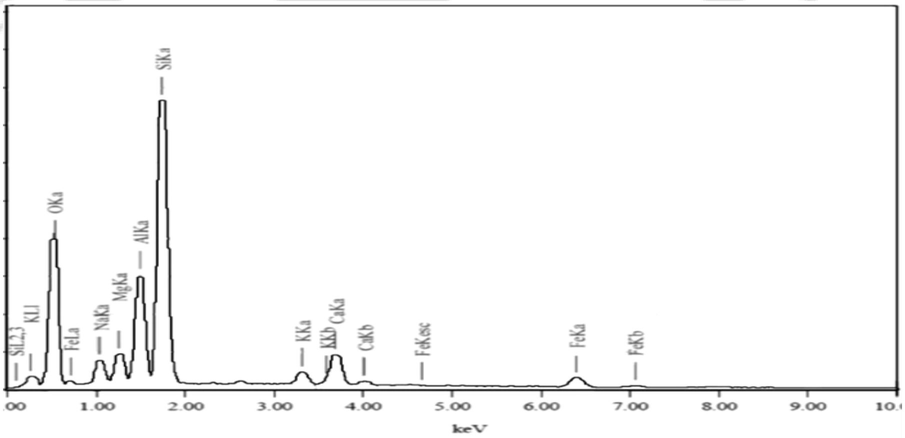


Fig.4.9 EDX pattern for FBent

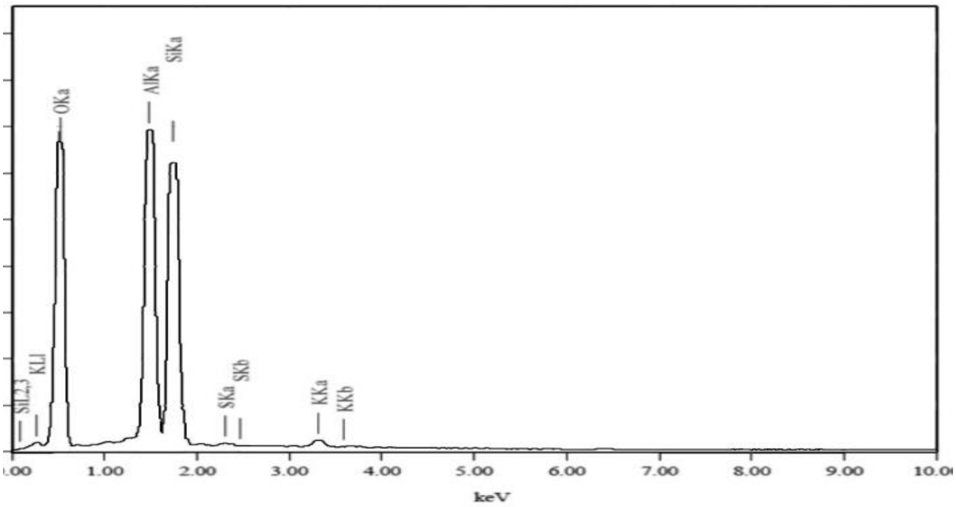


Fig.4.10 EDX pattern for Kao

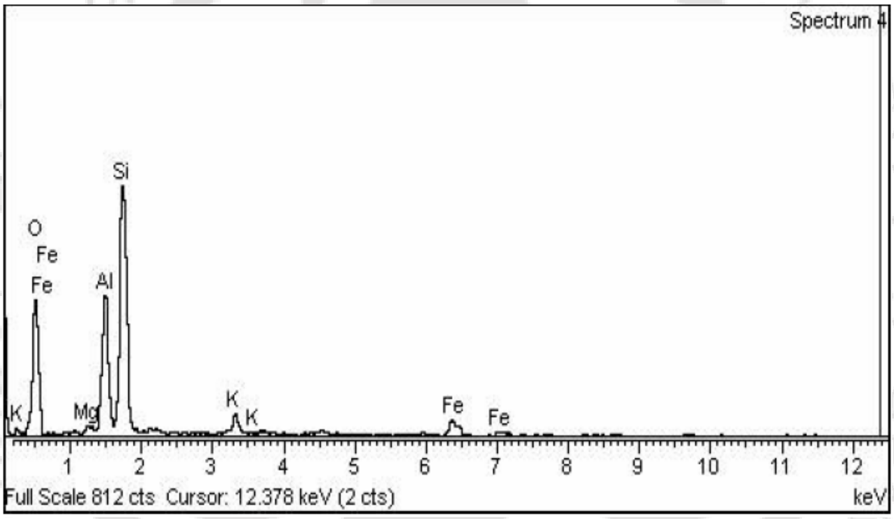


Fig. 4.11 EDX pattern for RS

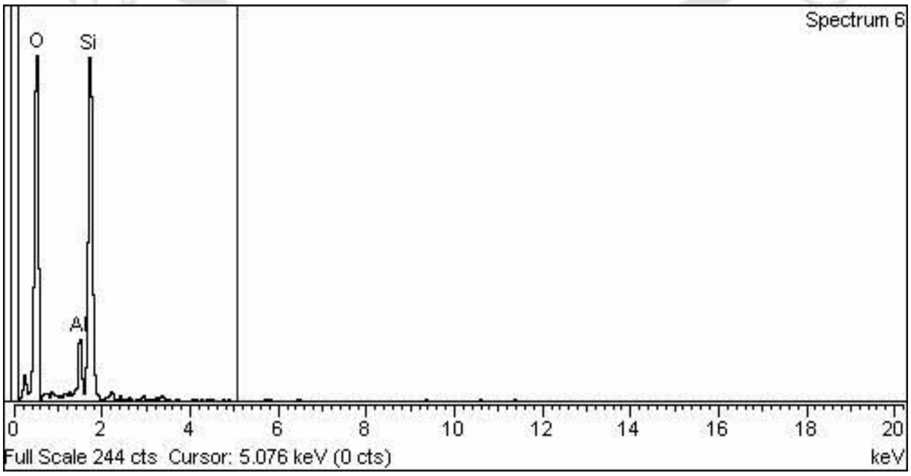


Fig. 4.12 EDX pattern of FC

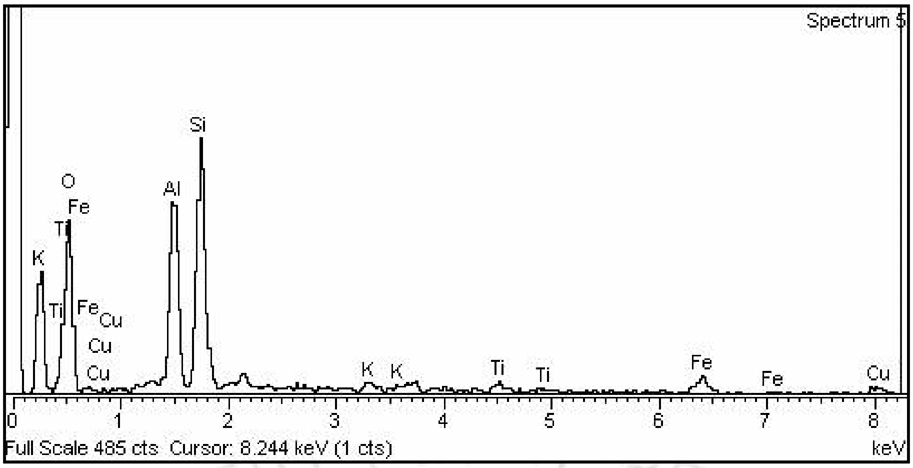


Fig. 4.13 EDX pattern of FAsh

Table 4.3 Elemental composition obtained using EDX

Name of Soil	Element	Amount
IBent	O	59.39
	Al	12.37
	Si	24.12
	Fe	4.12
FBent	Na	5.59
	Mg	5.65
	Al	18.58
	Si	35.03
	K	5.39
	Ca	13.10
	Fe	16.65
Kao	Al	40.87
	Si	39.43
	S	12.40
	K	7.29
RS	O	49.30
	Mg	0.81
	Al	12.93
	Si	28.26
	K	2.29
FC	O	68.23
	Al	3.83
	Si	27.94
	O	57.30
	Ca	0.39
FAsh	O	57.30
	Ca	0.39
	Al	5.56
	Si	12.86
	Fe	23.69

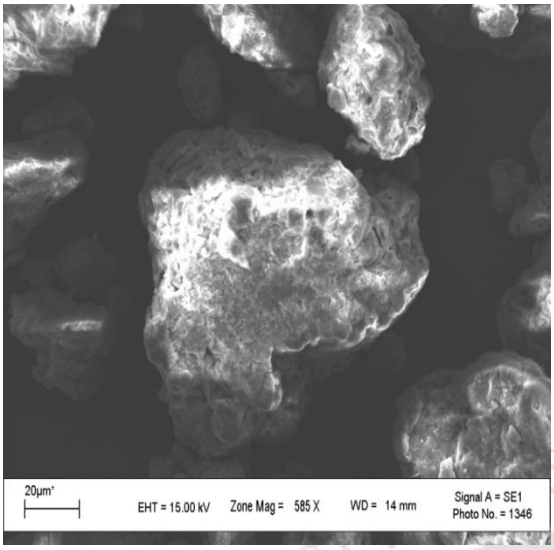


Fig. 4.14 SEM image of IBent

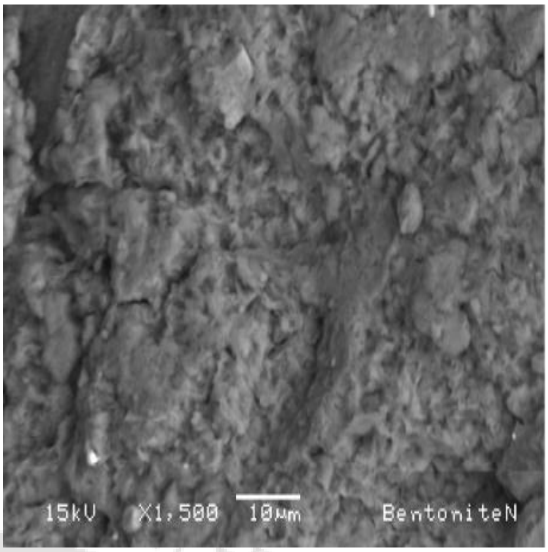


Fig.4.15 SEM image of FBent

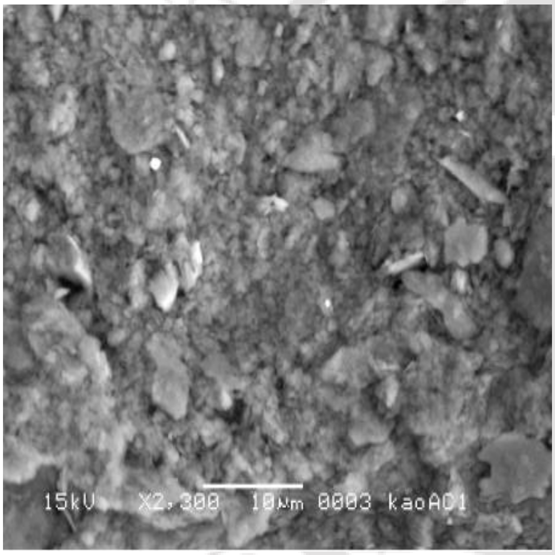


Fig.4.16 SEM image of Kao

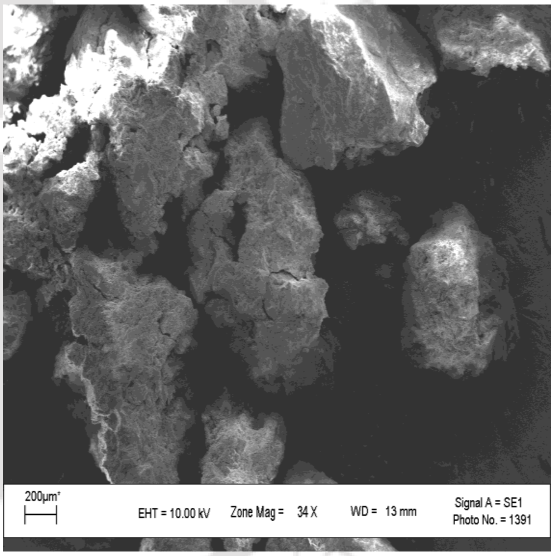


Fig. 4.17 SEM image for RS

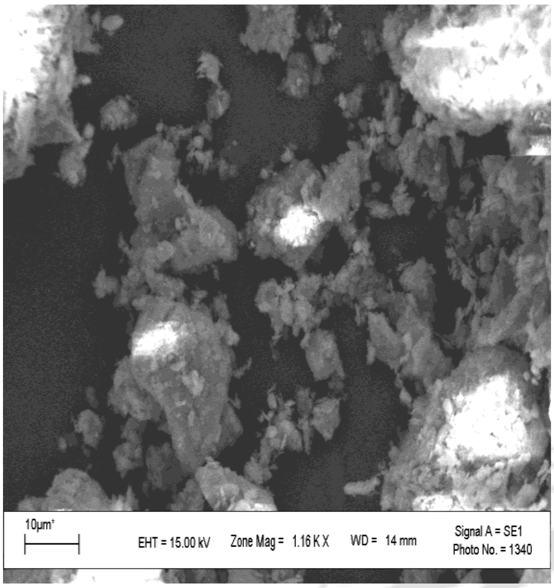


Fig. 4.18 SEM image of FC

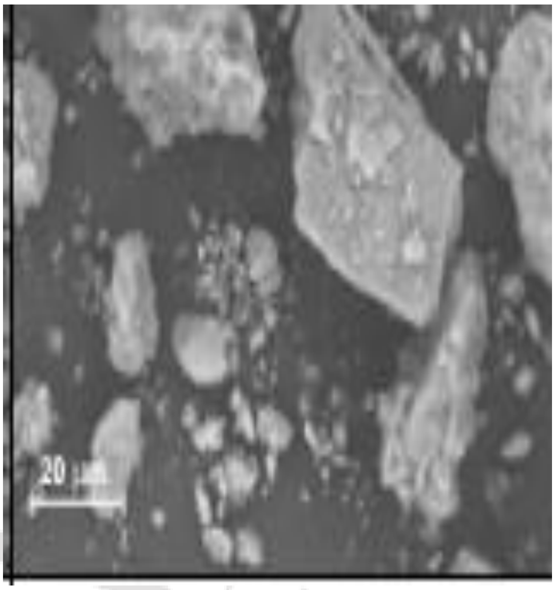


Fig.4.19 SEM image of LS

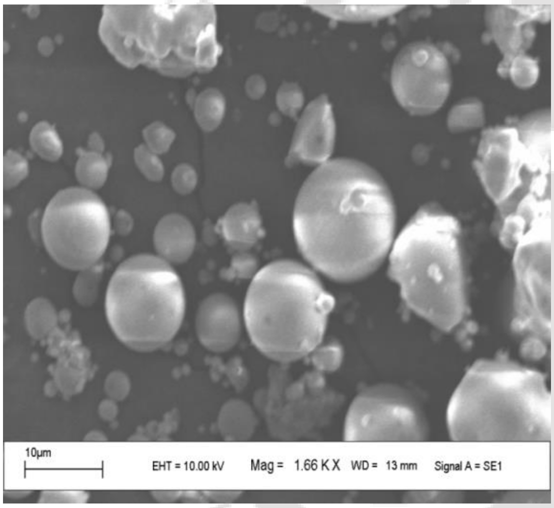


Fig. 4.20 SEM image of FAsh

4.3.2 Cation Exchange Capacity

4.3.2.1 Ammonium replacement method

This method involves saturation of the cation exchange sites on the soil surface with ammonium, and removal of the excess ammonium with ethanol. Further leaching of exchangeable ammonium was replaced with protons from HCl acid. It must be noted that this method is less suited for soils containing carbonates, vermiculite, gypsum and zeolite minerals. The procedure adopted in this study is as follows:

1. Take about 10g of soil, in 125ml flask, add 50ml of ammonium acetate solution and place the flask in reciprocating shaker for 30min. The shaking process is repeated for blank solution as well.

2. 1-liter vacuum extraction flask is connected to a funnel with Whatman no.5 filter paper. The soil sample is then transferred to the funnel and leached with 175ml of 1N ammonium acetate. The leached solution is analyzed for extractable K, Ca, Mg, and Na.
3. The soil sample in the funnel is further leached with ethanol and the leachate is discarded.
4. Transfer the soil to a 500ml suction flask and leach the soil sample with 225ml of 0.1N HCl to replace the exchangeable ammonium. Make up the leachate to a final volume of 250ml in a standard flask using deionized water.
5. The concentration of ammonium in the final leachate is measured using UV spectrophotometer, and CEC is calculated using Eq. 4.1.

$$\text{CEC} = (\text{ammomium concentration})\,\text{X}\,\frac{0.25}{14}\,\text{X}\,\frac{100}{\text{sample size (g)}} \tag{4.1}$$

$$= (\text{meq./100g of soil})$$

The CEC values of all the soils are listed in table 4.3.

4.3.3 Soil pH

The pH of the soil is a useful variable in determining the solubility of soil minerals and the mobility of ions in the soil and assessing the viability of the soil-contaminant interaction. The pH measurements procedure adopted in this study is as follows (GTM-EB 07-039).

1. The test soil must be sieved through a (2 mm sieve size).
2. The soil is weighed and placed into the glass beaker.
3. 30±0.1 g of distilled water is added to the soil sample. The solution is stirred to obtain a soil slurry and then cover with watch glass.
4. The sample is made to stand for a minimum of one hour, stirring every 10 to 15 minutes. This procedure allows the pH of the soil slurry to stabilize.
5. After one hour, the temperature of the sample should be stabilized. The temperature of the sample is measured and adjusted with the temperature controller of the pH meter to that of the sample temperature. This adjustment is done just prior to testing.
6. Immediately before immersing the pH electrode(s) into the sample, the sample is stirred well with a glass rod and the electrode is placed into the soil slurry solution and gently the beaker is turned to make good contact between the solution and the

electrode. Care was taken not to place the electrode into the soil but only into the soil slurry.

7. The electrode(s) require immersion 30 seconds or longer in the sample before reading to allow the meter to stabilize.
8. The pH value is read and recorded to the nearest tenth of a whole number. The pH values for all soil are listed in table 4.3.

Table 4.4 Chemical properties of the soils

Property	**Soil**						
	IBent	**FBent**	**Kao**	**RS**	**FC**	**LS**	**FAsh**
CEC (meq/100g)	56.90	77.60	15	16.17	8.74	11.7	1.23
Soil pH	10	9.5	6.3	6.32	5	5.8	9

4.4 Physical characterizations of soil

4.4.1 Specific gravity

The specific gravity (G) of the soils was determined by following the guidelines provided in IS: 2720 (Part III); ASTM D 854 with the help of specific gravity bottles. For the sake of accuracy, the average specific gravity was obtained from the results of minimum 5 tests. The results are presented in table 4.3.

4.4.2 Gradational characterization

The particle size characteristics of the soils are determined based on ASTM D 422-63. The results of percentage size fractions of the soils obtained from grain size curve are listed in table 4.4.

4.4.3 Atterberg limits

The consistency limits of the soil samples were determined as per guidelines provided by ASTM D 4318 and IS: 2720 (Part V) for liquid limit (LL) and plastic limit (PL).

4.4.4 Soil classification

Based on the physical characteristics, the classification of the soils was done by following unified soil classification system (USCS) (ASTM D 422). The details of the classification are listed in table 4.4.

4.4.5 Specific Surface Area

4.4.5.1 Desiccator method

In this method, specific surface area is calculated by considering the formation of unimolecular layer of water formed on the soil surface (Sridharan and Rao., 1972). The procedure adopted is as follows:

1. About 5gm of oven dried soil sample and was kept in a desiccator at a constant relative humidity of 20% with partial pressure of 0.20.
2. An aqueous solution of sulphuric acid as per ASTM E 104-85 was used to maintain the required relative humidity about 20% at 25ºC, with a density of 1.4789gm/cm^3.
3. The solution is placed at the bottom of the desiccator. The soil is placed in this desiccator for 24hr to 48hr depending up on type of soil.
4. The equilibrium moisture content was determined using a balance with a sensitivity of 0.0001gm; and the specific surface area can be obtained from the Eq. 4.2

$$SSA= \left(w \times \frac{N}{M} \times 10^{4} \times \right) \times A \times 10^{-16} \qquad (4.2)$$

where S is the specific surface area in m^2/gm, w is the equilibrium moisture content in gm adsorbed per gm of soil, N is Avogadro's number(6.025x10^{23}), M is the molecular weight of water (18.016 gm), and A is the area in square Angstroms per water molecule (10.8 Å^2).

4.4.5.2 EGME method

By conducting Ethylene Glycol Monoethyl Ether (EGME), adsorption on soil surface the total specific-surface area was determined (Carter et al., 1986; Cerato and Lutenegger., 2002).

1. 2 g of air-dried material was spread uniformly on the bottom of a glass dish (40 mm internal diameter and 20 mm in height) and covered with a perforated watch-glass.Six such dishes, with sample in them, were placed in a vacuum desiccator containing 250 g of P2O5. This helps in maintaining a constant vapour pressure inside the desiccator.
2. The sample was evacuated by applying vacuum for 2 h and was weighed. This process was repeated several times, until sample attains almost a constant weight.
3. 6 ml of analytical grade EGME solution was added to the sample and the mixture was swirled, gently, until it becomes slurry.

4. The slurry was then placed in the desiccator over a desiccant (mixture of 100 g $CaCl_2$ and 20 ml EGME) for 12 h.
5. This helps in maintaining a constant vapour pressure which is just sufficient to form monolayer on the sample.
6. Initial weight of the slurry along with the glass dish was measured using the precision balance and the dish was replaced in the desiccator for evacuation under vacuum.
7. The glass dish was taken out of the desiccator, weighed and replaced in it several times, till it attains a constant weight.
8. Calculation of SSA for soil is given below, (Cerato and Luteneggerl 2002)

$$SSA = \frac{W_a}{0.000286W_s} \tag{4.3}$$

Where SSA = Specific Surface Area in m^2/g.

Wa = weight of ethylene glycol monoethyl ether (EGME) retained by the sample in grams (final slurry weight – Ws)

0.000286 = weight of EGME required to form a monomolecular layer on a square meter of surface (g/m^2)

Ws = oven dry weight of soil (g)

4.5 Geotechnical Characteristics

4.5.1 Proctor compaction characteristics

The compaction characteristics of the soil samples used in the study have been established by using standard Proctor compaction procedure (IS: 2720: part 7; ASTM D 698). The compaction characteristics of the soils are presented in the form of relationship between dry unit weight, γ_d and moisture content, w, as depicted in Fig.4.27. The salient characteristics such as maximum dry unit weight, γ_{dmax}, the optimum moisture content (OMC), of the soil are listed in table 4.5.

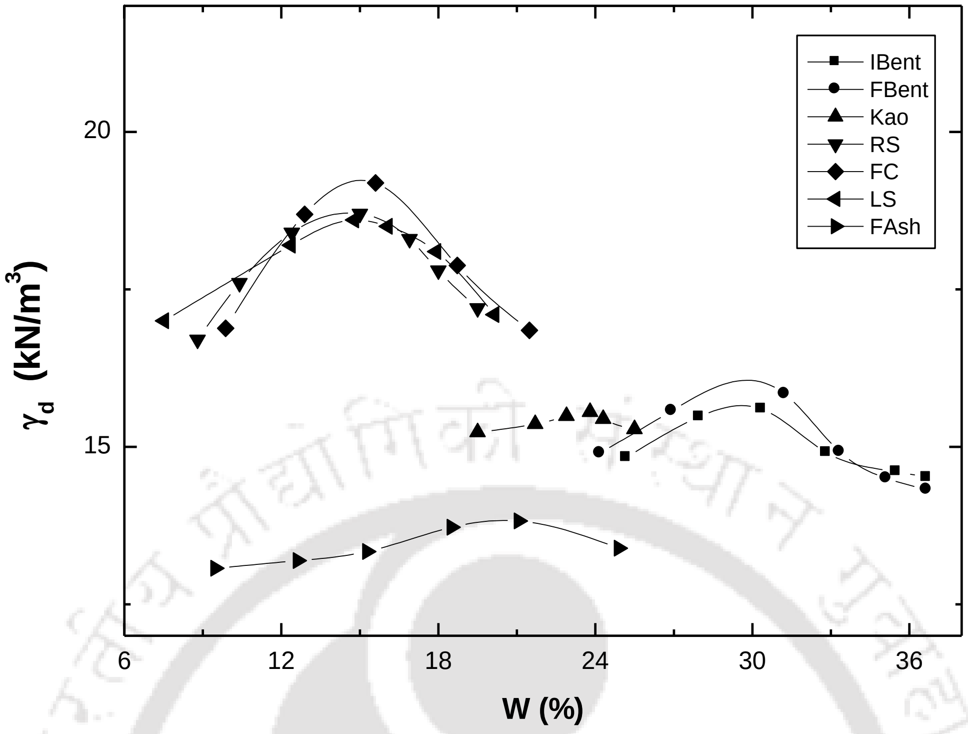


Fig.4.21 Compaction characteristics for all soils

Table 4.5 Physical properties and classification of the soils

Property	**Soil**						
	IBent	**FBent**	**Kao**	**RS**	**FC**	**LS**	**FAsh**
Specific gravity (G)	2.61	2.65	2.6	2.62	2.71	2.74	2.12
Particle size characteristics (%):							
Sand (4.75-0.075 mm)	5	1.17	3	26	46	11	34
Coarse sand (4.75-2 mm)	0	0	0	0	0	0	0
Medium sand (2-0.425)	0	0	0	5	22	0	0
Fine sand (0.425-0.075)	5	4.18	10	21	24	11	34
Silt (0.075-0.002 mm)	31	30.09	80.85	67	38	59	66
Clay (<0.002 mm)	64	64.45	50.97	7	16	30	0
Atterbergs Limit							
Liquid limit	272	345	52	46	28	42	-
Plastic limit	51	56	35	27	16	20	-
Plasticity index	221	289	17	19	12	22	-
USCS(Classification)	CH	CH	CL	CL	CL	CL	SM /class
SSA (m^2/g) (Dessicator)	136.50	112.45	12.56	50.62	11.23	9.34	1.21
SSA (m^2/g) (EGME)	244	219.12	36.62	94.12	26.12	20.12	2.66

Table 4.6 Compaction characteristics

Soil	IBent	FBent	Kao	RS	FC	LS	FAsh
γ_{dmax} (kN/m^3)	28.66	29.8	23.5	18.68	19.23	18.6	20.32
OMC (%)	15.70	16.05	15.552	14.56	14.98	14.88	13.76

4.6 Determination of retention characteristics

Retention characteristics of the soils with selected contaminants has been obtained. The different methods employed are discussed as follows:

4.6.1 Batch method (ASTM D 4646-03)

The aim of this method is to determine the retention affinity of contaminants by geomaterials in aqueous solution, which is expressed in terms of distribution coefficient (K). This test method is applicable to both organic and inorganic constituents, but fully prohibitive for volatile chemical constituents.

Apparatus: a) A rotary solid waste extractor equipment for agitation b) 0.45 micrometer pore size membrane filter equipment for phase separation, for organic matter glass or stainless steel used. c) Generally round, wide mouth bottles are used. But high density, linear polyethylene bottles are used for nonvolatile inorganic constitute with 125ml, 250ml, 2lit bottles for sample sizes of 5, 10, 70gm respectively. d) A balance having a minimum capacity of 70g and sensitivity of ±0.005g shall be used. e) Reagents: chemicals of high purity, and water having a lower conductivity i.e deionised or pure water. The brief procedure of the test is given below

1. Air dried soil sample is sieved through 2-mm sieve and the required amount is weighed.
2. The weighed soil sample is then transferred into polyethylene bottle and mixed with contaminant solution in the ratio of 1:10 (solid:liquid).
3. Place the closed container with soil solution on a shaker and agitate continuously for 24 hrs 25 ± 2°C.
4. Open the container and note any change in solution such as color, odor, temperature pH etc.
5. The solution is filtered through 0.45-µm pore size membrane and stored in a refrigerator at 4±2°C until analyzed.

6. The results of the analysis are then used to develop retention isotherm.

4.6.2 Preparation of single and multiple contaminant solution

Single and multiple contaminant stock solution were prepared by dissolving appropriate amounts of salt/ salts of analytical reagent grade in ultrapure water. For example, a single stock solution of monovalent Na^+ was prepared by mixing 2.54 gms of NaCl salts in 1000ml of ultrapure water. A multiple stock solution comprising of binary common ions of Na+K for 1000mg/L was prepared by mixing 2.54 gms and 1.91 gm of NaCl and KCl in 1000 ml of ultrapure water. The different ranges of desired concentration were achieved by diluting the solution again in ultra pure water.

Chapter 5

Experimental evaluation of soil-single contaminant interaction

5.1 General

The main objective of this research is to understand multiple contaminant interaction in different soils. To establish this, it is important to determine the interaction between soil and the single contaminant. This becomes the reference value for understanding the extend of multiple contaminant-soil interaction. Single contaminant-soil interaction studies would also help to understand how soil particle surface respond to a particular contaminant under a given condition. The model contaminants used in the study are classified as common ions (sodium, potassium, calcium, ammonium) and also heavy metals (lead, copper, zinc and nickel). The possibility of the correlation between soil specific surface area and retention characteristics is explored. Seven different soils varying in index properties and specific surface area (Table 4.1) has been used. Such studies will be important for waste containment liners where such soil contaminant interactions govern the performance of the system. Also the present study does not try to differentiate processes of interaction like sorption, complexation and precipitation. The usage of the term retention hence forth include all possible soil contaminant interactions occurring at a particular condition.

5.2. Batch results for Na^+ ion from NaCl solution

All batch tests analysis were performed in triplicate. Only those results with less than 2% variability are considered. The close results were averaged for plotting retention isotherms. Batch tests were performed for a range of NaCl concentrations varying from 10 mg/l to 1200 mg/L. Fig 5.1a and 1b shows the retention characteristics of all the soils for Na^+. From the figures it can be noted that soils like IBent, FBent and FAsh there is no definitive trend for retained concentration (Q_e) of Na^+ versus equilibrium concentration (C_e) for the entire range of concentration. There is a scatter of data and hence no isotherm could be fitted. It should be mentioned that the release of Na^+ from soils was higher for the IBent and FBent. This possibility of release can be attributed to the high amount of Na^+ present in bentonite. However, for the rest of the soils Kao, FC, LS and RS retention of Na^+ was observed. For soil RS retention is negligible for Ce less than 500 mg/L and in some cases exhibits release of Na^+. Langmuir (La) and Freundlich (F) isotherms fitted to soil Kao is depicted in Fig 5.2. For the sake of brevity trends for other soils are not presented. The fitting parameters of the retention isotherms for all the four soils (Kao, FC, LS and RS) along with the goodness of fit

(R^2) are listed in table. 5.1 It was observed that Kao has the highest Freundlich retention coefficient K_F followed by FC, LS and RS. The maximum retention capacity (Q_m) obtained from Langmuir isotherm followed the sequence RS > Kao > LS > FC. The isotherms that gave best fitting for different soils are listed in the table. The experimental results show that soils exhibit a low affinity towards Na^+ ion.

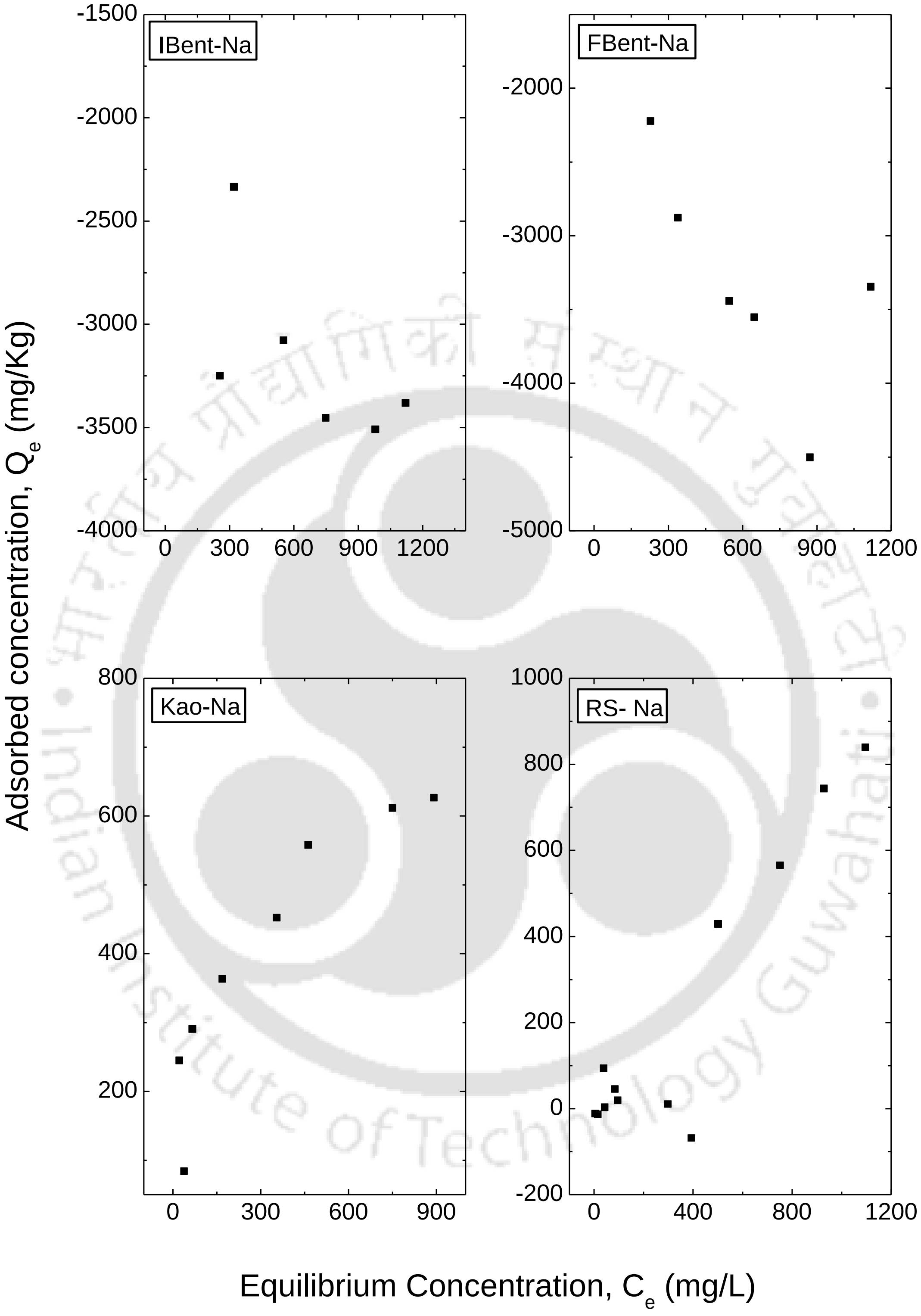


Fig.5.1a Retention characteristics of Na^+ on 4 soils from NaCl solution.

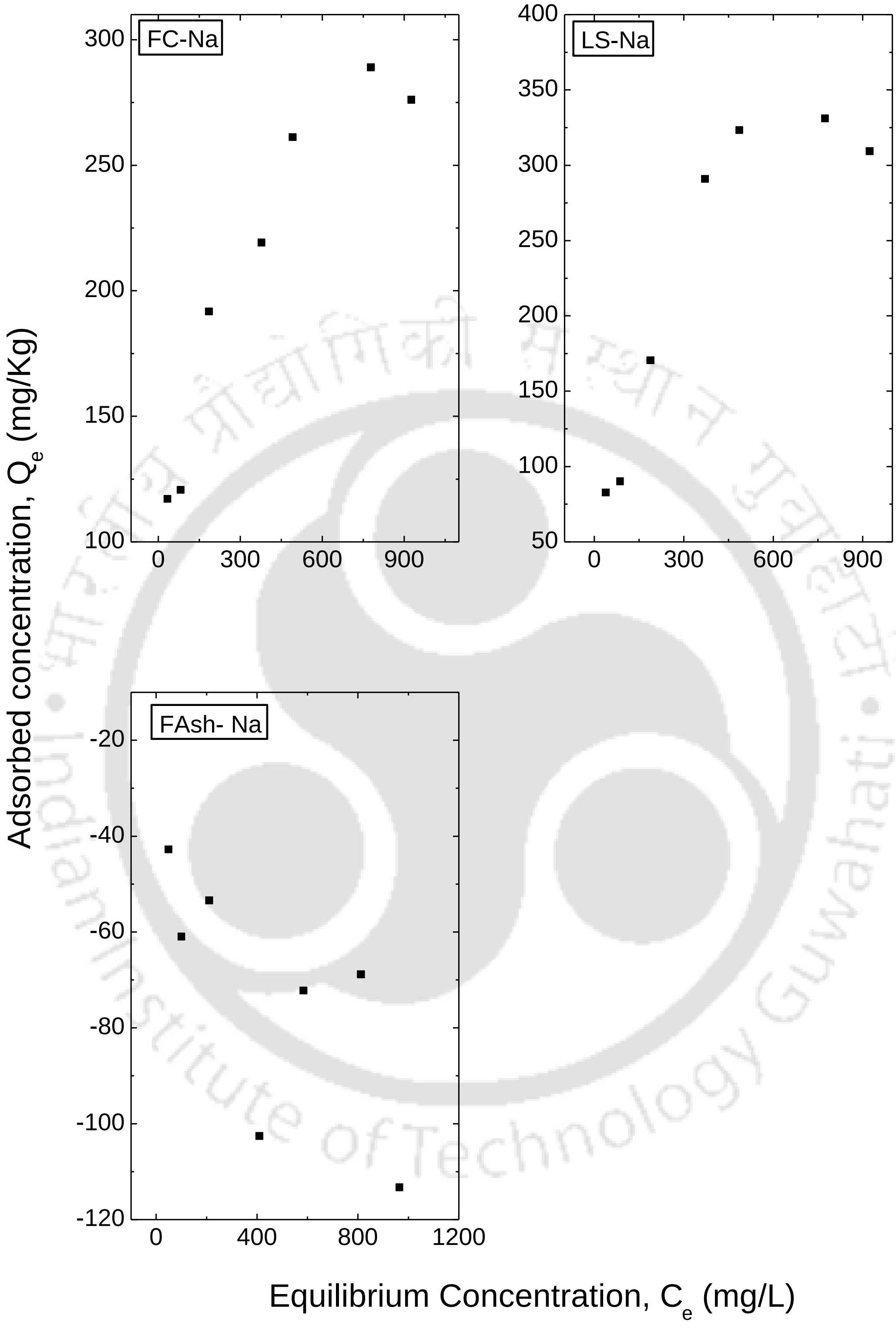


Fig. 5.1b Retention characteristics of Na^+ on 3 soils from NaCl solution

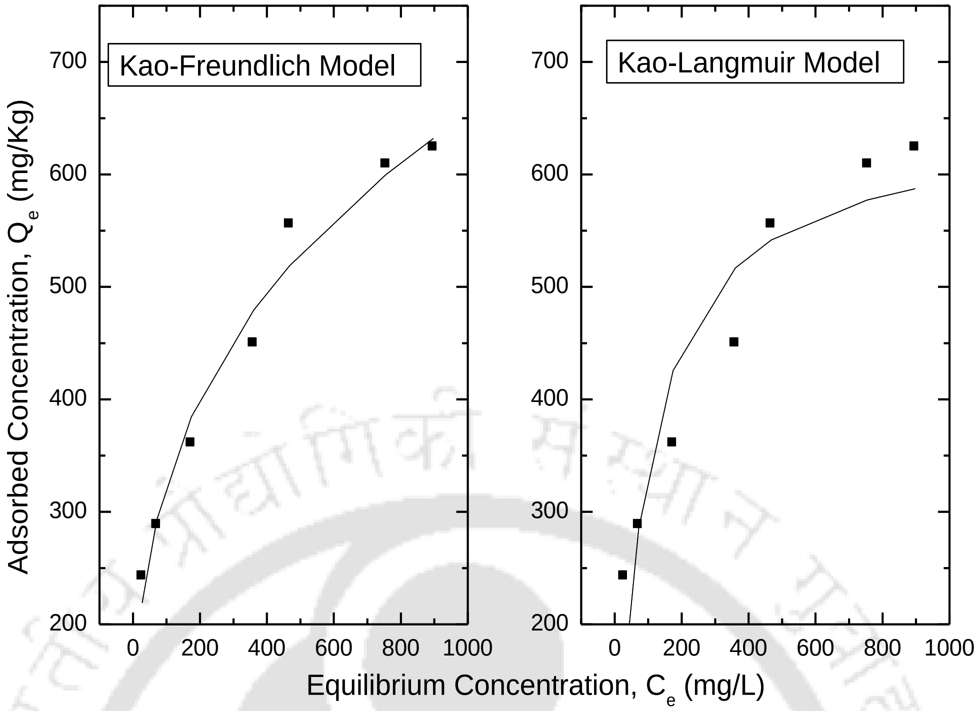


Fig. 5.2 Langmuir and Freundlich isotherm model for Na^+ in single salt solution

Table 5.1: Retention isotherm parameters for Na^+ from NaCl

Soil	Parameters						Best Fit
	Freundlich			Langmuir			
	K_F(L/Kg)	N	R^2	K_L(L/mg)	Q_m(mg/Kg)	R^2	
RS	1.35	0.92	0.98	0.001	8263.81	0.98	Langmuir
FC	35.50	0.31	0.95	0.0091	309.63	0.92	Freundlich
Kao	80.48	0.30	0.97	0.011	646.43	0.86	Freundlich
LS	18.54	0.43	0.87	0.0042	429.41	0.94	Langmuir

5.3. Batch results for K^+ ion from KCl solution

K^+ is present in the soil in water-soluble, exchangeable and non-exchangeable forms. The availability of K^+ in the soil is primarily controlled by retention processes. Although K^+ does not pose potential environmental concerns, an understanding of K^+ retention is required to appraise its influence on retention of other ions. Batch tests were performed for a range of KCl concentrations varying from 10 mg/L to 1000 mg/L. The retention characteristics of K^+ for all the seven soils are plotted in Fig 5.3a and 5.3b. All the soils except for FAsh exhibited higher retention of K^+ than Na^+ for entire the range of concentration investigated in this study. This finding is similar to Levy and Torrento (1995) that soil affinity for K^+ was about

10 times greater than Na^+. Both Langmuir and Freundlich isotherms fitted the data well and the fitting parameters are tabulated in table. 5.2. Comparison among the retention performance showed the following trend for the different soils IBent > FBent > Kao > FC > RS > LS > FAsh according to Freundlich isotherm parameter K_F. The trends according to Langmuir isotherm parameter Q_m is IBent > FBent > Kao > FC > LS > FC > RS > FAsh.

The soil mineralogy plays a pivotal role for the retention of K^+. Wang et al., (2000) and Rahman and Rowell, (1979) indicates that the preference for K^+ result from higher content of clay minerals such as smectite or illite than vermiculite soils. In the present study, smectite rich soil such as IBent and FBent exhibited high retention of K^+. Different clay variety may affect soil selectivity of K^+. Understandably, the distribution of different sites for retention depends on quantity and quality of clay minerals, their degree of depletion and complementary ions (Hannan 2007). FAsh had very little affinity for K^+, indicated by its negligible retention at low concentration and release at higher concentration.

By comparing the experimental data, it has been found that K^+ has more retention in soils than Na^+. This can be attributed to the fact that for cation of equal valence (Na^+ and K^+), the one with lower hydrated radius is retained more. In the present case, K^+ has a smaller hydrated radius than Na^+ (hydrated radius of K^+ is 0.330 nanometer and for Na^+ it is 0.360 nanometer).

5.3.1. Influence of range of concentration on retention characteristics

Literature have highlighted that different ranges of initial concentrations are used for establishing retention isotherms. Therefore, the present study purports to evaluate the importance of range of concentration on retention isotherm parameters for the soil RS. For this purpose, three ranges of C_e has been considered for fitting isotherms such as (i) $C_e < 60$ mg/L (low range); (ii) $C_e > 60$ mg/L(high range); and (iii) entire range of C_e (low range and high range together).

The details of different isotherm fits (linear, Langmuir, Freundlich), for the three ranges mentioned above are depicted in Figs. 5.4 to 5.6. Linear isotherm is considered to account low concentration range. The details of the various fit parameters of these retention isotherms are presented in table 5.3. In the table, Li is linear, F is Freundlich and La is Langmuir. It can be noted from Fig 5.6 that there is more scatter of data for the range of $C_e <$ 60 mg/L. The table depicts that for this range of concentration, linear isotherm gave a relatively better fit as compared to other isotherms. This observation is in agreement with the observations reported in the literature that linear isotherm is suitable for low range of concentration (Barone et al., 1989). For C_e > 60 mg/L, non linear isotherm exhibited fairly good fit, with Freundlich isotherm exhibiting the best fit. When the entire range of data is considered, the trends exhibit a clear non-linearity. As expected, the linear isotherm does not represent the data efficiently. Freundlich isotherm exhibited the best fit for entire range of C_e. The observation clearly indicates that the range of C_e influences the suitability of isotherm and hence batch test need to be conducted for the range of concentration anticipated in the field. Also, for Linear isotherms, the slope changes drastically for C_e <60 mg/L and C_e > 60 mg/L. Therefore, there should be proper discretion while using linear isotherm results as the distribution coefficient, K_d is applicable only for a small range of data. For a wide range of data, the slope (K_d) changes with C_e. For better understanding the partition coefficient corresponding to different isotherms and C_e ranges are plotted as shown in 5.7. It can be noted from the figure that the partition coefficient values for different isotherms are entirely different. The results of C_e > 60 mg/L are similar to the entire range of concentration investigated in this study. The physical significance of these values in each of the isotherms will be different and hence cannot be compared. The main intention of this figure is only to investigate the variation of the partition coefficient for different range of C_e corresponding to a particular isotherm.

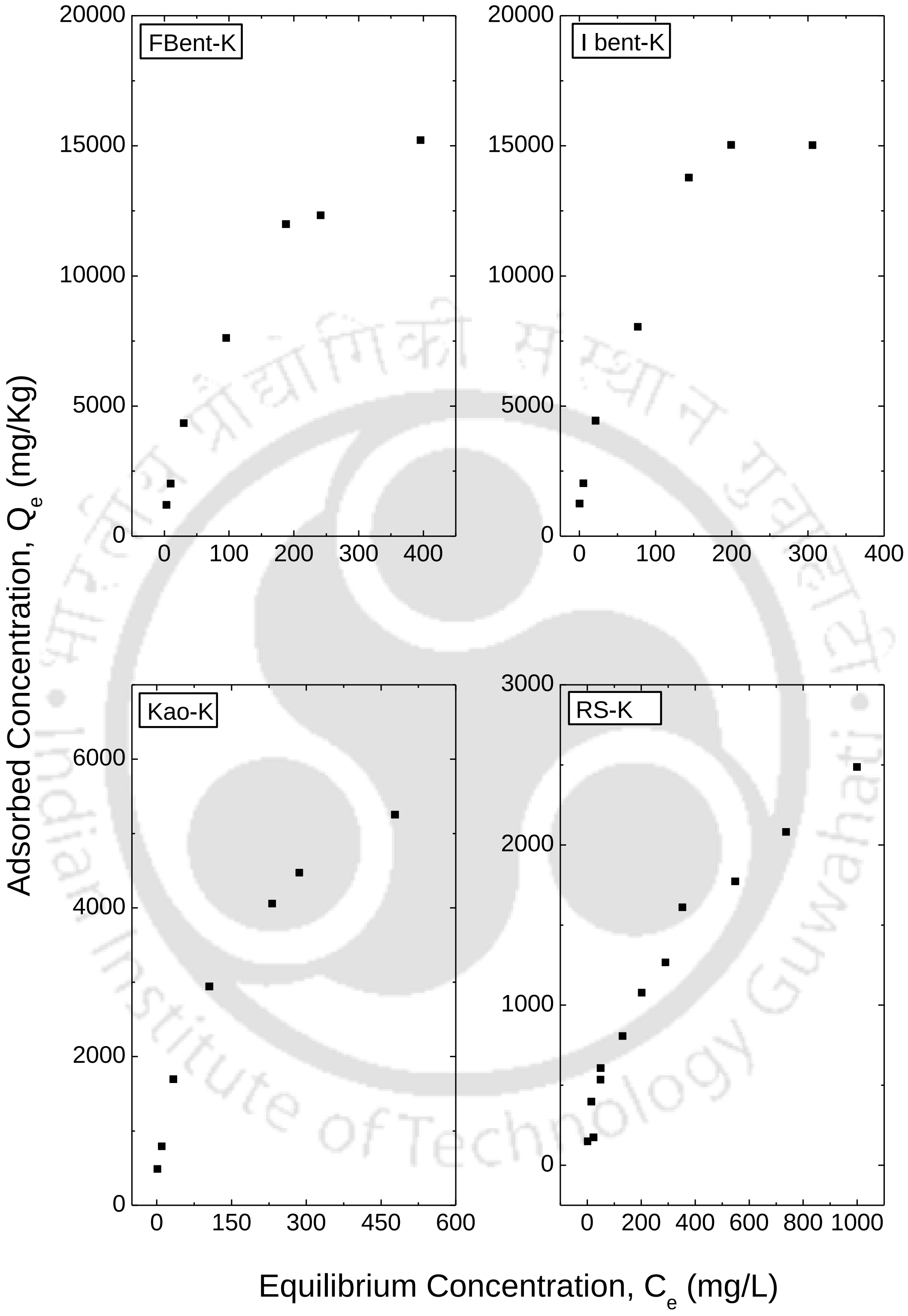


Fig. 5.3.a Retention characteristics of K^+ on 4 soils from KCl solution.

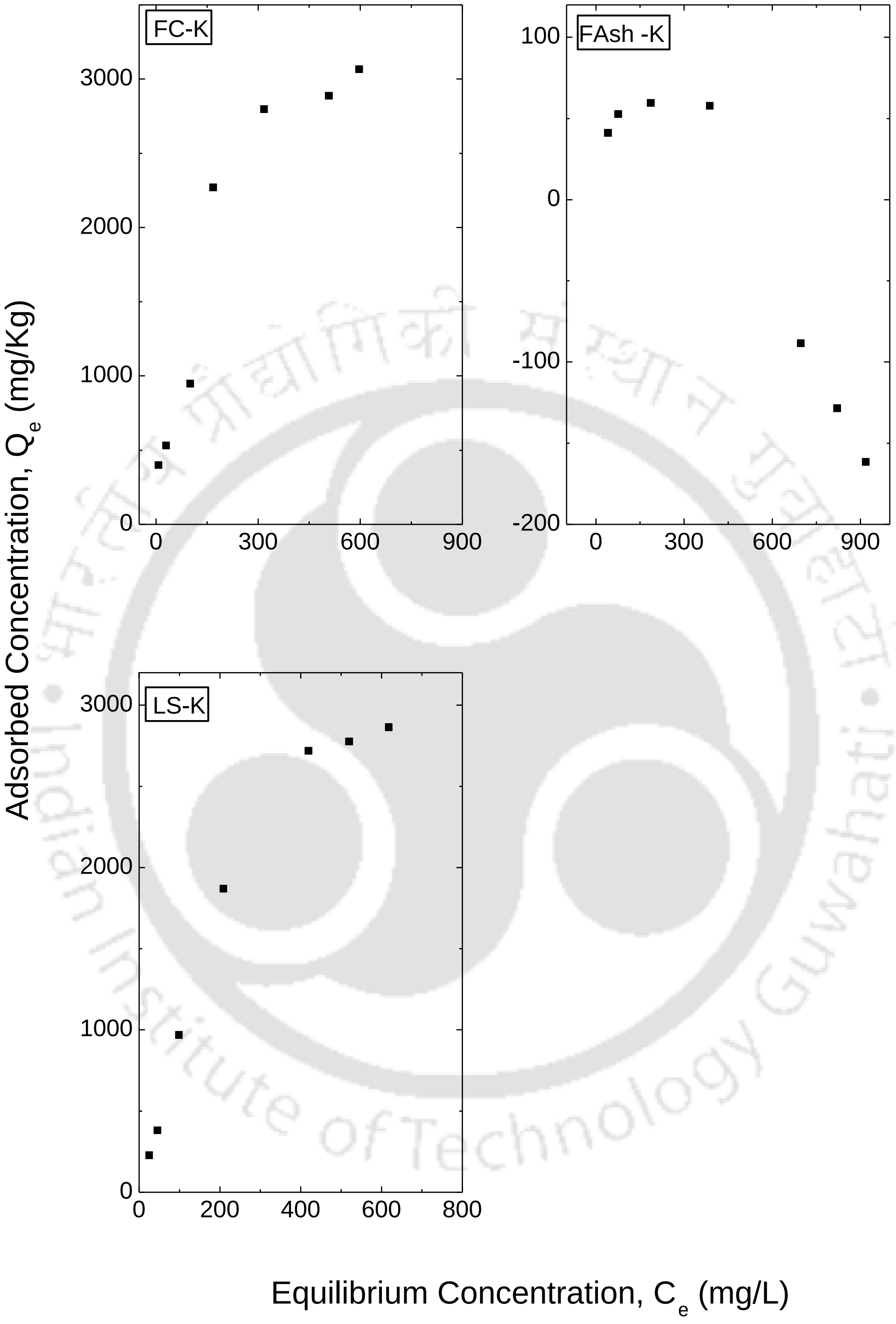


Fig. 5.3b Retention characteristics of K^+ on 3 soils from KCl solution.

Table 5.2: Retention isotherm parameters for K^+ from KCl

Soil	Parameters						Best Fit
	Freundlich			Langmuir			
	K_F(L/Kg)	N	R^2	K_L(L/mg)	Q_m(mg/Kg)	R^2	
IBent	1039.30	0.48	0.95	0.01084	20569.74	0.97	Langmuir
FBent	685.88	0.52	0.98	0.0069	20217.49	0.99	Langmuir
RS	59.710	0.54	0.99	0.00249	3263.94	0.97	Freundlich
FC	131.77	0.50	0.91	0.00473	4236.37	0.94	Langmuir
Kao	314.53	0.46	0.99	0.00878	6250.62	0.99	Freundlich
LS	52.017	0.63	0.96	0.00263	4814.18	0.98	Langmuir
FAsh	26.14	0.14	0.72	0.045	62.73	0.89	Langmuir

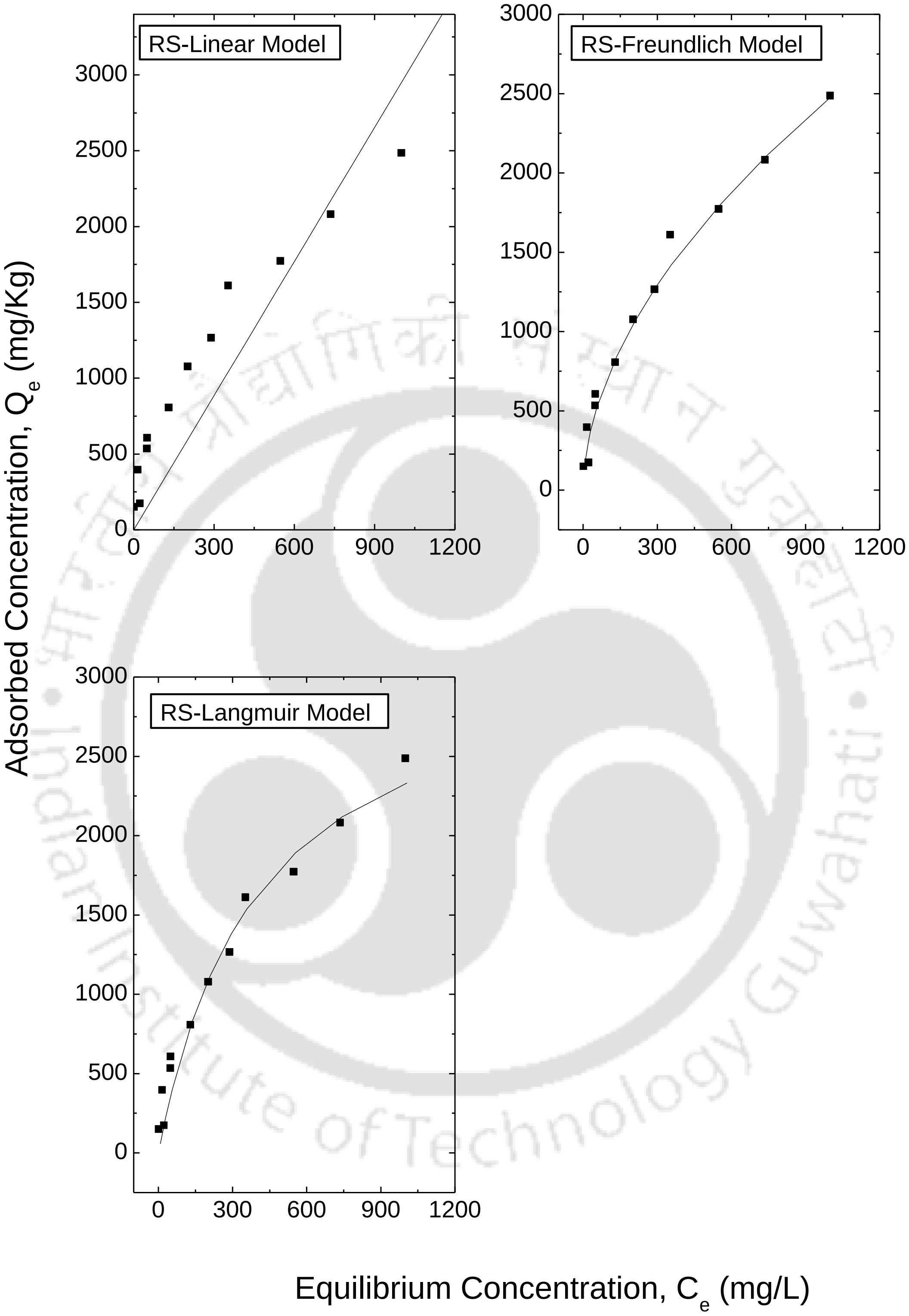


Fig. 5.4 Retention characteristics for K^+-RS interaction corresponding to entire range of C_e

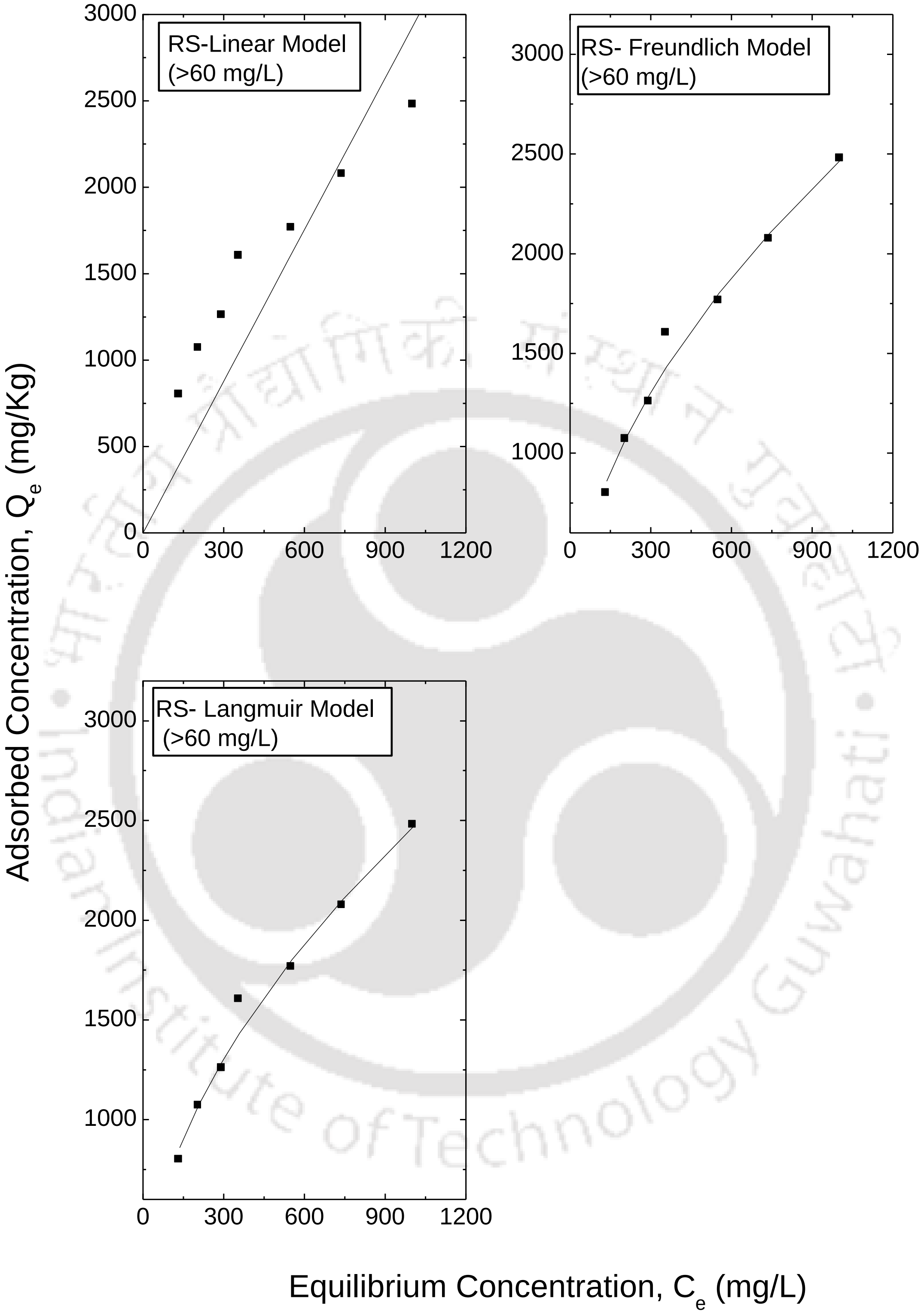


Fig. 5.5 Retention characteristics for K$^+$-RS interaction corresponding to C$_e$ >60 mg/L

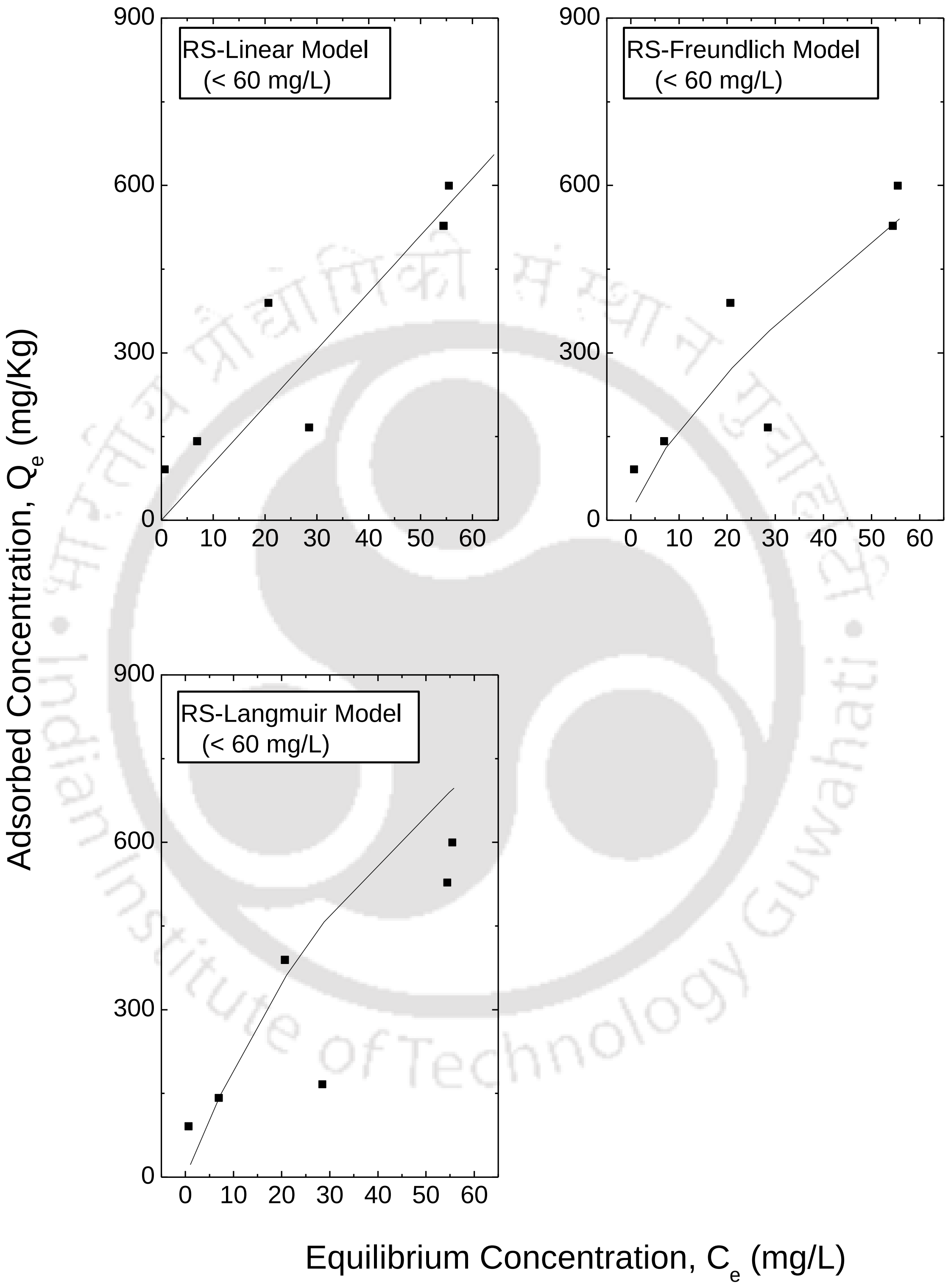


Fig. 5.6 Linear, Freundlich and Langmuir isotherm for K^+ and RS corresponding to $C_e < 60$ mg/L

Table 5.3 Retention isotherm parameters for K^+ (single salt) for different ranges of C_e for RS

Range	Li	F	La
C_e < 60 mg/L	K_d=10.20 L/Kg R^2=0.8990	K_F=32.36 L/Kg N=0.699 R^2=0.7830	K_L=0.0078 L/mg Q=17.000 mg/Kg R^2=0.7620
C_e > 60 mg/L	K_d=2.924 L/Kg R^2=0.8720	K_F=64.20 L/Kg N=0.527 R^2=0.9820	K_L=0.0019 L/mg Q=3602.74 mg/Kg R^2=0.9762
Entire range	K_d=2.95 L/Kg R^2=0.8531	K_F=60.04 L/Kg N=0.538 R^2=0.9872	K_L=0.0025 L/mg Q=3262.3 mg/Kg R^2=0.9751

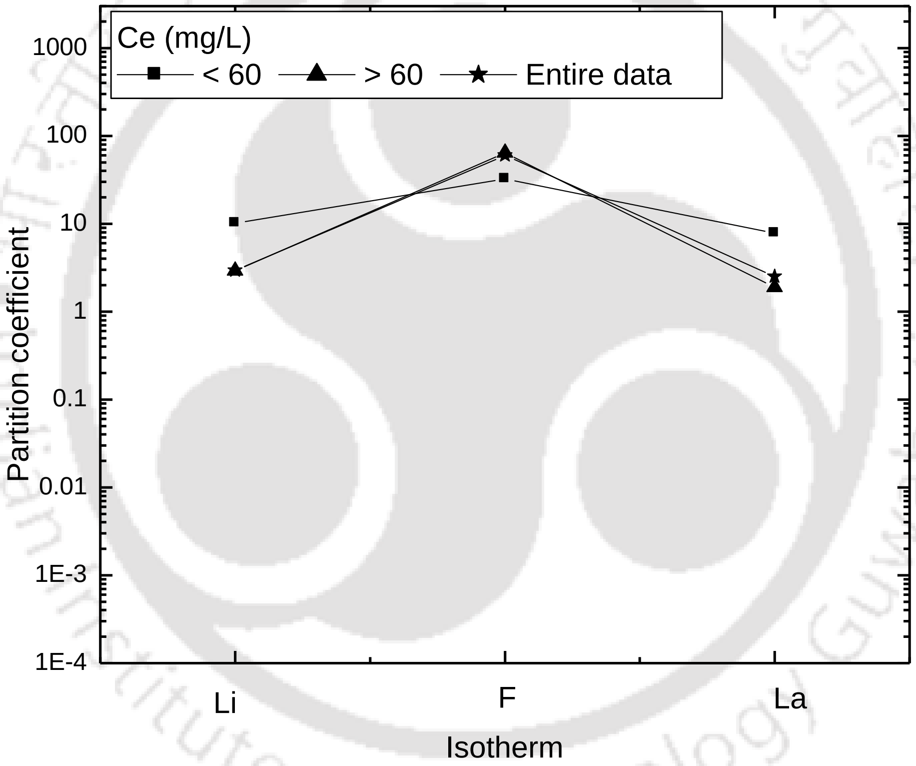


Fig. 5.7 Comparison of partition coefficient of K^+ in single salt solution for different isotherms and range of data for RS

5.4. Batch results for Ca^{+2} ion from $CaCl_2$ solution

From the perspective of soil fertilization, the retention of calcium is important for determining their availability to plants and their movement through soils. It is one of the essential elements for agricultural production. Calcium is an alkaline metal of Group IIA on the periodic chart, fifth most abundant element in the earth's crust and is widely distributed in nature. Even though there are a few studies appraising calcium retention on soils, its influence on other ions needs to be investigated. Retention isotherms for $CaCl_2$ was determined for concentration varying from 50 to 1200 mg/L as depicted in Fig. 5.8a and 5.8b for all seven soils. From the Figs., it can be noted that there is a definitive trend for retained concentration (Q_e) versus equilibrium concentration (C_e). Langmuir and Freundlich isotherms were fitted to the retention data by nonlinear regression analysis. Both the Langmuir and Freundlich models fit the Ca^{+2} retention data satisfactorily, with comparable R^2. The various isotherm parameters for all the soils are reported in Table 5.4. The retention of Ca^{+2} based on Freundlich isotherm paramter K_F is ranked as IBent > FBent > Kao > FC > RS > LS and according to Langmuir isotherm, maximum adsorption value Qm value is ranked as IBent > FBent > Kao > FC > LS > RS. For FAsh there is a net release of Ca^{+2} and therefore no isotherm could be quantified.

The resulting curves associated is classified according to the Giles' model (Sposito, 1989) as an L type for I Bent, F Bent and Kao which indicated an initial curvature, implying that the sites in the soils are rapidly filled by Ca^{+2} added, and the subsequent increase of solute on the soil surface becomes difficult. S type of isotherm is followed by RS and FC and LS where the initial curvature of type S shows gradual retention in the initial phase with the addition of Ca^{+2} ions in solution. This S type of curve occurs when there is moderate intermolecular attraction (Giles et al., 1960)

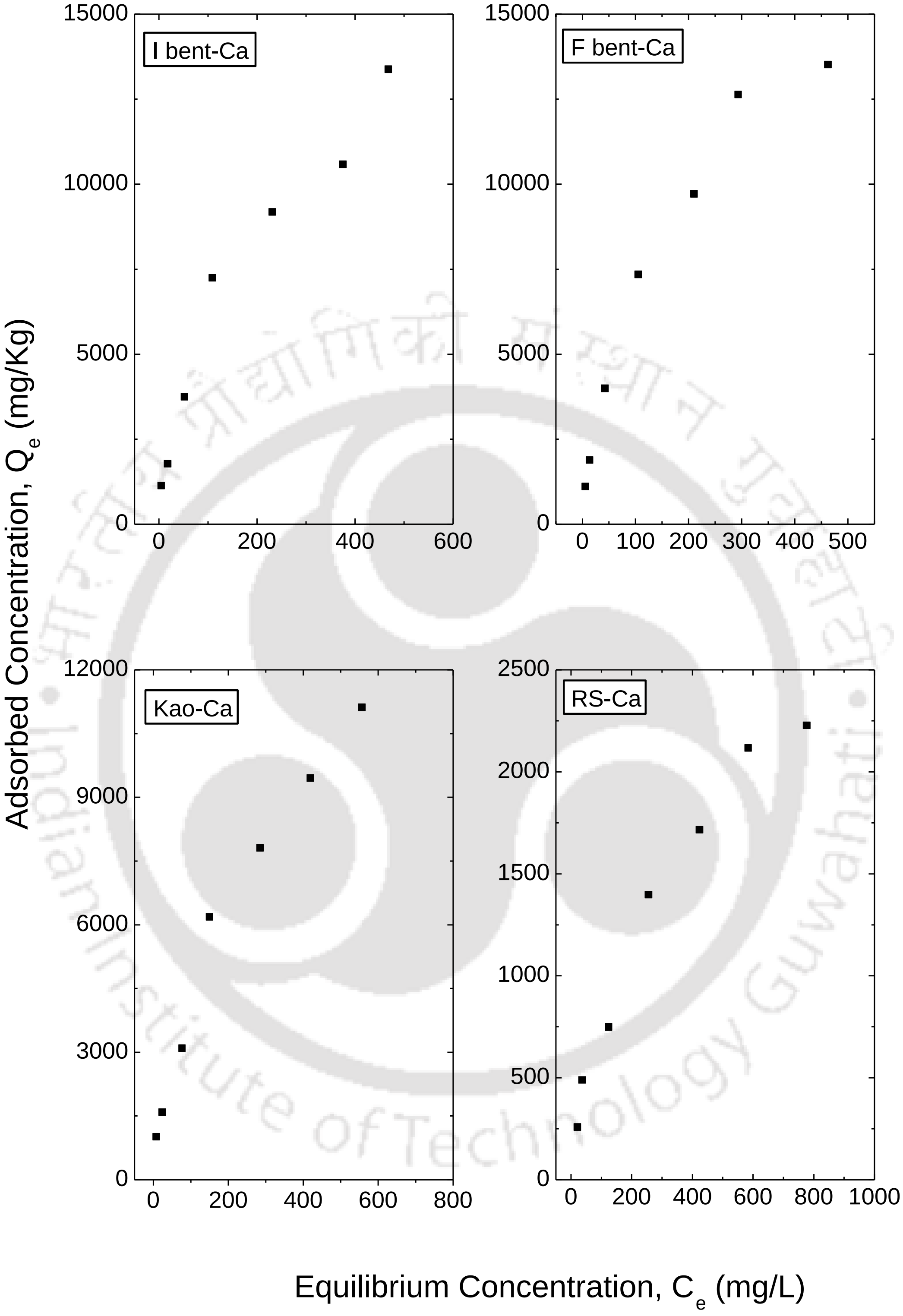


Fig. 5.8a Retention characteristics of Ca^{+2} on 4 soils from $CaCl_2$ solution

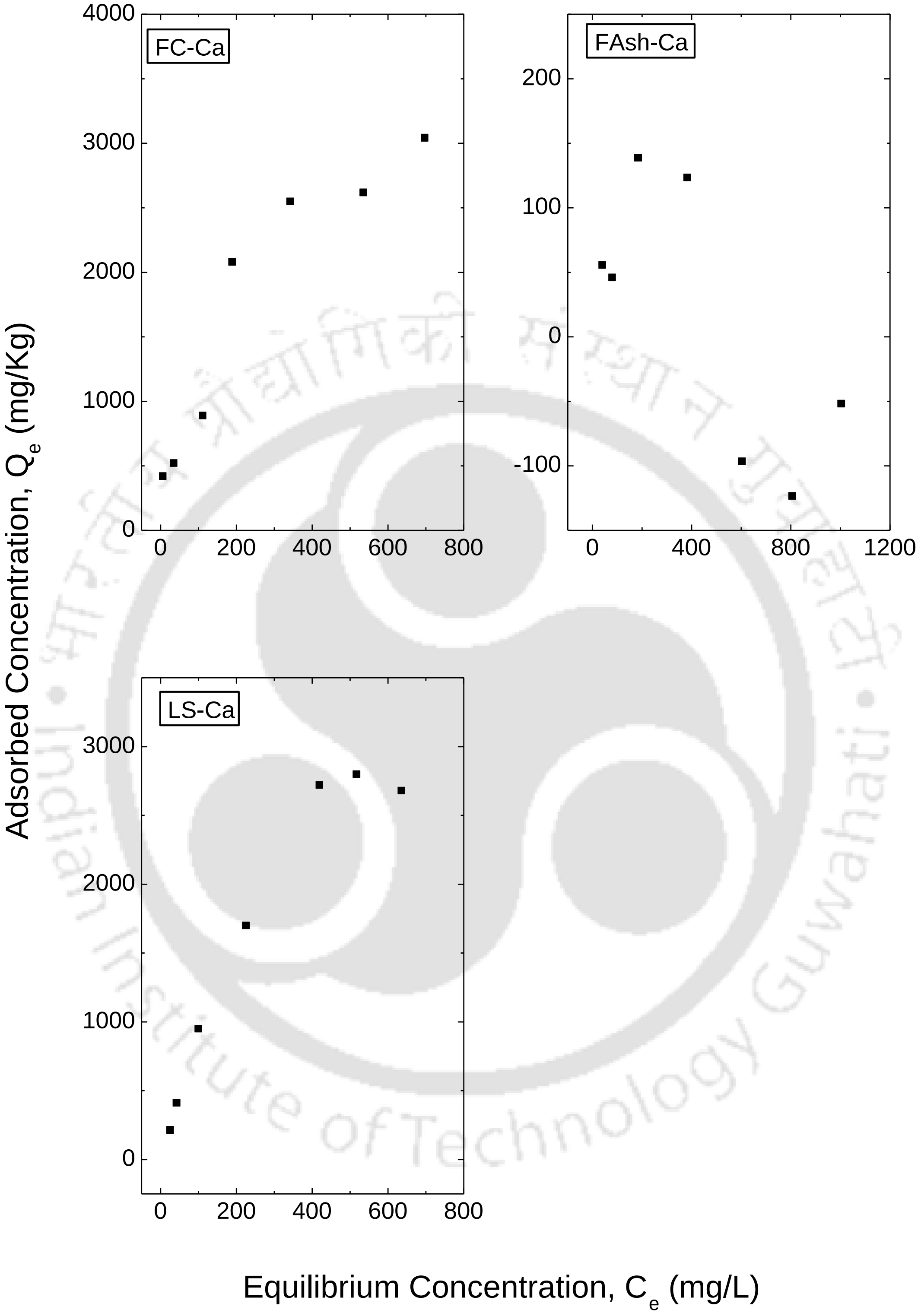


Fig. 5.8b Retention characteristics of Ca^{+2} on 3 soils from $CaCl_2$ solution

Table 5.4: Retention isotherm parameters for Ca^{+2} from $CaCl_2$ solution

Soil	Parameters						Best Fit
	Freundlich			Langmuir			
	K_F(L/Kg)	N	R^2	K_L(L/mg)	Q_m(mg/Kg)	R^2	
I Bent	558.14	0.53	0.97	0.00588	18633.56	0.99	Langmuir
FBent	458.81	0.54	0.97	0.00538	17211.77	0.98	Langmuir
RS	55.98	0.56	0.98	0.00264	3331.95	0.99	Langmuir
FC	114.79	0.51	0.93	0.00387	4123.10	0.95	Langmuir
Kao	264.77	0.54	0.98	0.00323	16752.23	0.99	Langmuir
LS	49.79	0.64	0.95	0.0025	4747.92	0.98	Langmuir
FAsh	-	-	-	-	-	-	-

5.5. Batch results for ammonium (NH_4^+) ion from NH_4Cl solution

Nitrogen is one of the essential elements for plants, and its depletion limits agricultural production. The frequent use of industrially manufactured nitrogen (N) fertilizers becomes a major source of ammonium in groundwater and surface water (Goodlass et al., 2003; Monaghan et al., 2007). The retention inhibits the movement of NH_4^+ through the soil to groundwater and thereby increasing its availability for plants. NH_4^+ also originate from diverse sources such as landfills, foul sewerage systems and contaminated industrial sites, animal manure, biological N fixation, mineralization from soil organic N. The presence of excess N compounds also causes environmental and water pollution. The NH_3 and NH_4^+ ions are the more commonly encountered N compounds in wastewater.

NH_4^+ has been regarded as a key indicator of groundwater contamination and it is considered for assessing groundwater pollution risk. Moreover, it is found in high concentrations even after centuries since it is not degraded under anaerobic conditions (Vrba and Romijn, 1986; Mikolajków 2003). Most of the reported literature deals with NH_4^+ retention on natural and commercially available zeolites (Kithome et al., 1998; Weber et al., 1983; Bernal and Lopez- Real, 1993; Lee et al., 2003). It is felt that studies are required to quantify the $NH4^+$ retention in soils (Buss et al., 2003; Pivato and Raga 2006; Wang et al., 2011). $NH4^+$ retention is explicitly related to the proportion of clay minerals (Griffin et al., 1976; Thornton et al., 2001) and it is implicitly related to lithology and/or mineralogy (Desimone et al., 1996; Kjeldsen and Christensen 1984; Thornton et al., 2000; Jackson 1989, Colley 1991). In the case of clay minerals, it has been found that mixed-layer clays (e.g. montmorillonite/smectite, including bentonite) generally attenuate ammonium more strongly than double layer clays (e.g. illite), which again attenuate more strongly than single layer clays (e.g. kaolinite) (Environment Agency 2000b; Griffin et al., 1976). This observation is common in many studies of cation exchange and is related to the respective specific cation exchange capacities of the different clays (Stumm 1992). It should also be noted that retention of NH_4^+ to illite and other 2:1 type clay minerals may be an effectively irreversible process since the NH_4^+ ion fits into the intra-layer clay lattice. In soils with considerable illite content, interlayer-fixed ammonium can typically account for 20 to 40% of the total nitrogen (Brady and Weil 2002). Even though there are studies appraising ammonium retention on clay minerals, further efforts are required to quantify ammonium interaction with natural soils. Such studies are required for predicting the fate of ammonium and the results can be used for risk assessment for landfills, effluent soak ways, contaminated sites etc. where mostly natural soils are present apart from engineered landfills.

In this study, NH_4^+ retention has been quantified for seven soils of varying physical characteristics using NH_4Cl solution ranging from 50 to 1000 mg/L. Solution pH of 7 is considered in the study. Literature indicates that NH_4^+ equilibrium in solution is largely pH dependent. Studies conducted by Wang et al., (2011) state that retention of NH_4^+ ion below pH 6 is relatively less due to the competition for exchange sites from hydrogen ions present in the solution. However, as pH increased to alkaline values, the adsorption capacity decreased slightly (Lin et al., 2007) because of the formation of ammonia. The reaction followed is $OH^- + NH_4^+ > H_2O + NH_3$. At pH 7, the capacity of adsorption reached a maximum. The equilibrium isotherms of NH_4^+ are shown in Fig 5.9a and 5.9b. It is observed from experimental data that an increase in the initial concentration led to an increase in the amount of NH_4^+ retained by almost all the soils. The various fitting parameters of the retention isotherms along with the goodness of fit (R^2) are listed in table. 5.5. Initially a sharp increase in capacity can be observed with increasing concentration, reaching a maximum. This maximum value is indicative of the fact that the ion exchange surface is increasingly saturated with the NH_4^+ ion. This is the maximum amount of NH_4^+ which can be exchanged on to the surface of the material under the experimental conditions and after this point further increases in solution concentration are ineffective in raising the soils retention capacity. The results also show that an increase in the initial NH_4^+ concentration led to a reduction in the retention at higher concentration, showing the process to be highly dependent on the initial concentration, this may lead to a possible saturation of the mono-layer coverage on the surface of almost all the soils by the NH_4^+ ions.

According to Gibes model the isotherm curves follows L type for IBent, FBent, Kao and RS indicating high affinity for retention of NH_4^+ ions at lower concentration and S type for soils FC, LS and FAsh indicating low affinity. It can be observed from table 5.5 that though both the isotherms (Langmuir and Freundlich) fitted well to the experimental data, there were some contradictions in the order of NH_4^+ retention of soils based on Freundlich K_F and langmuir Q_m values. Like previous cases, it was observed that soils with higher CEC and SSA exhibited high NH_4^+ retention and among all the soil FAsh has the least potential. .

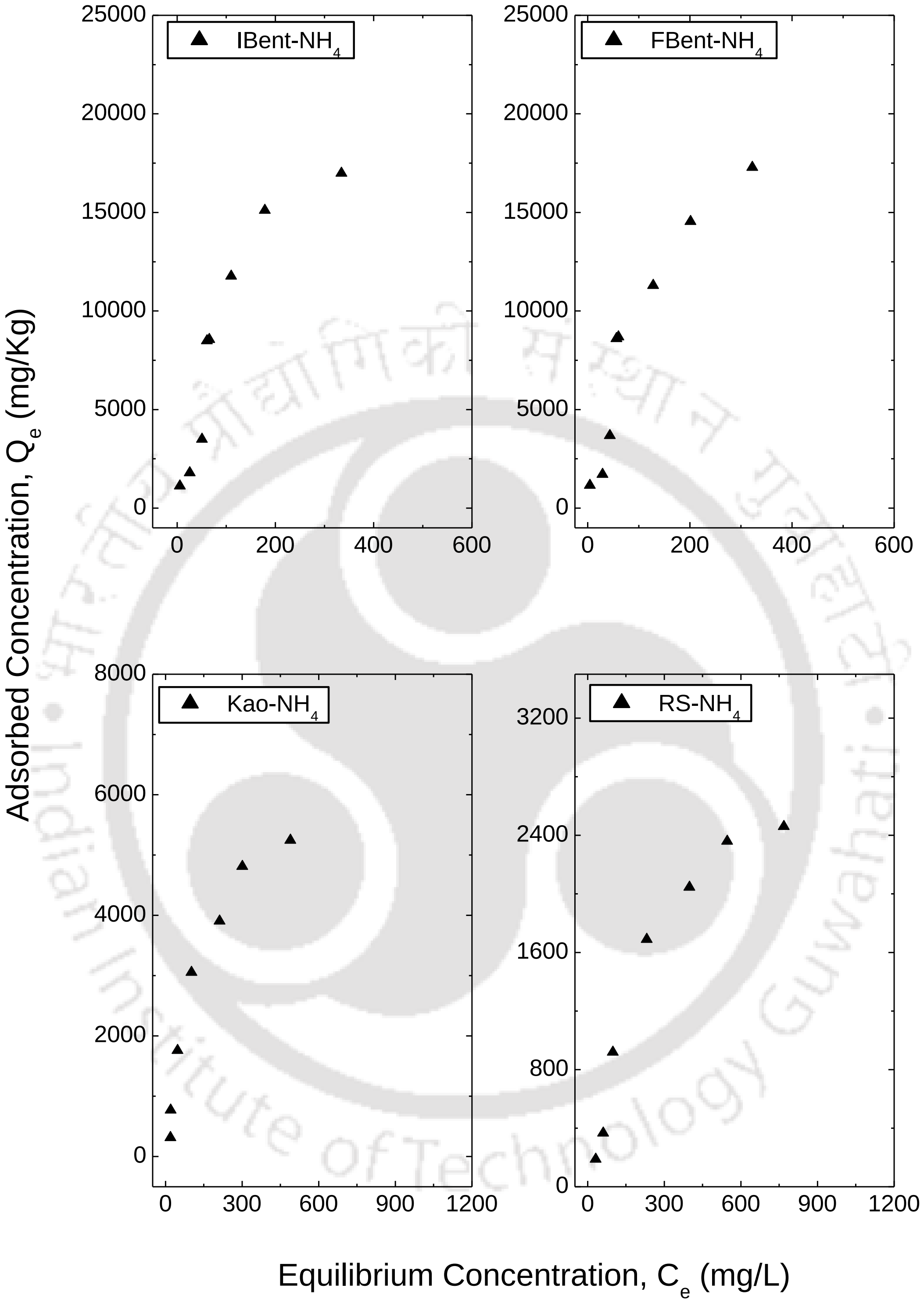


Fig. 5.9a. Retention characteristics of NH_4^+ on 4 soils from NH_4Cl solution

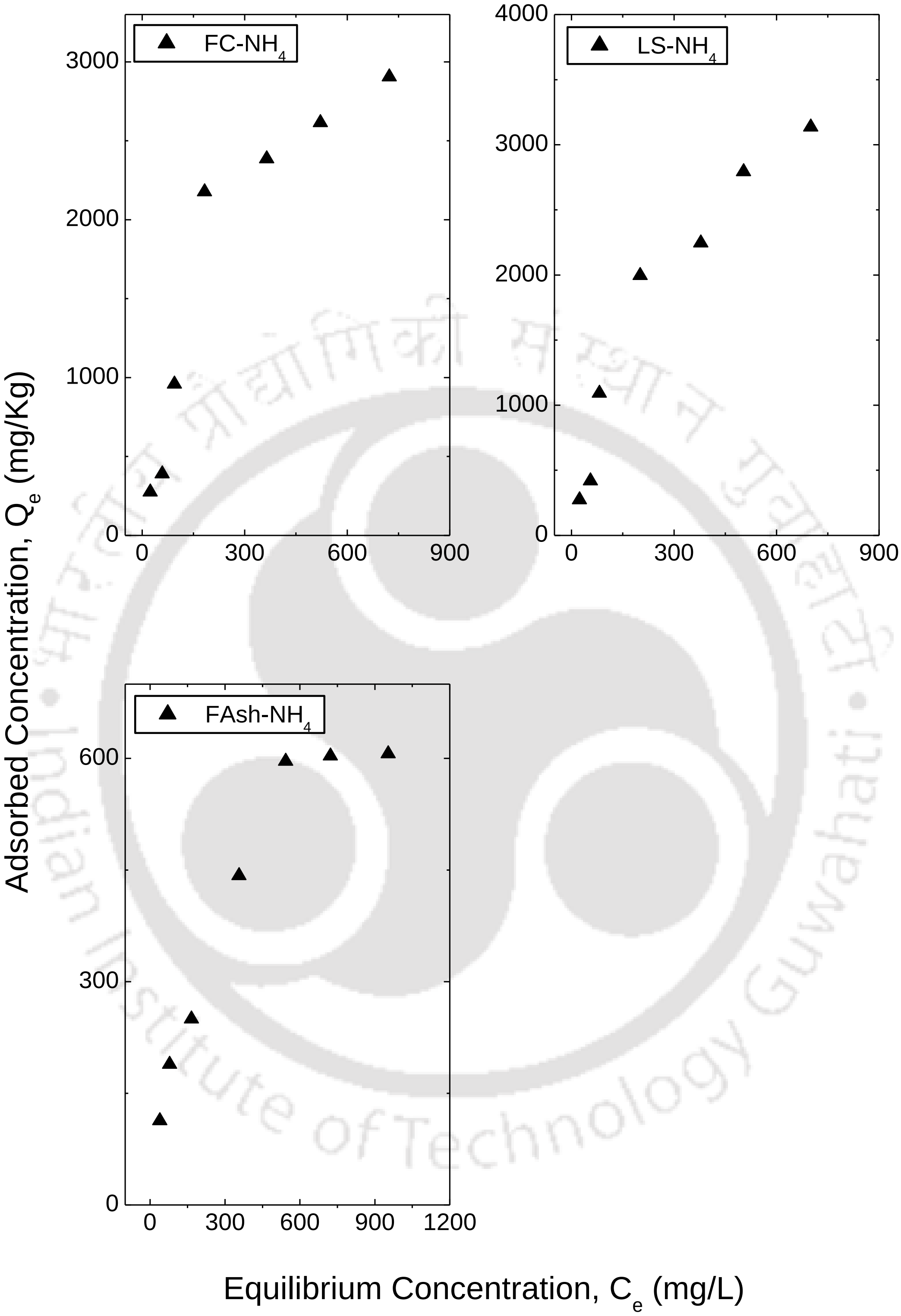


Fig. 5.9b. Retention characteristics of NH_4^+ on 3 soils from NH_4Cl solution

Taleb 5.5 Retention isotherm parameters for NH_4^+ from NH_4Cl solution

Soil	Parameters						Best Fit
	Freundlich			Langmuir			
	K_F(L/Kg)	N	R^2	K_L(L/mg)	Q_m(mg/Kg)	R^2	
IBent	682.49	0.57	0.88	0.00621	26596.63	0.93	Langmuir
FBent	628.22	0.58	0.91	0.00478	26300.21	0.93	Langmuir
RS	60.83	054	0.98	0.00247	3273.198	0.98	Freundlich
FC	99.83	0.52	0.89	0.0041	3951.42	0.94	Freundlich
Kao	229.53	0.52	0.94	0.0066	6983.96	0.98	Langmuir
LS	79.41	0.57	0.95	0.00337	4395.84	0.97	Langmuir
FAsh	23.80	0.49	0.94	0.0032	848.29	0.97	Langmuir

5.6 Batch results for divalent lead (Pb^{+2}) ion from $Pb(NO_3)_2$ solution

Pb^{+2} is one of the most commonly encountered heavy metals found at hazardous-waste sites (Sims et al., 1986). It is considered as toxic because of its tendency to bioaccumulate and damage the skeletons, internal organs, and nervous systems of animals (Luoma, 1983; Chaney et al.,1988; Gunn et al., 1988). Nitrate salt of lead was chosen because of its poor ability to complex metallic cations (Msaky and Calvet, 1990). Solutions at different concentrations were obtained by adding appropriate amounts of the stock solution to deionized water to obtain ion range of concentrations varying from 50 mg/L to 1200 mg/L. Literature indicates that the most important factor in controlling the partitioning of a metal to soil is the solution pH (Sposito 1984; Basta and Tabatabai 1992), thus Pb^{+2} equilibrium retention is largely pH dependent. Griffin and Shimp (1976) showed that clay minerals adsorbing increasing amounts of lead with increasing pH may also be attributed to the formation of lead carbonate precipitates which was observed when the solution pH value exceeded 5. The amount of Pb^{+2} retained on the soils increased sharply with pH, up to pH 5 and reached a maximum at pH 8.0 with only marginal increase between pH 6 and 8. The high dependence of Pb^{+2} retention on pH can be explained by the fact that pH will affect the surface charge of the adsorbent, degree of ionization and the speciation of adsorbate (Elliot and Huang 1981). According to Sparks (1995) there is a continuum between surface complexation (retention) and surface precipitation, and the separation of these processes is very difficult. The precipitation mechanism is often associated with neutral to alkaline soil conditions, relatively high concentrations of the heavy metal concerned, or low specific retention sites (Brummer 1986). At pH values above 6, lead is either retained on clay surfaces or forms lead carbonate. Therefore, a pH value of 5 is considered in this study. The solution pH was adjusted using dilute hydrochloric acid or sodium hydroxide solutions. The retention characteristics curves for Pb^{+2} contaminant solution is shown in Fig 5.10a and 5.10b. The retention curves showed that the amount of Pb^{+2} retained by all soil samples increased with the increasing amount of initial concentration. As can be noted from the figures, the experimental isotherm obtained for the retention of Pb^{+2} for lower concentration (unique for each soil) was nearly vertical line, revealing its total retention and its high affinity for the soil. This is in accordance with the findings of McLaren et al., (1981) who stated that at low concentration the retention of metals are essentially linear. Mohamed et al (1992) have stated that at low concentration, clay particles tend to disperse due to the full development of the diffuse double layer, and hence the surface area in contact with the solution will be maximum. After a certain point for some soils (FC, LS and FAsh) the retention approaches almost constant value. This phenomenon indicates that the retention sites on those soil retention sites become saturated with Pb^{+2}, and hence the retention decreases with further increasing of Pb^{+2} in the solution. On the basis of isotherm classification described by Giles et al., (1960) it can be observed that for Pb^{+2} retention data followed the H and L type of curve, which signifies a strong affinity between metallic cations and the sorbent surface for the entire concentration range and lower range respectively.

The retention data fitted well with both Freundlich and Langmuir retention isotherms as can be observed in table 5.6. The retention capacity for all soils follows the sequence FBent > IBent > Fash > RS > FC > Kao > LS based on Freundlich K_F parameter and IBent > FBent > Kao > LS > FC > RS > FAsh based on Langmuir Q_m values. It was observed that the soils vary in their metal binding strength. The maximum retention capacity of Kao compared to other clay IBent and FBent is less because of its non-expanding nature and highmolecular stability as a result of which isomorphous substitution is limited or nonexistent thus becoming the least reactive clay (Suraj et al., 1998). Also, the metal retention is usually accompanied by the release of hydrogen (H^+) ions from the edge sites of the mineral. It should be mentioned that interestingly, K_F and Q_m for FAsh was high demonstrating FAsh has a good retention potential for the Pb^{+2} metal species which generally behaved as a inert material for all the common ions. FAsh is a strong alkali material, and its pH value normally varied from 10 to 13 when added to water. So it can be expected that Pb^{+2} ions can be retained by precipitation or electrostatic retention. The pH value of the solution could affect the surface electricity property of FAsh, ionic strength and the existing form of metal ions in the solution. Under the strong acidic condition, the H^+ ions in the solution could neutralize the basic anhydride on the surface of FAsh, which decreased the retention ability of FAsh.

Under the strong alkaline condition, precipitation could occur. The mechanism of retention of ions is assumed to be the combination of the retention at the surface of FAsh together with the precipitation from the solution.

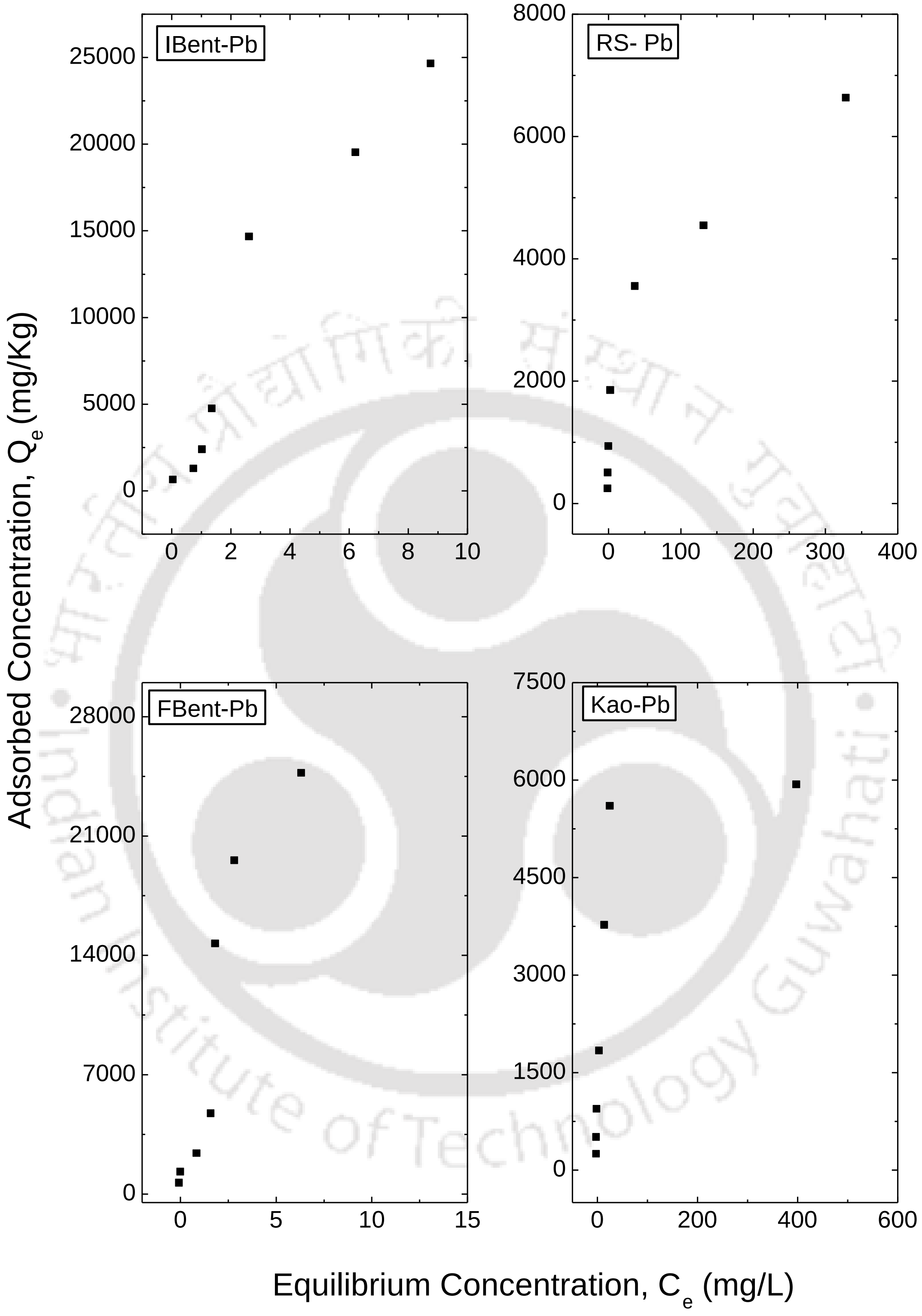


Fig.5.10a Retention characteristics of Pb^{+2} on 4 soils from $Pb(NO_3)_2$ solution

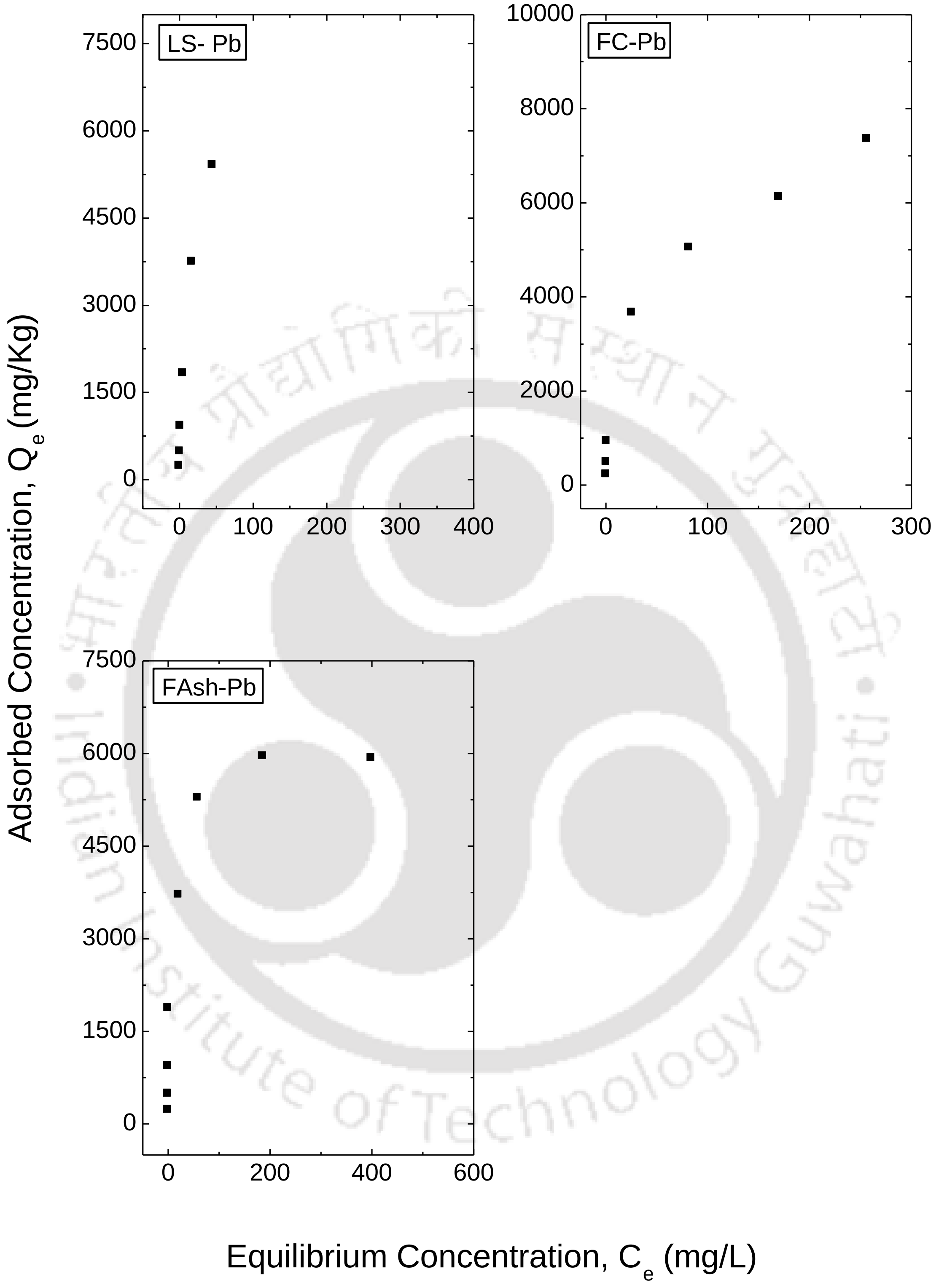


Fig.5.10b Retention characteristics of Pb^{+2} on 3 soils from $Pb(NO_3)_2$ solution

Table 5.6 Retention isotherm parameters for Pb^{+2} from $Pb(NO_3)_2$ solution

Soil	Parameters						Best Fit
	Freundlich			Langmuir			
	K_F(L/Kg)	N	R^2	K_L(L/mg)	Q_m(mg/Kg)	R^2	
IBent	4427.523	0.804	0.936	0.0803	59721.24	0.948	Langmuir
FBent	6575.96	0.746	0.855	0.122	58840.07	0.873	Langmuir
RS	858.252	0.351	0.979	0.0496	6103.928	0.931	Freundlich
FC	840.365	0.393	0.978	0.0301	7664.73	0.979	Langmuir
Kao	802.32	0.559	0.995	0.024	13982.53	0.992	Freundlich
LS	594.351	0.599	0.992	0.019	13697.19	0.974	Freundlich
FAsh	1410.82	0.263	0.885	0.132	5919.666	0.948	Langmuir

5.7. Batch results for divalent Cu^{+2} ion from single salt solution ($Cu(N0_3)_2.2.5\ H_20$)

Widespread use of Cu^{+2} in many anthropogenic activities like mining activities, waste emissions, and also being added to soils in the form of fertilizers, pesticides, live stock manures, sewage sludges, and industrial emissions has been reported by various researchers (Adriano, 1989; Flemming and Trevors, 1989; Tran et al.,1998; USEPA, 2009; Covelo et al., 2008; Lau and Stenstrom, 2005; USEPA, 2009). An understanding of the behaviour of Cu^{+2} in the soil is fundamental for the prediction of the environmental consequences of its incorporation in the environmental-ecosystem. The fate of Cu^{+2} is controlled by retention/release reactions, precipitation and complexation. These interactions influence the partition of the metal in the liquid and soil phases and are responsible for its mobility and bioavailability in the system. Copper exhibits strong retention properties to many mineral surfaces as well as soil organics (Kabata- Pendias, 2001; McBride et al., 1997; Elliott et al., 1986; McBride and Bouldin, 1984; Hickey and Kitrick, 1984; Vega et al., 2007; Yu et al., 2004). In many cases, clays have a little influence on Cu^{+2} retention (Vega et al., 2007). The 1:1 clays such as kaolinite have little affinity for Cu^{+2} (McBride,1978a). However, Martinez-Villegas and Martinez (2008) showed that Cu^{+2} retention was found in the order organic matter > montmorillonite > ferrihydrite (Martinez-Villegas and Martinez, 2008). Despite their limitations, the Freundlich and the Langmuir models have been used in various studies of Cu^{+2} retention (Petruzzelli et al., 1985; Temminghoff et al., 1994; Yuan and Lavkulich, 1997; Jordão et al., 2000) and may be useful to predict the behavior of metals in the soil.

A stock solution of Cu^{+2} was prepared by dissolving known amount of $Cu(N0_3)_2.2.5H_20$ (AR Grade) in deionized water for a range of concentration 50-1200 ppm. Literature indicates that Cu^{+2} equilibrium in solution is largely pH dependent. The solution pH was adjusted to 5 using dilute hydrochloric acid and sodium hydroxide solutions. The retention characteristics curves for Cu^{+2} contaminant solution is shown in Fig.5.11a and 5.11b. The figures show that the amount of Cu^{+2} retained by all soil samples increased with the increasing amount of Cu^{+2} used in the experiment, especially at lower concentration. As the concentrations increased, the increase in the retention progressively reduced. The process of Cu^{+2} retention probably occurred in two stages, with the saturation of different adsorptive sites. With the increase in the metal concentration, more sites were filled and Cu^{+2} retention reduced (Petruzzelli et al., 1985). Similar results were obtained by Jordão et al., (2000), who demonstrated the occurrence of two phases in the retention curve. The initial phase of the retention curve corresponded to high bonding energy, although some soils like (FC, FAsh and LS) had a low capacity for the retention of high quantities of the metal. In those case, although the soil retained a lower quantity of copper, the energy which kept it retained was sufficient for the metal not to be free in the system. The experimental isotherm obtained for the retention of Cu^{+2}, for all the soils followed a L type curve portraying its high affinity for the soil at lower concentration. In the second phase, higher quantities of Cu^{+2} are retained, although the retention energy is lower. Thus, each linear portion of the retention curve suggests different types of retention sites responsible for Cu^{+2} retention in the soil. All retention curves show linear pattern at lower concentration, and approach maximum retention (Q_m) with increasing equilibrium concentration of Cu^{+2}. The maximum retention values were obtained for bentonites, highlighting its higher capacity for retaining Cu^{+2} compared to other soils. The higher values of Cu^{+2} retention for I Bent and F Bent could be related to the mineralogy, high SSA, pH and CEC. Kuo and Baker (1980) reported that the Cu^{+2} retention occurs even when the pH values of the soil are below the zero point of charge .This is evident with the case of FAsh that inspite of although has low CEC, no clay content, and low SSA, the values of Q_m were close to those found for RS and LS.

As can be observed from Table 5.7 both Freundlich and Langmuir were used to quantify the Cu^{+2} retention. The best fit coefficients obtained in the present study varied between 0.865 and 0.99, indicating that these isotherms can represent soil-Cu^{+2} interaction conditions very well. The parameters derived from the isotherms fit were convenient for comparative assessment of different soils. Atanassova and Okazaki (1997) observed correlation coefficients of approximately 0.96 and 0.99 for the Langmuir and the Freundlich equations, respectively, in soils with different mineralogical compositions and physico-chemical properties. Yuan and Lavkulich (1997) found high correlation between the retention of Cu^{+2} and the “K” parameter of the Freundlich model (R^2 = 0.98 to 0.99) for different soil samples. The Freundlich distribution coefficient, K_F ranged from 305.083 to 4159.567 L/Kg . The retention capacity for all soils based on K_F paramter can be ranked as follows: IBent > FBent > Kao > FC > LS > RS > FAsh. The Freundlich constant N which indicates retention intensity (Jalali and Mohharrami 2007; Hosseinpur and Dandanmozd 2010) ranged from (0.192 to 0.621). The maximum retention capacity, Q_m obtained from Langmuir isotherm can be ranked as FBent > IBent > LS > RS > Kao > FC > FAsh. It was observed that the soils vary in their metal binding strength. The Q_{max} ranged from 1333.23 (FAsh) to 38737.93 (FBent). This thirty times variation was associated to the soil type, especially to the mineralogy.

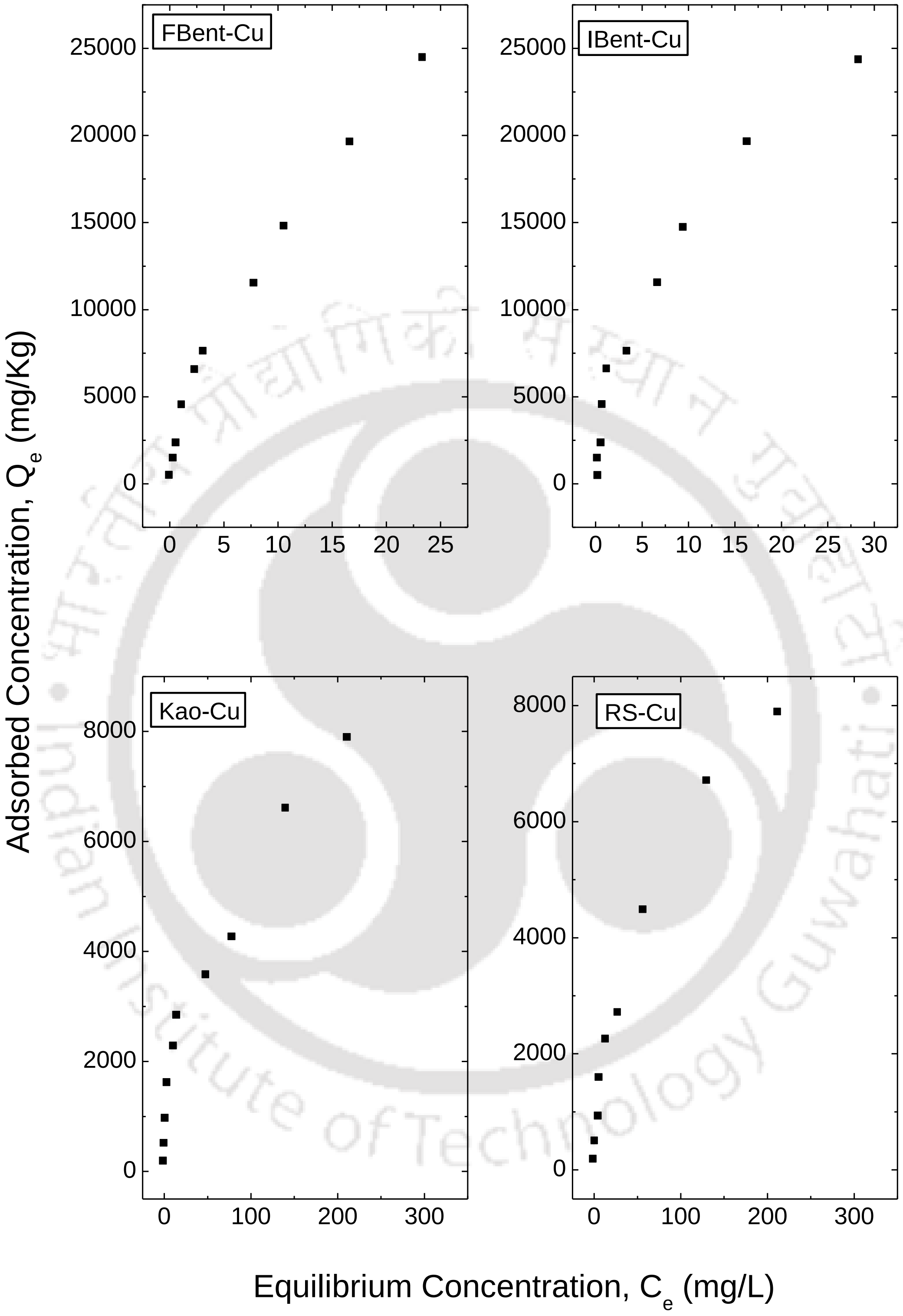


Fig.5.11a Retention characteristics of Cu^{+2} on 4 soils from $Cu(N0_3)_2.2.5H_20$ solution

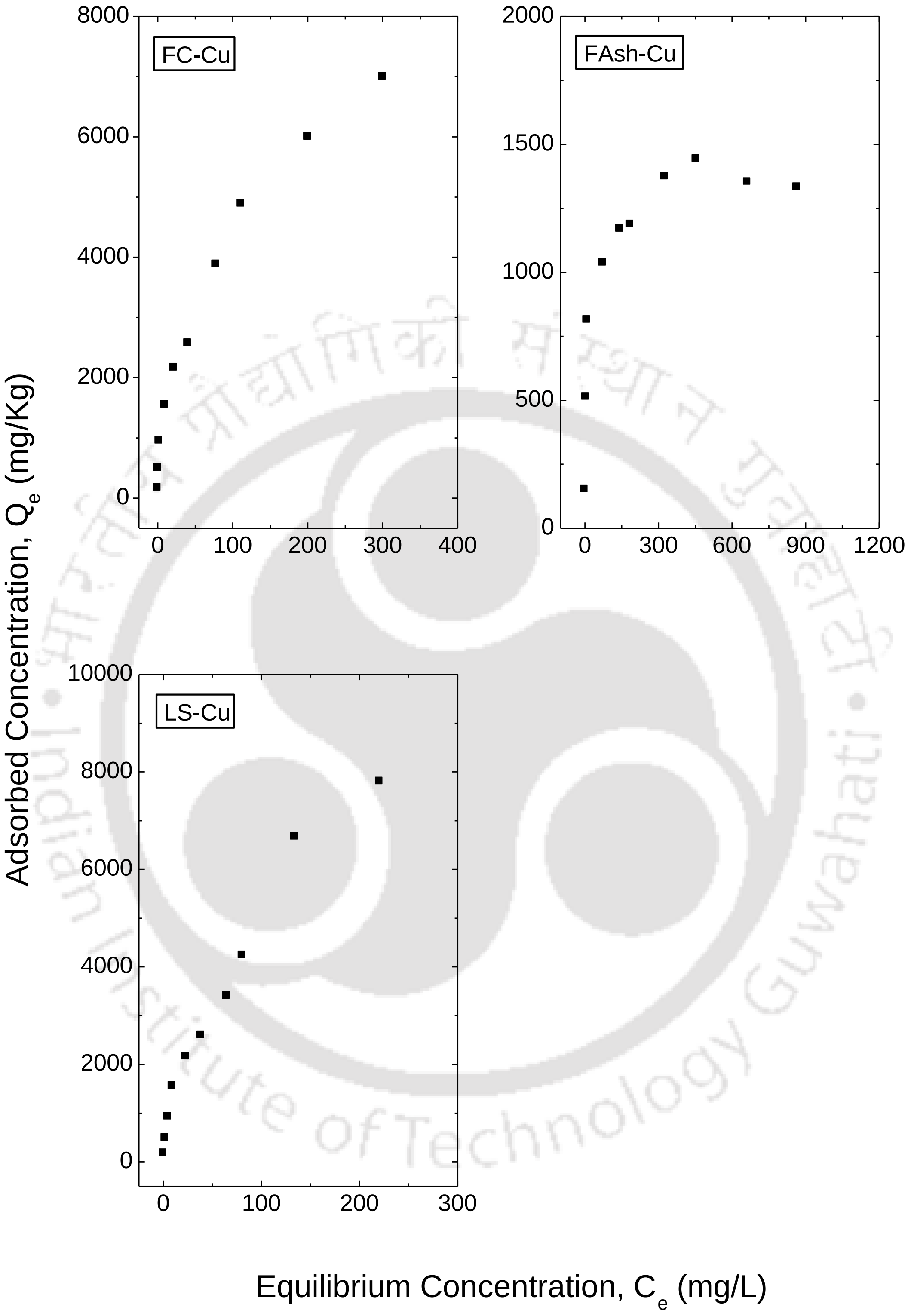


Fig. 5.11b Retention characteristics of Cu $^{+2}$ on 3 soils from $Cu(N0_3)_2.2.5H_20$ solution

Table 5.7 Retention isotherm parameters for Cu^{+2} (single salt) for all soils

Soil	Parameters						Best Fit
	Freundlich			Langmuir			
	K_F(L/Kg)	N	R^2	K_L(L/mg)	Q_m(mg/Kg)	R^2	
IBent	4159.56	0.54	0.98	0.0948	32340.95	0.97	Freundlich
FBent	3414.45	0.62	0.99	0.0643	38737.93	0.98	Freundlich
RS	516.821	0.51	0.99	0.01529	10081.58	0.99	Freundlich
FC	509.45	0.46	0.99	0.0122	8569.17	0.97	Freundlich
Kao	662.89	0.46	0.98	0.01922	8895.06	0.92	Freundlich
LS	305.08	0.60	0.98	0.00646	13314.06	0.97	Freundlich
FA	412.82	0.19	0.86	0.10663	1333.24	0.95	Langmuir

5.8. Batch results for divalent Ni^{+2} ion from ($Ni(NO_3)_2.6H_2O$) solution

Nickel among other toxic metals, are discharged into the environment from a wide range of industries, including microelectronics, electroplating, battery manufacture, dyestuffs, chemical, pharmaceutical, metallurgical, tanneries etc (Tchobanoglous and Burton, 1991; Volesky and Holan, 1995; Slacka et al., 2005; Amarasinghe et al., 2007; Mohan et al., 2009 ; Musapatika et al., 2010). Because of their extreme toxicity and non-biodegradable nature it has become a major health hazards in living organisms even in relatively low concentrations (Malakul et al .1998; Mohan et al., 2002 ; Bansal et al., 2009; Babarinde et al., 2011). Ni^{+2} retention depend greatly on the pH, regardless of soil, and increased sharply with the increase in pH from 4.0 to 6.0, where 20-90% Ni^{+2} retention occurred (Soares 2011). Many retention studies with mineral soils have shown increase in Ni^{+2} retention with increase in pH (Harter, 1983; Elzinga and Sparks, 2001). Harter (1983) and Beukes et al., (2000) reported that metal retention was pH-dependent and that the intensity of the phenomenon increased drastically above pH 7.0. In the present study a pH of 5 is considered. A stock solution of Ni^{+2} ions was prepared by dissolving known amount of Ni^{+2} in the form of hydrated A.R. grade nitrate salt ($Ni(NO_3)_2.6H_2O$) in deionized water . Solutions at different concentrations were obtained by adding appropriate amounts of the stock solution to deionized water to obtain ion range of concentrations varying from 50 mg/l to 1200 mg/L.

Fig 5.12a and 5.12b shows the retention characteristics of soils of Ni^{+2} on seven soils .All curves showed a non linear shape and the amount of Ni^{+2} retained by all soil samples increased with the increasing amount of Ni^{+2}. It can be observed that the experimental isotherm obtained for the retention of Ni^{+2} for lower concentration in all the soils revealed its high retention and affinity for the soil. This phenomenon can be the result of inner-sphere type surface complexing mechanisms, or to significant retention processes mediated by van der Waals interactions (Sposito, 1989), or to the predominance of hydrolyzed metallic species (James and Healy, 1972, Echeverría et al., 2003). On the basis of isotherm classification described by Giles et al.,(1960), it is observed that Ni^{+2} retention data followed the S type for LS, FC and FAsh characterized by a small initial slope which remained constant and was not related to the equilibrium concentration (Sposito, 1989). The high initial slope in the H-type isotherms is shown by IBent, FBent and Kao which suggest high affinity of the soil for Ni^{+2}, L type was observed for soil RS which signifies a strong affinity between metallic cations and the sorbent surface at lower concentration. Sparks (1995) argued that in soils where kaolinite and illite minerals are dominant, (Kao, LS, FC) sorption is due to ion exchange (electro-static) formation of outer-sphere complexes. Whearas for soils dominated with smectite type minerals (IBent, FBent and RS) nner-sphere complexes are formed. Serrano et al. 2005 have stated that Ni^{+2} retained as outer-sphere complexes is considered mobile whereas with inner-sphere complexes strong affinity of heavy metals is expected

As can be observed from table 5.8, the retention for all soils according to K_F and Q_m parameter can be ranked as follows: IBent > FBent > FC > Kao > RS > FC > LS > FAsh. It was observed that the soils vary in their metal binding strength. The Ni Q_{max} ranged from 1457.34 mg/Kg (RS) to 17059.52 mg/Kg (FBent). It was seen that FAsh has the potential to adsorb Ni^{+2} and its retention performance are comparable to other soils like LS and RS. However, in most of these seven soils, Langmuir's retention isotherm was predominant than Freundlich models which conflicted with the earlier studies of Al-Hamden and Reddy (2006) and Sunil Kumar et al., (2009) as observed in Table 5.8. Freundlich's K_F values varied from 269.101 L/Kg for FAsh to 3391.576 L/Kg for IBent. But different trends was followed in Langmuir retention isotherm where Q_m values were found to be minimum for RS and maximum for FBent.

Earlier researchers have reported about the enhanced retention of metals with increasing soil pH (Harter, 1983; Msaky and Calvet,1990; Basta and Tabatai, 1992; Raghupathi and Vasuki, 1993), which is attributed to the generation of pH-dependent sites on colloids, reduced competition with H-ions and a change in the hydrolysis state of ions in solution. According to Gomes et al., (2001), soils having higher pH values were the ones with highest relative capacity to absorb metal ions. The enhancement in Ni^{+2} retention at higher alkaline pH levels may be attributed to the hydroxide precipitation reactions with Ni^{+2} and

$NiOH^+$ species as reported by Sen Gupta and Bhattacharyya (2006). The findings obtained in the present study retaliates that the retention capacity of the soil cannot be governed solely by its pH value. As for example even though FAsh had a very high pH value around 9 its K_F and Q_m value was less compared to other soil with relatively low pH. The findings obtained in the present study are in agreement with Reddy and Dunn (1986), Jalali and Moharrami (2007) who reported that the abundance of exchange sites available for Ni^{+2} on high CEC and SSA soils were responsible for higher K_F and Q_m. The presence of Al^{+3} in acidic soils like FC, LS and RS and its competition for exchange sites might have resulted in reduced Ni^{+2} retention in these soils (Cavallaro and McBride, 1978). In addition, the Fe-oxides present in acidic soils FC may be responsible for the low retention capacity of Ni^{+2} by blocking access of Ni^{+2} to exchange sites as reported by Cowan et al., (1992). As observed for the soil FAsh in Fig. 5.12b, it was found that a fall in the curve at higher range of concentration, which indicated that the retention sites become saturated with Ni^{+2}, and the retention decreases with further increasing of Ni^{+2} in the solution. This unusual reduction (not being constant when saturation is reached) may be linked to the decrease of bonding energy at higher concentration leading to some retained ions being free. For the other soils (RS, FC and LS) the retention curves show linear pattern at lower concentration, and become constant, i.e. reach the maximum retention (Q_m) with increasing concentration of Ni^{+2}. For I Bent, F Bent and Kao there was an increase in retention with the increase of concentration which indicates that the retention sites are not completely occupied.

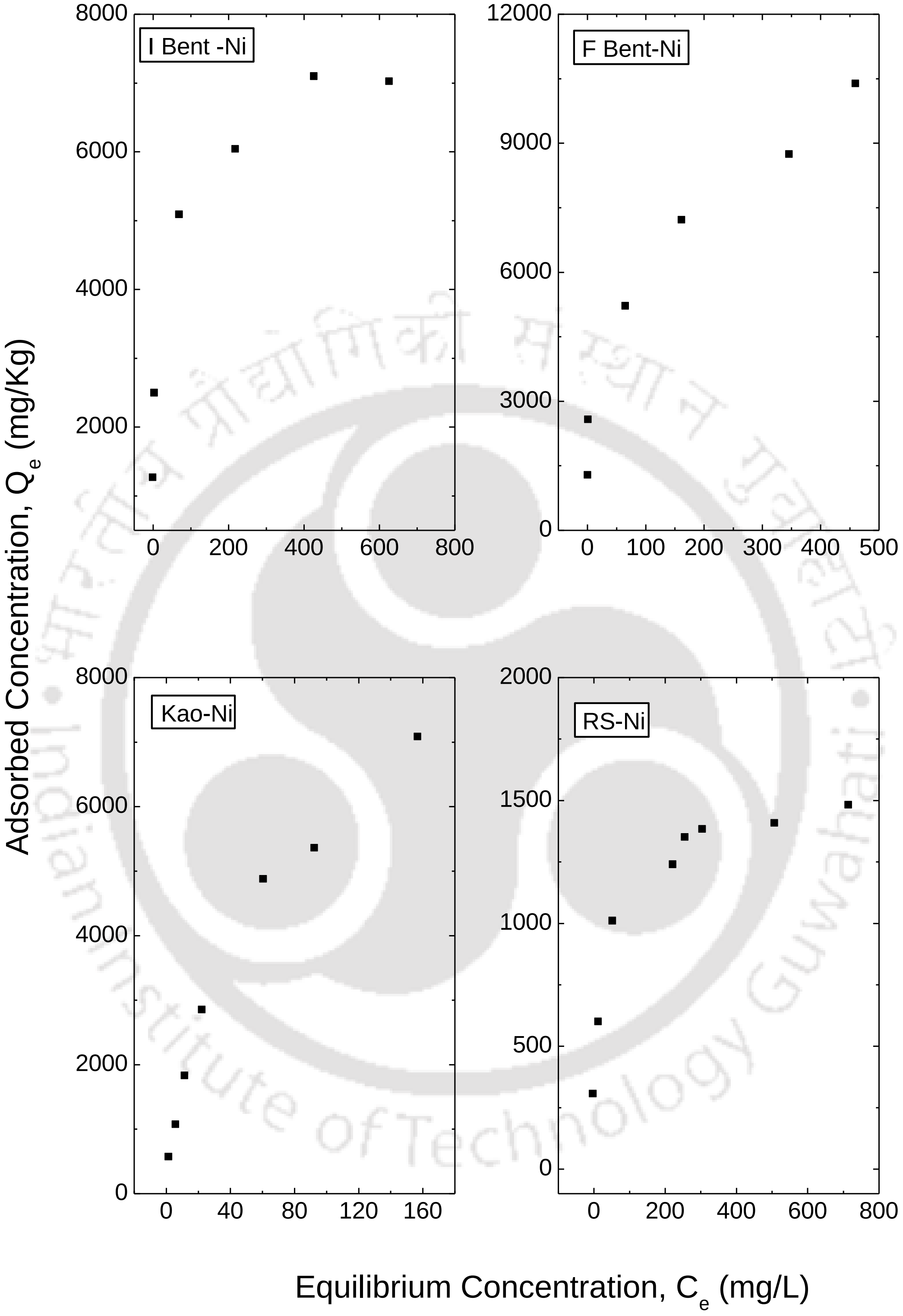


Fig.5.12a Retention characteristics of soils in Ni^{+2} on 4 soils from $Ni(N0_3)_2.2.5H_20$ solution

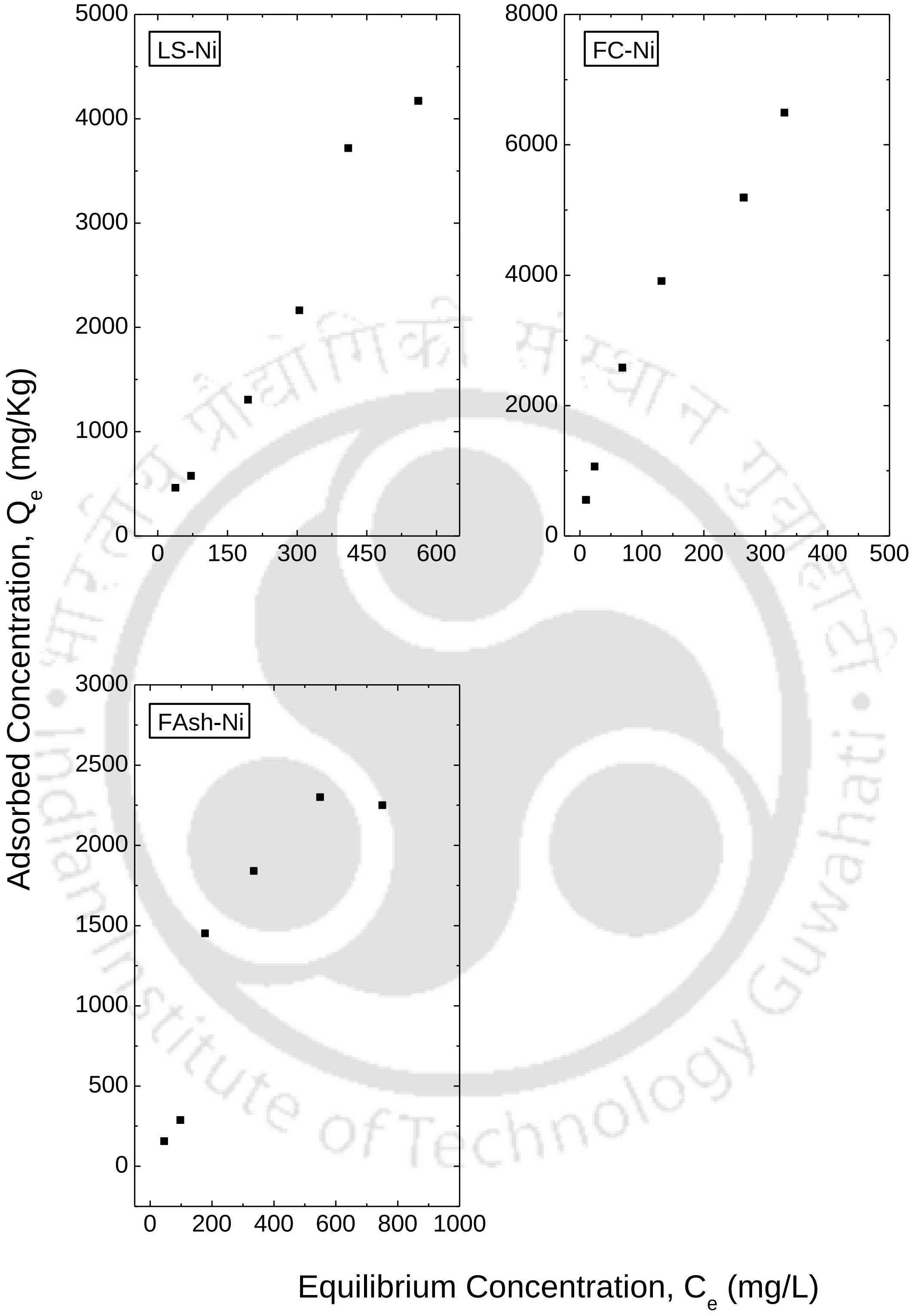


Fig. 5.12b Retention characteristics of soils in Ni^{+2} on 4 soils from $Ni(N0_3)_2.2.5H_20$ solution

Table 5.8 Retention isotherm parameters for Ni^{+2} (single salt) for all soils

Soil	Parameters						Best Fit
	Freundlich			Langmuir			
	K_F(L/Kg)	N	R^2	K_L(L/mg)	Q_m(mg/Kg)	R^2	
IBent	3391.58	0.25	0.94	0.195	12417.94	0.95	Langmuir
FBent	2735.79	0.36	0.98	0.059	17059.52	0.89	Freundlich
RS	360.81	0.22	0.96	0.044	1457.34	0.96	Langmuir
FC	639.85	0.31	0.95	0.175	2705.86	0.94	Freundlich
Kao	501.72	0.53	0.98	0.019	9066.55	0.99	Langmuir
LS	451.77	0.20	0.91	0.060	1587.04	0.96	Langmuir
FA	269.10	0.27	0.91	0.0201	1594.25	0.98	Langmuir

5.9. Batch results for divalent Zn^{+2} ion from $Zn(NO_3)_2$ solution

Zinc is considered one of the most mobile heavy metals in surface waters and groundwater because it is present as soluble compounds at neutral and acidic pH values. At higher pH values, zinc can form carbonate and hydroxide complexes which control zinc solubility. Zinc readily precipitates under reducing conditions and in highly polluted systems when it is present at very high concentrations, and may co precipitate with hydrous oxides of iron or manganese (Smith et al., 1995). The availability of Zn^{+2} in soil is mostly regulated by retention-release process and its partitioning between the solution and solid phases (Gaudalix and Pardo, 1995; Catlett et al., 2002). Several studies have been reported on Zn^{+2} retention of soils (Gerritse et al., 1982; Christensen, 1984; Gerritse and Van Driel, 1984; Fuller and Davies, 1987, Abraham et al., 1989; Basta and Tabatabai, 1992; Chairidchai ; Ritchie, 1992; Schulte and Beese, 1994; Escrig, 1995).

Many investigators have reported that Zn^{+2} retention increases with increasing pH (Bart-Tal et al., 1988; Bar- Yousef, 1979; Guadalix and Pardu, 1995; Harter 1983; Bar-Tal, Bar-Yosef, and Chen 1988; Stahl and James 1991; Dang et al., 1994). On the contrary, some investigators, such as Saeed and Fox (1977) reported that Zn^{+2} retention decreased with increasing pH. In general, the shapes of Zn^{+2} retention isotherms at identical equilibrium solution differ among soils and vary with pH for a particular soil. The number of exchange and specific retention sites increases with pH (Mann and Ritchie 1993). Zn^{+2} retention by oxides and hydroxides has also been reported to be strongly pH dependent (Kalbasi, Racz, and Loewen-Rudgers 1978). Hence, pH plays a predominant role in the partitioning of Zn^{+2} between solid and liquid phases of soils. Indeed, it was observed by Fotovat et al., (1996) that solubility of Zn^{+2} in soil is directly related to pH, irrespective of the total Zn^{+2} concentration in the soil. Reduction of Zn^{+2} solubility based upon solution concentrations in the soil has been shown to be about 30-fold for every unit of pH increase in the pH range of 5–7 (McBride and Blasiak 1979). In the present study, a pH value of 5 is considered. Fig 5.13a and 5.13b shows the retention characteristics of Zn^{+2} in seven soils. The isotherm parameters obtained is listed in Table 5.9. The trend based on Freundlich isotherm parameters for retention capacity follows IBent > FBent > Kao > RS > FC > LS > FAsh and based on Langmuir Q_m value, the maximum retention of Zn^{+2} was seen on IBent soil and the minimum in FAsh. The maximum retention of Zn^{+2} in IBent soil is attributed to high amount of clay and relatively high pH. The soil pH influences not only the amount of Zn^{+2} retained but also the shape of the retention isotherm (Barrow et al., 1981; Harter 1983; Barrow 1986; Msaky and Calvet 1990). The higher pH increased the retention of Zn^{+2} as a result of complexation of Zn^{+2} by OH ions and a higher net negative charge (Shuman, 1986). Research conducted by Ford et al., (1999), Voegelin et al., (2002), and Manceau et al., (2005) have confirmed in their studies that when Zn^{+2} ion get released into the soils, it gets sorbed to various soil components such as clay minerals, organic matter, Fe and Mn oxides, and to carbonates. Referring to the elemental composition of FAsh it was observed that a high amount of FeO was present (23.69) and MgO (0.80) which might be responsible for its comparable value of retention with respect to other soils inspite of its negligible clay content, CEC and SSA. It was observed that during the process of metal retention to clay minerals under ambient soil conditions, metal surface precipitates may also form. In other words, metal retention onto soil minerals not only results in retained (outer- and inner-sphere complexes) phases but may also result in precipitated phases occurring at the surfaces of phyllosilicate minerals. These 'precipitate phases' or 'newly forming mineral phases' include layered double hydroxide (LDH), phyllosilicate type and hydroxide type precipitates, which explains the high retention capacity of soils rich in smectite minerals (IBent, FBent, RS and Kao). Another type of layered Zn^{+2} phase may form under acidic conditions when Zn^{+2} enters the Al-hydroxy (Al-OH) interlayers of clay minerals (Voegelin et al., 2005; Scheinost et al., 2002).

With increasing pH values slow retention reactions and Zn^{+2} incorporation into new formed precipitates tend to become more prominent (Nachtegaal and Sparks, 2004; Voegelin et al., 2002). The formation of Zn^{+2} containing phyllosilicate, layered double hydroxide, or formation of inner sphere retention complexes are unlikely under strongly acidic conditions. Therefore, a higher pH favours Zn^{+2} retention. In addition, the clays have high retention sites that allow the non-exchangeable (specific) retention of Zn^{+2} (Randal and Bruce, 1991). It can be noted in the present study that though pH influences the retention, it itself is not the dominant factor in retention of Zn^{+2} for all soils. CEC, SSA, mineralogy plays a major role in the retention capacity capacity (Shukla and Mittal, 1979). According to Giles et al.,1960 are thought to reflect the type of retention mechanism taking place. It was observed that Zn^{+2} retention data followed the ‘L’ type of curve for IBent, FBent and Kaolinite whearas for LS, RS, FC and Fash it follows the 'S' type of curve which indicates less affinity.

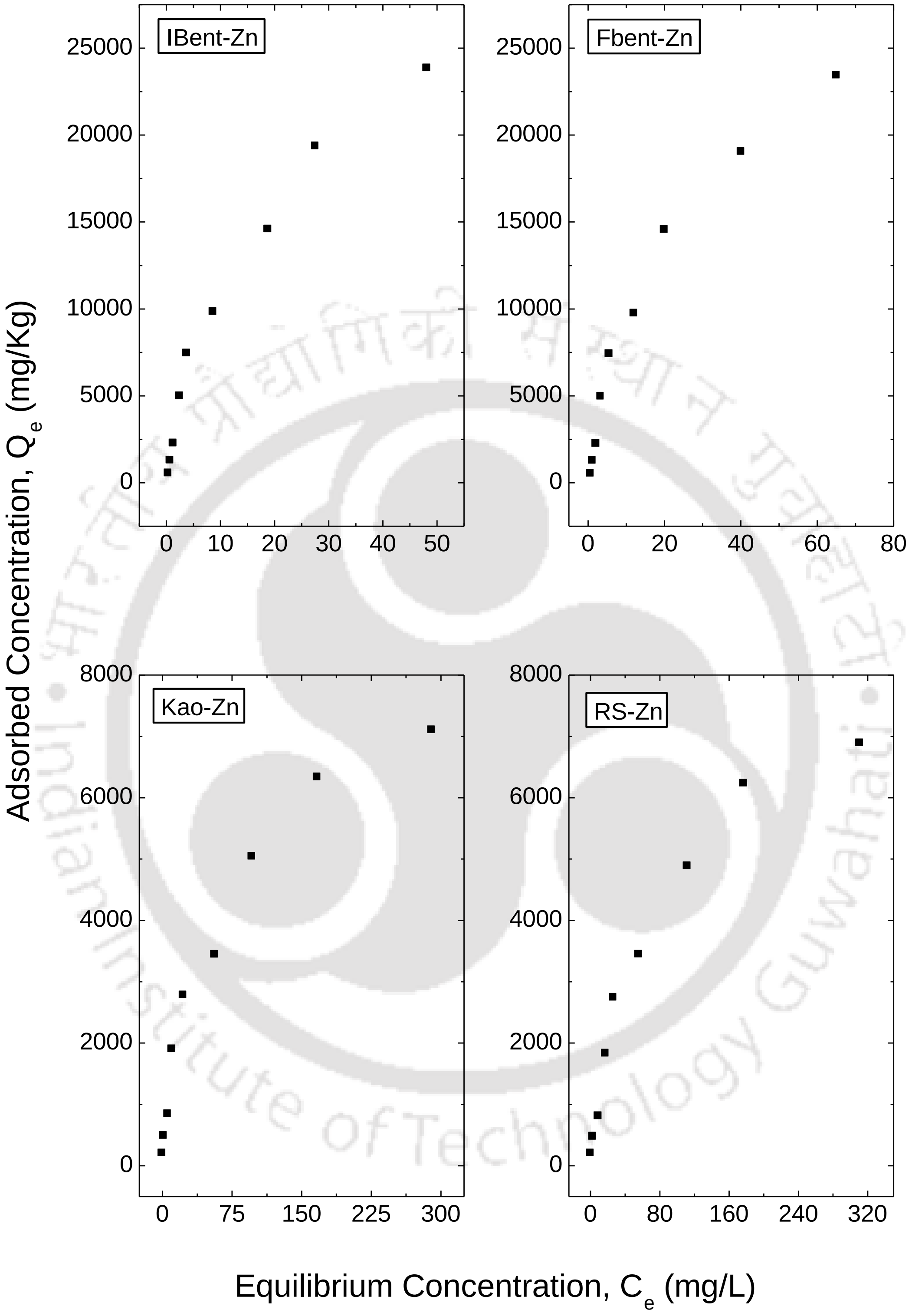


Fig. 5.13a Retention characteristics of Zn^{+2} on 4 soils from $Zn(NO_3)_2$ solution

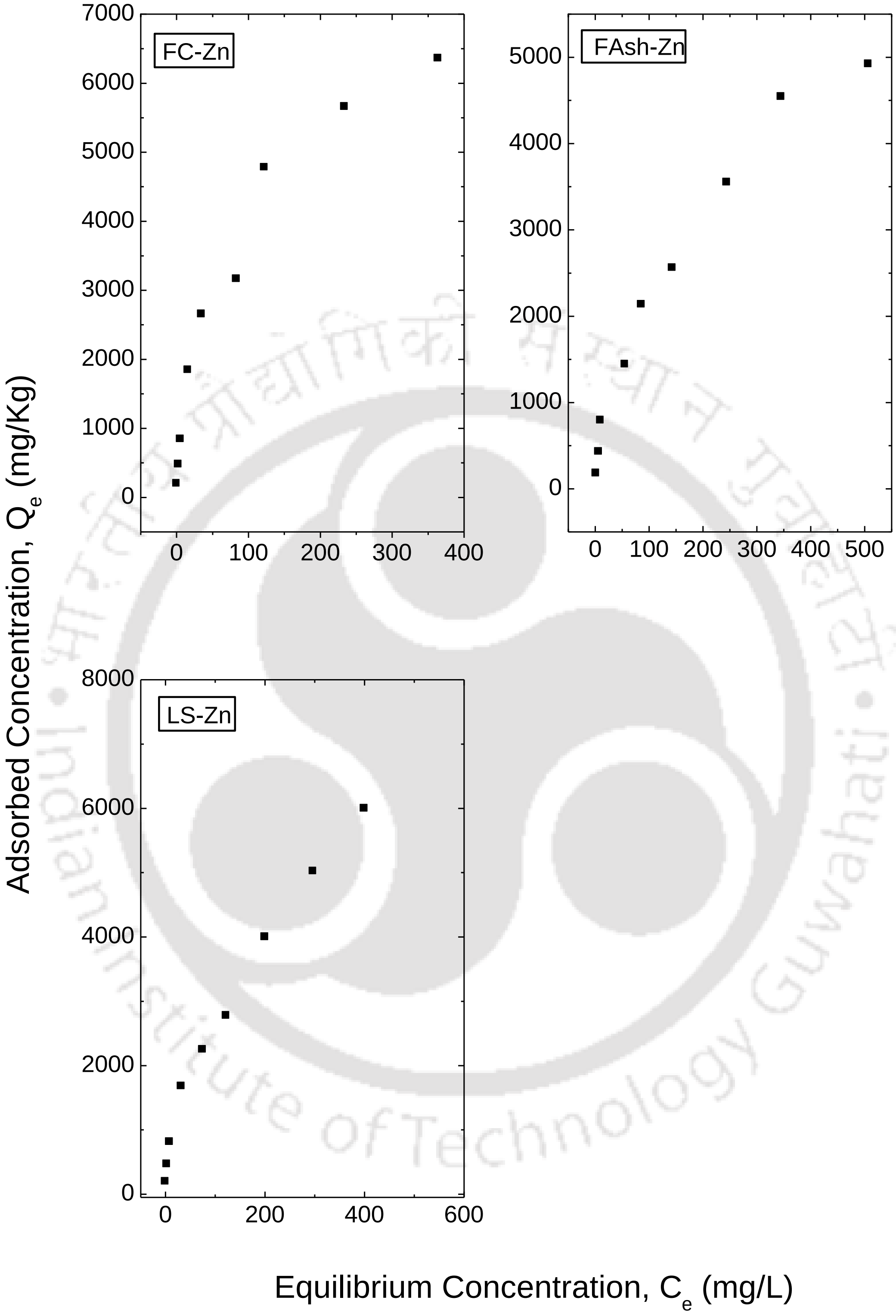


Fig. 5.13b Retention characteristics of Zn^{+2} on 3 soils from $Zn(NO_3)_2$ solution

Table 5.9 Retention isotherm parameters for Zn^{+2} (single salt) for all soils

Soil	Parameters						Best Fit
	Freundlich			Langmuir			
	K_F(L/Kg)	N	R^2	K_L(L/mg)	Q_m(mg/Kg)	R^2	
IBent	2735.15	0.568	0.98	0.0524	32291.16	0.98	Freundlich
FBent	2290.87	0.566	0.97	0.041	312565	0.99	Langmuir
RS	471.03	0.48	0.97	0.0135	8488.91	0.99	Langmuir
FC	486.48	0.444	0.98	0.014	7394.24	0.97	both
Kao	576.66	0.453	0.97	0.0169	8347.25	0.98	Freundlich
LS	190.97	0.573	0.99	0.0041	9276.42	0.98	Langmuir
FAsh	182.07	0.537	0.989	0.0045	7070.95	0.98	Freundlich

6.0 Summary

This section of the study investigates single contaminant soil interaction for common ions (Na^+, K^+, $NH4^+$ and Ca^{+2}) and heavy metals (Cu^{+2}, Pb^{+2}, Zn^{+2} and Ni^{+2}) in seven different soils.

1. The study indicates that for soil dominant with smectite minerals (IBent and FBent) there was a huge release of Na^+ for the entire range of concentration considered in this study. The same was observed for FAsh but the release was noticeably less. For soil RS at lower range of equilibrium concentration there was scatter of data and desorption was observed whereas at higher range of concentration sorption was observed and isotherm fitting were done. For the remaining soils FC, Kao and LS a minimal amount of retention of Na^+ was observed.
2. For most of the soils, the retention behaviour of K^+ and NH_4^+ is comparable because of its unique characteristics. It can be noted that for FAsh at higher range of concentration there was a small amount of release happening for K^+ whereas for Ca^{+2} there was release for the entire range of concentration this was attributed to the abundance of Ca^{+2} ion present in FAsh. For soil Kao, Ca^{+2} was found to retain much better than the remaining soils. It can be observed that the retention of K^+, NH_4^+ and Ca^{+2} was much higher than that of Na^+ in all the cases.
3. The retention results on single heavy metals indicates that for majority of the soils Pb^{+2} was found to be the highest sorbing metal followed by Cu^{+2} (except FAsh), Zn^{+2} (except Kao) and Ni^{+2}.

4. It can be highlighted from the present study that range of concentration has significant effect on single ions retention in soils. Simple linear isotherms are appropriate only for small range of concentration and for low concentration.
5. It was observed that FAsh and the locally available soils (RS. LS) proved to be efficient in retaining many heavy metals which is advantageous from environmental and economical perspective

Chapter 6

Experimental evaluation of soil -multiple contaminant interaction

6.1. General

Competing ions can have a marked effect on ion retention by soils (Murali and Aylmore, 1983). Complexities of the soil system have generally constrained researchers to use a single ion at near-zero ionic strength. Extensive studies were conducted on the interaction of single metal ions with various minerals and soils (Vasudevan et al., 2002; Vega et al., 2006; Scheinost et al., 2001; Trivedi 2001; Gomes et al., 2001; Serrano et al., 2005; Saha et al., 2002; Spark et al., 1995). There are a few studies to understand competitive retention of heavy metals on various adsorbents like pure minerals (Forbes et al.,1976; Saha et al., 2002; Spark et al., 1995), organic compounds (Elliott et al., 1986; Saha et al., 2002) and acid soils (Arias et al., 2006, Fontes and Gomes 2003; Fontes et al., 2000; Gao et al., 1997; Gomes et al., 2001; Naidu et al.,1998; Serrano et al., 2005). Not many systematic efforts were made to comprehend the interaction of various model multiple contaminants (common ions and heavy metals) with wide variety of soils, which is attempted in this study. This chapter deals with the multiple contaminant interaction of common ions and heavy metals with soils. For this purpose, the single ions discussed in chapter 5 are used in combination.

Another important note to be specified is that Ni^{+2}, Cu^{+2} and Zn^{+2} are consecutive elements belonging to the same period in the table of elements with identical molar weights (58.7, 63.5 and 65.4 g mol^{-1}, respectively), and hence can be considered equimolar in these batch studies. Pb^{+2} belongs to a different period of the Mandeleev Periodic Table and has an atomic mass of 112.4 g mol^{-1} i.e, is nearly twice those of Ni^{+2}, Cu^{+2} and Zn^{+2}. This would influence the results when concentration is expressed in ppm (mg/L) of multiple contaminant studies. However, the aim of the present study is to investigate the interaction of a particular combination of contaminants whose concentration is expressed in ppm (mg/L). This study does not purport to quantify and compare different soils as adsorbents and hence the importance of milliequivalence unit of concentration is not prominent. The influence of multiple contaminants on soil-contaminant interaction is the main aim of this study. In addition, the present study does not try to differentiate processes of interaction like sorption, complexation and precipitation. The usage of the term retention henceforth includes all possible soil contaminant interactions occurring at a particular condition.

6.2. Batch tests results for common ions

6.2.1 Batch test results for Na^+ and K^+ in binary (Na +K) solution

Na^+ and K^+ retention and its influence on each other was quantified for seven different soils of varying index properties. Solutions of different concentrations were prepared by mixing equivalent amount of Na^+ and K^+ chloride salts in deionised water to obtain range of concentrations varying from 10 mg/L to 1200 mg/L of (Na+K) binary solution. Literature indicates that retention equilibrium is largely pH dependent and acidic condition may attribute increased number of hydrogen ions in solution giving rise to more competition for exchange sites. Therefore, a neutral initial pH is preferred in this study. The results of the batch test for Na^+, K^+ in binary salt solution (Na+K) for the above range of concentration is plotted as shown in Fig 6.1a and 6.1b. The index given in the figure is explained as follows IBent-K-(Na+K) means the data represents the results of K^+ retention on soil IBent from a multiple solution of (Na+K). The retention characteristics of model contaminants Na^+ and K^+ from individual salt solution and multiple salt solutions was compared. The non-linear Langmuir (La) and Freundlich (F) isotherms describing retention characteristics were fitted to the retention data. The various fitting parameters of the retention isotherms for soils (Kao, FC, LS and RS) along with the goodness of fit (R^2) are listed in table. 6.1 for Na^+ and table 6.2 for K^+. It was observed that soil (Kao) has the highest retention coefficient followed by FC, LS and RS. Both the isotherms gave a satisfactory fitting. It should be noted that soil FAsh desorbed at higher range of concentration. It was observed from the retention parameter table that the retention potential of all the soils for K in presence of Na is I Bent > FBent > FC > Kao > RS > LS. It can be noted that there is no definite trend for the retention results of Na^+ for most soils except for FC and Kao. Soils dominated with more smectite mineralogy (IBent and FBent) have the least preference for Na^+ but have the greatest preference for K^+. This is attributed to the presence of high SSA of these soils and high amount of exchangeable Na^+ ions present. These findings suggest that Na^+ leach out from soils (Parfitt, 1992). As such, no isotherms could be obtained for these cases. Such release behaviour of Na^+ for batch test has been reported in the literature (Du and Hayashi 2004) where the authors found that net release occurred for the entire range of concentration. Na^+ is one of the most abundant exchangeable cations present in soils. Also another important finding by Parfitt, 1992 stated that the retention of K^+ is preferred to Na^+ when soils contain more exchangeable Na^+ than exchangeable K^+. This preference decreases as more K^+ is added to the soil

The results of retention of K^+ follows a far better trend than Na^+ as illustrated in the figures 6.1 a, b. It can be noted that soil retained more K^+ than Na^+ for all soils. This can be because of the fact that among K^+ and Na^+ the non-hydrated atom K^+ has the largest radius (r=0.133 nm) compared to Na^+ (r=0.098) which attributes to its greater retention. K^+ also has larger polarization energy (0.0876) than Na^+ (0.0196) and is preferred in ion exchange reactions leading to preferential retention (Sparks, 1987).

Haghnia and Pratt, (1988) have stated that the degree of retention preference for K^+, as compared to Na^+ depends apparently on the nature of the exchangeable complex. Li and Ji (1992) in their study have portrayed that variable charge soils saturated with hydrogen (H) and aluminium (Al) ion tend to adsorb K^+ preferentially to Na^+. Singh et al., (1993) demonstrated that for smectite-dominant soils there is a preference for Na^+ retention than for K^+. The reverse occurs in soils with equal amounts of smectite and mica in the clay fraction. The present experimental results contradict this findings and it was observed that for soils dominated by smectite mineralogy it gave net release of Na^+. Levy and Torrento (1995) reported that soil affinity for K^+ was about 10 times greater than Na^+. Li and Ji, (1992) in their study reported that soils saturated with hydrogen (H) and aluminium (Al) tend to adsorb K^+ preferentially to Na^+.

6.2.2 Investigation on the range of concentration:

One particular soil RS is used to demonstrate the importance of range of concentration on retention characteristics of K^+. The retention of monovalent K^+ from binary solution (Na+K) solution was also investigated for different range of C_e mentioned in section 5.3.1. For better understanding, the partition coefficient and different isotherms (Linear, Langmuir and Freundlich) and C_e ranges are shown in Fig. 6.2. The various retention isotherm fitting parameters are tabulated in Table 6.3. It can be noted from Fig.6.2 that the partition coefficient values for different isotherms are entirely different. This is mainly because physical significance of these values in each isotherm will be different and hence cannot be compared. From table 6.3 it can be noted that linear isotherm based on $C_e < 60$ mg/L data gave maximum partition coefficient and was comparable with Freundlich and Langmuir isotherm. For $C_e > 60$ mg/L and for the entire range of data the values of linear isotherm parameter, K_d are nearly same and lesser than $Ce < 60$ mg/L for Freundlich. The partition coefficients obtained from single and multiple contaminant solution is compared as shown in Fig. 6.3. It can be noted from the figure that the difference in partition coefficient is more for lower range of C_e. For higher range and the entire data taken together, the difference is not appreciable. However, there is a need to understand how small change in partition coefficient influences contaminant fate prediction

6.2.3 Comparison of Na^+ and K^+ corresponding to single and binary (Na+K) solution

An effort was made to compare the retention results of Na^+ and K^+ corresponding to single and binary salt solution (Na+K) and thereby understand the influence of the latter on soil-contaminant interaction. The comparison of Na^+ and K^+ corresponding to single and binary (Na+K) solution is shown in Fig. 6.4a,b. From the figures it can be stated that there is a significant influence of K^+ on the retention of Na^+ when multiple soil solution is considered. For soils dominated with smectite minerals, release of Na^+ was observed from single and multiple ions. For Kao, Na^+ retention from binary was less than those obtained by single ion solution. For FC the presence of K^+ did not affect much on its retention performance. For soil RS, though for single ions there was retention observed at higher range of concentration but in a competitive system there was considerable scatter of results. For LS, this initially exhibited retention with single ion showed net release of K+ in the presence of K+. In FAsh there was no definite pattern of retention. Similar results was found by Liang et al.,(1992) who observed that a negative retention of Na^+ ions by latosol and lateritic red soil in a mixed system containing equal amount of Na^+ and K^+ ions at low pH. This was caused by a competitive interaction of Na^+ and K^+ ions and repulsive effect of positive charge on the surfaces of soil particles for cations.

Fig 6.5a, b shows the comparison of retention characteristics of K^+ on soils corresponding to single and binary salt solution (Na+K). It can be seen that the presence of Na^+ has a inhibitory affect on the retention performance. Even though Na^+ itself does not get retained for some soils its presence do effect the retention of K^+. This trend was observed for all soils. For FAsh, in the presence of Na^+ there was more release of K^+ in the higher range of concentration as compared to K^+ in the single system.

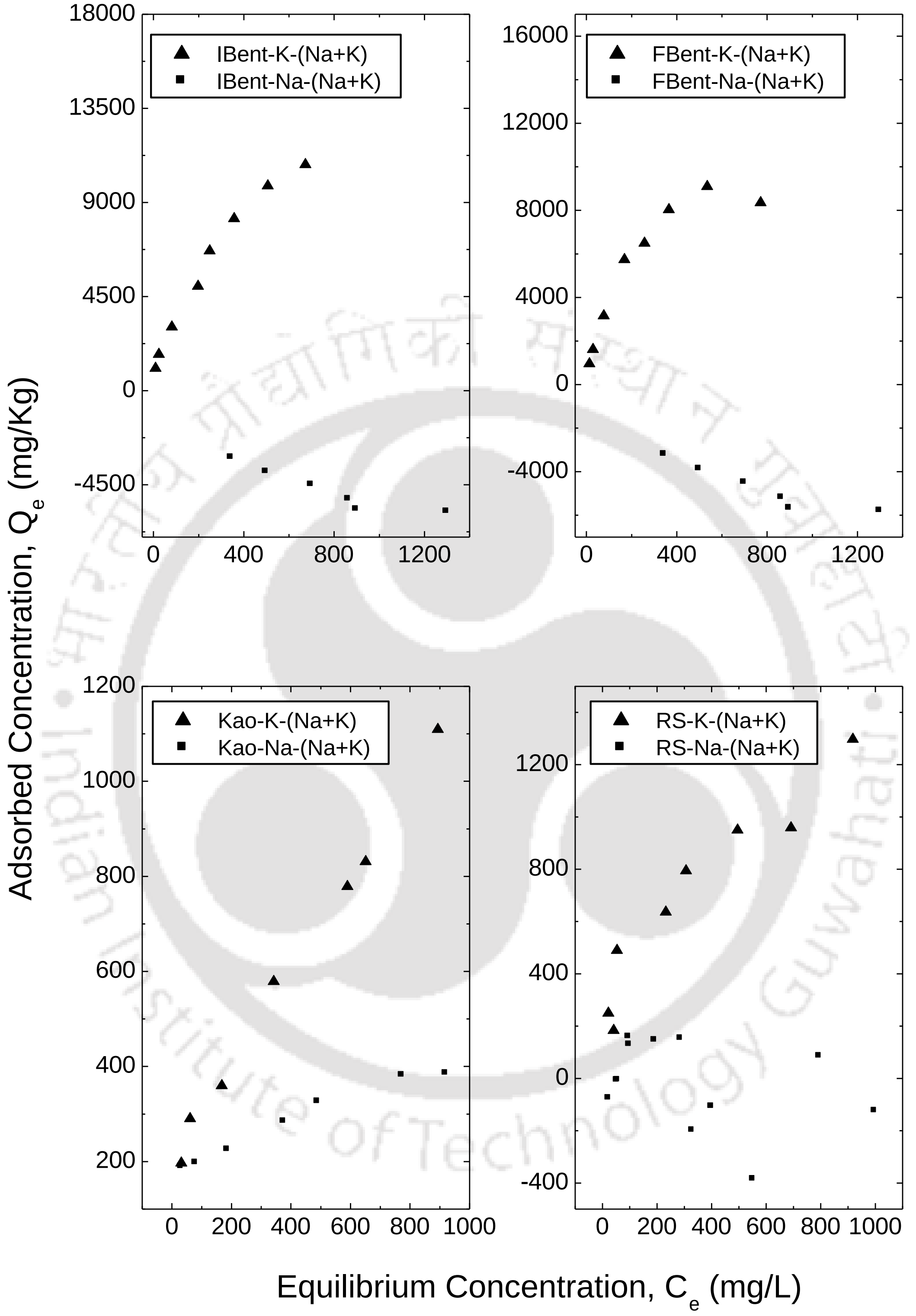


Fig.6.1a Comparison of retention characteristics of K^+ and Na^+ on 4 soils from binary (Na+K) solution

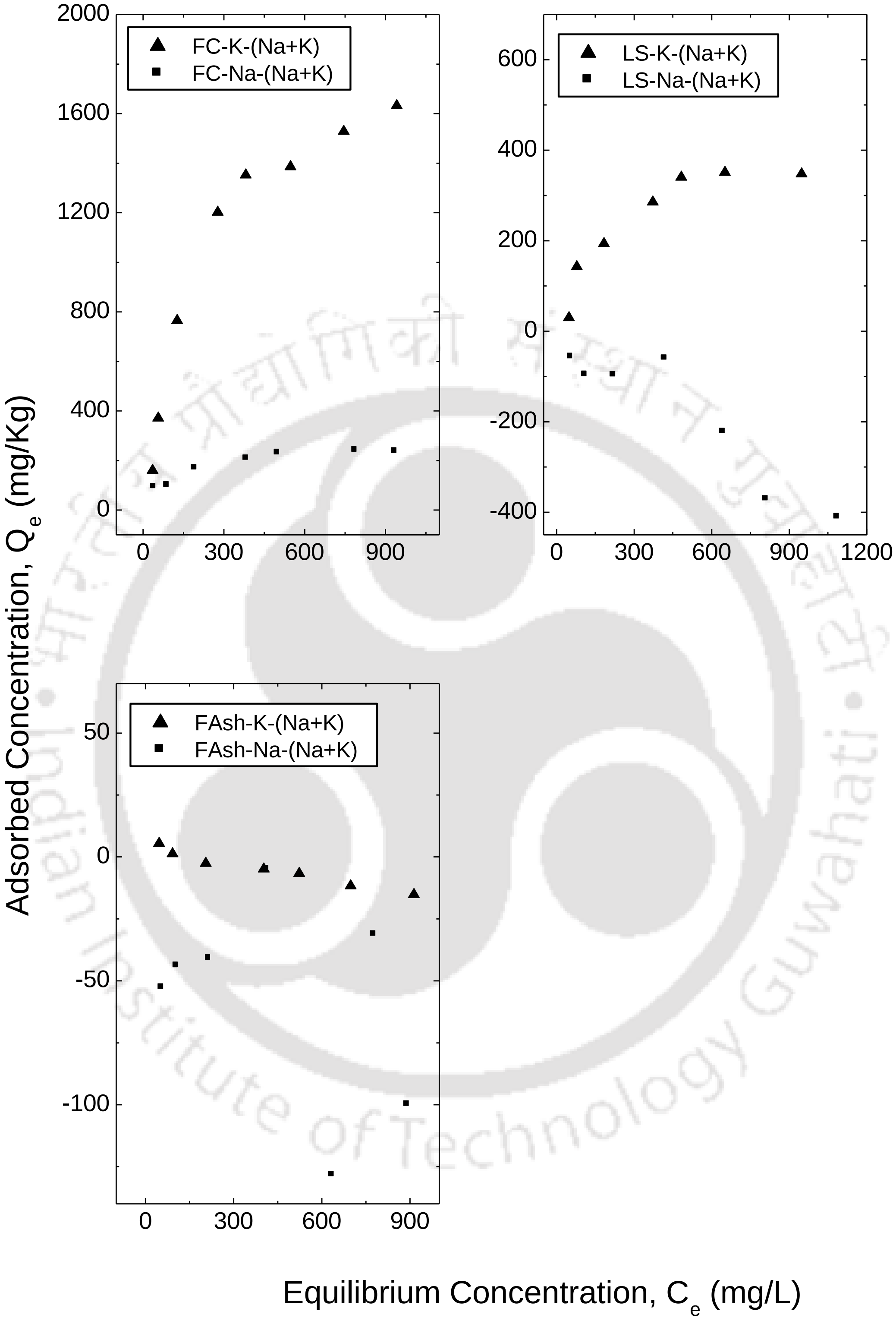


Fig.6.1b Comparison of retention characteristics of K^+ and Na^+ on 3 soils from binary (Na+K) solution

Table 6.1 Retention isotherm parameters for Na^+ from (Na-K) solution

Soil	Parameters-Na (Na+K)						Best Fit
	Freundlich			Langmuir			
	K_F(L/Kg)	N	R^2	K_L(L/mg)	Q_m(mg/Kg)	R^2	
FC	29.95	0.314	0.928	0.0085	272.95	0.962	Freundlich
Kao	63.15	0.263	0.946	0.0153	375.23	0.741	Freundlich

Table 6.2 Retention isotherm parameters for K^+ from (Na-K) Cl solution

Soil	Parameters-K (Na+K)						Best Fit
	Freundlich			Langmuir			
	K_F(L/Kg)	N	R^2	K_L(L/mg)	Q_m(mg/Kg)	R^2	
IBent	899.54	0.38	0.90	0.0095	11976.43	0.98	Langmuir
FBent	559.97	0.43	0.92	0.0062	10982.17	0.98	Langmuir
RS	55.01	0.45	0.95	0.0052	1359.58	0.92	Freundlich
FC	80.83	0.44	0.92	0.00461	2012.75	0.98	Langmuir
Kao	136.36	0.44	0.96	0.00375	3478.204	0.94	Freundlich
LS	30.25	0.56	0.87	0.0024	1943.57	0.92	Langmuir
FA	-	-	-	-	-	-	-

Table 6.3 Retention isotherm parameters of K^+ corresponding to (Na-K) Cl for different range of C_e for RS

Range	Linear	Freundlich	Langmuir
$C_e < 60$ mg/L	K_d=7.7 L/Kg	K_F=8.86 L/Kg N=0.9657 R^2=0.6824	K_L=0.0008 L/mg Qm=10085.3mg/Kg R^2=0.6298
$C_e > 60$ mg/L	K_d =.58 L/Kg	K_F =54.22L/Kg N=0.4574 R^2=0.9063	K_L =0.0025 L/mg Qm=1729.68mg/Kg R^2=0.8884
Entire range	K_d =1.603L/Kg	K_F =55.01 L/Kg N=0.4560 R^2=0.9522	K_L =0.0052 L/mg Qm=1359.74mg/Kg R^2=0.9183

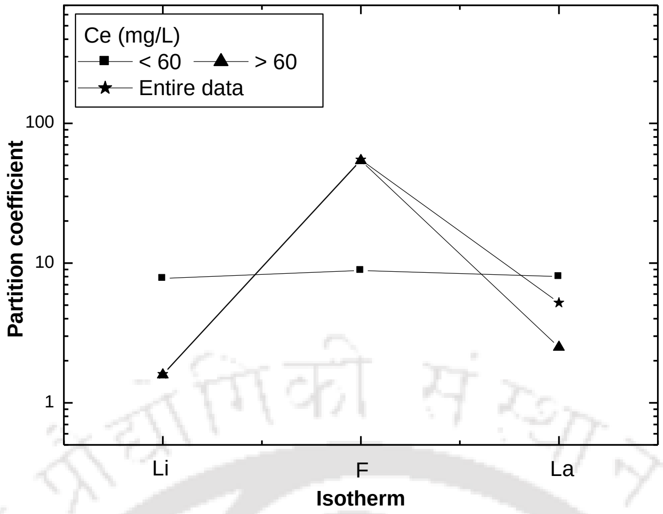


Fig.6.2 Comparison of partition coefficient of K^+ in (Na+K) multiple salt solution for different isotherms and range of data

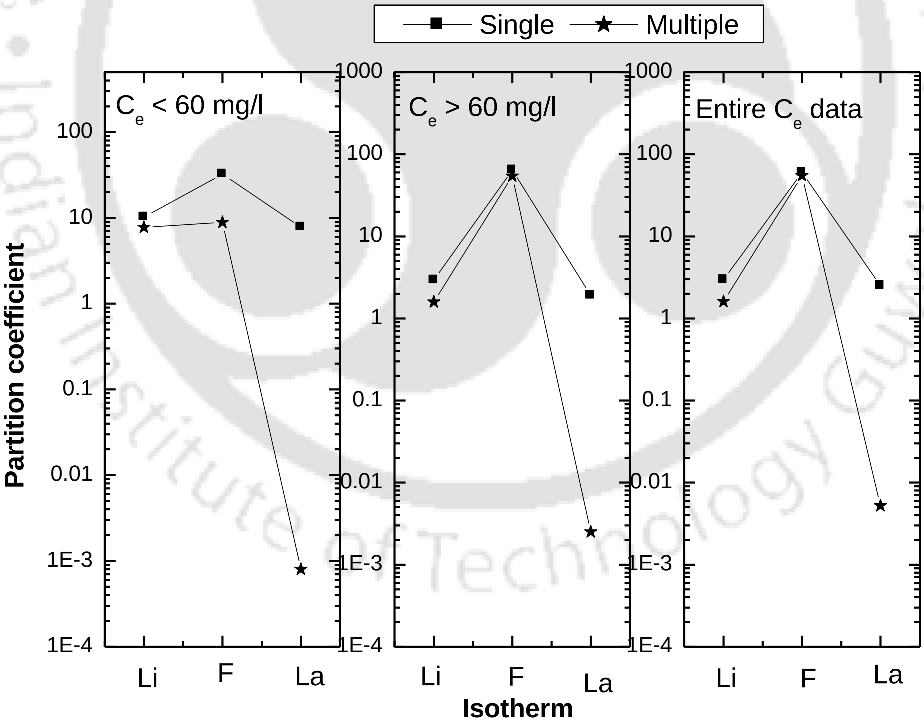


Fig. 6.3 Comparison of partition coefficient of K^+ obtained from single and multiple salt solutions for different isotherms and range of concentration

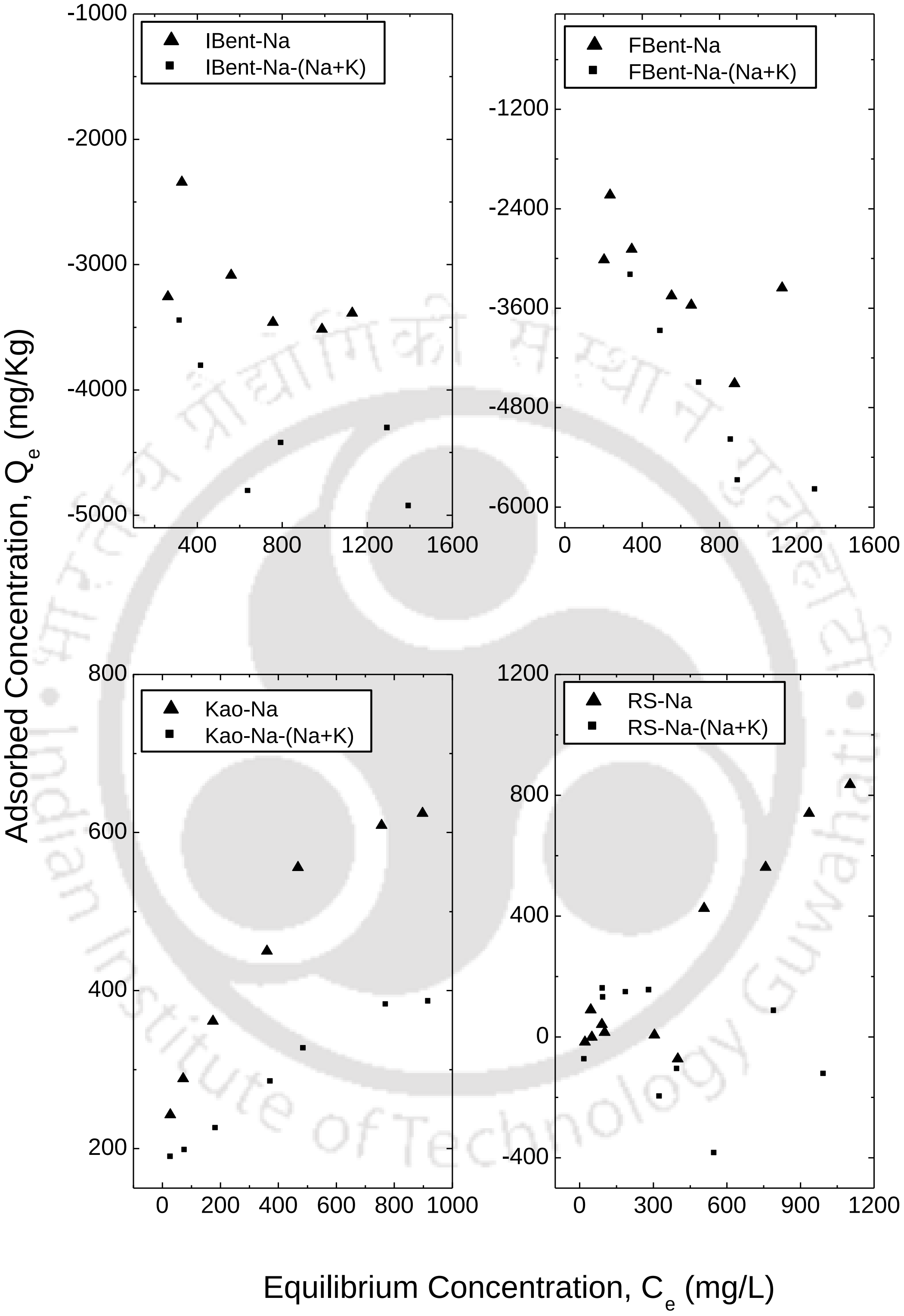


Fig.6.4a Comparison of retention characteristics of Na^+ on 4 soils corresponding to single and binary (Na+K) solution

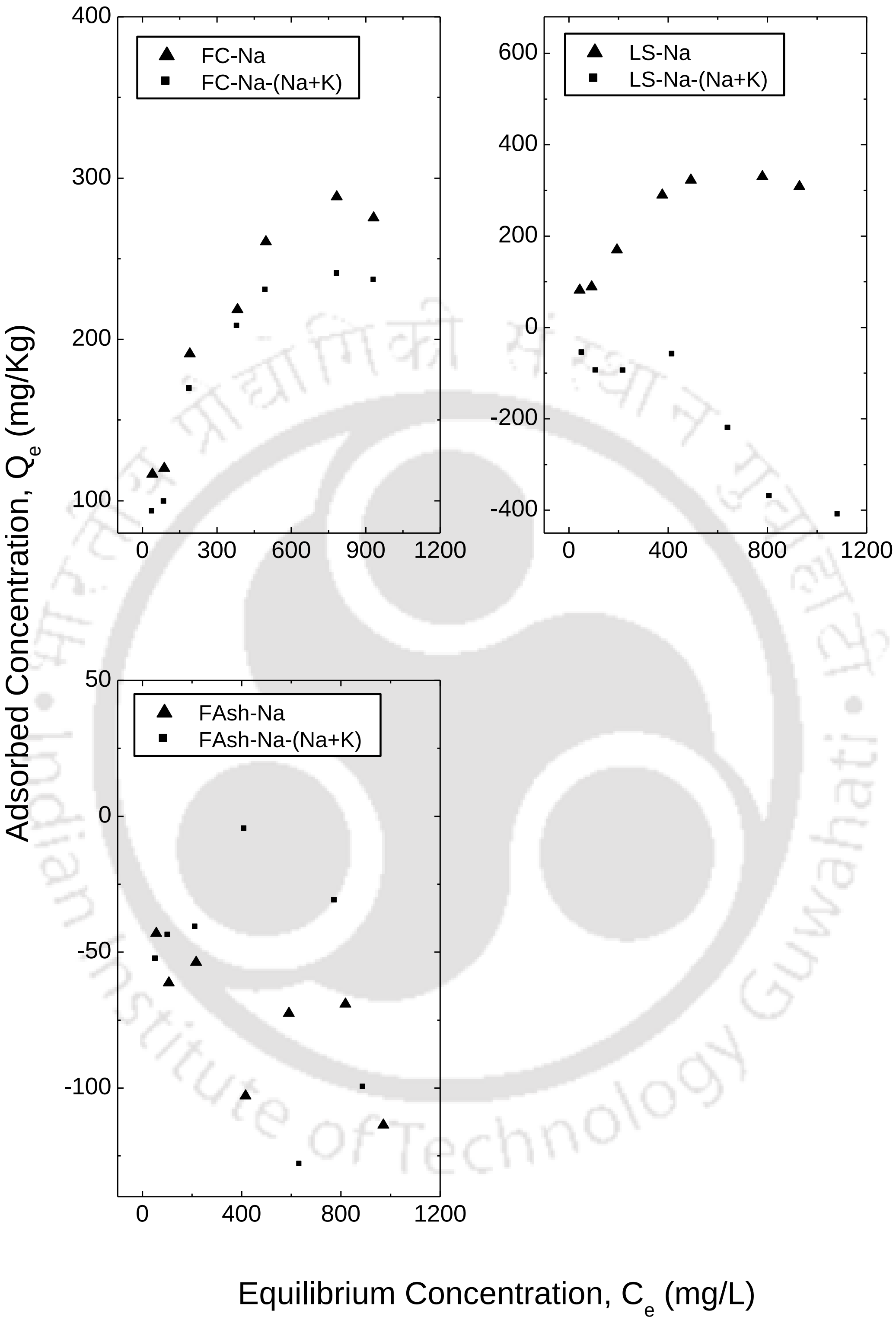


Fig.6.4b Comparison of retention characteristics of Na^+ on 3 soils corresponding to single and binary (Na+K) solution

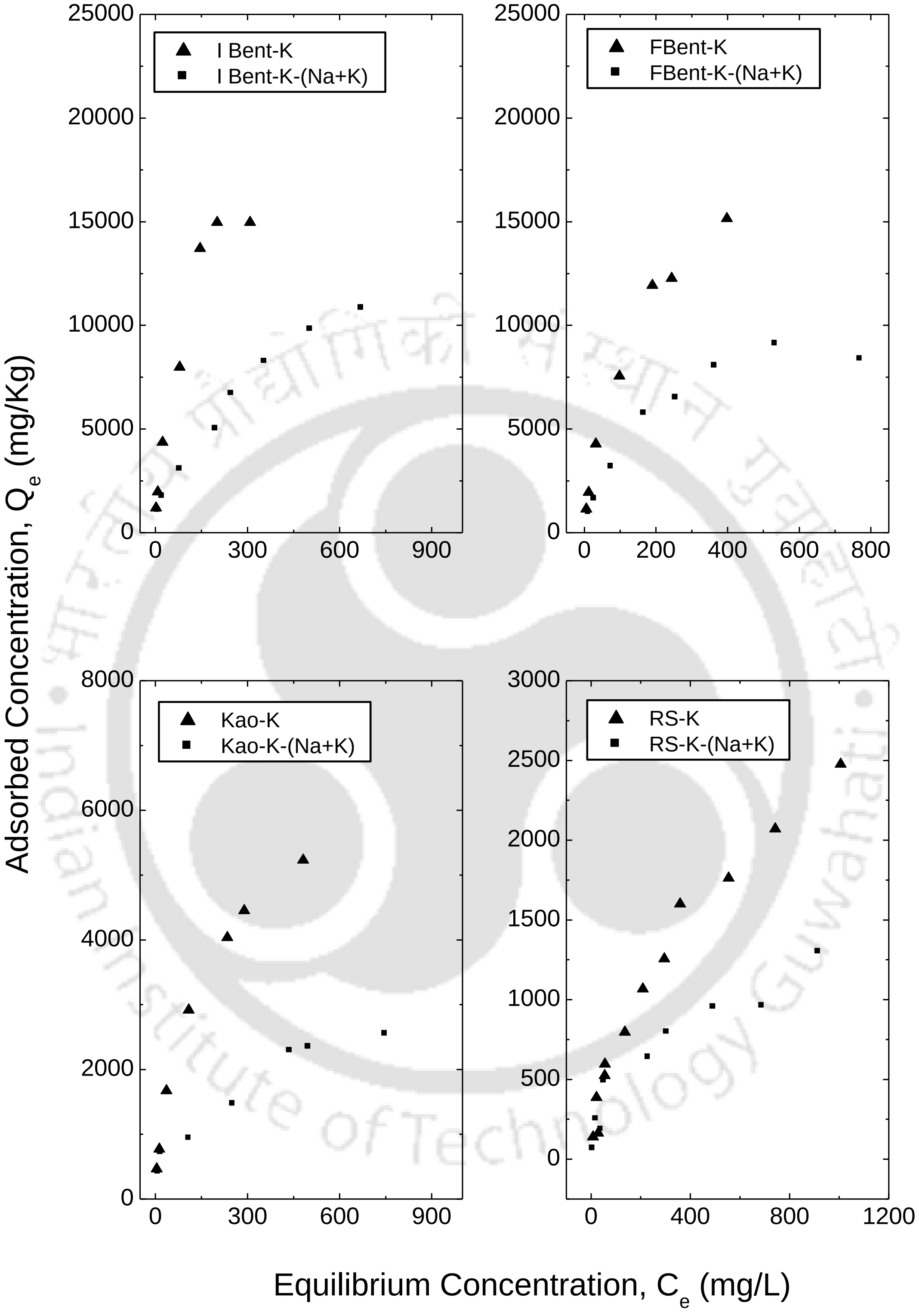


Fig.6.5a Comparison of retention characteristics of K^+ on 4 soils corresponding to single and binary (Na+K) solution.

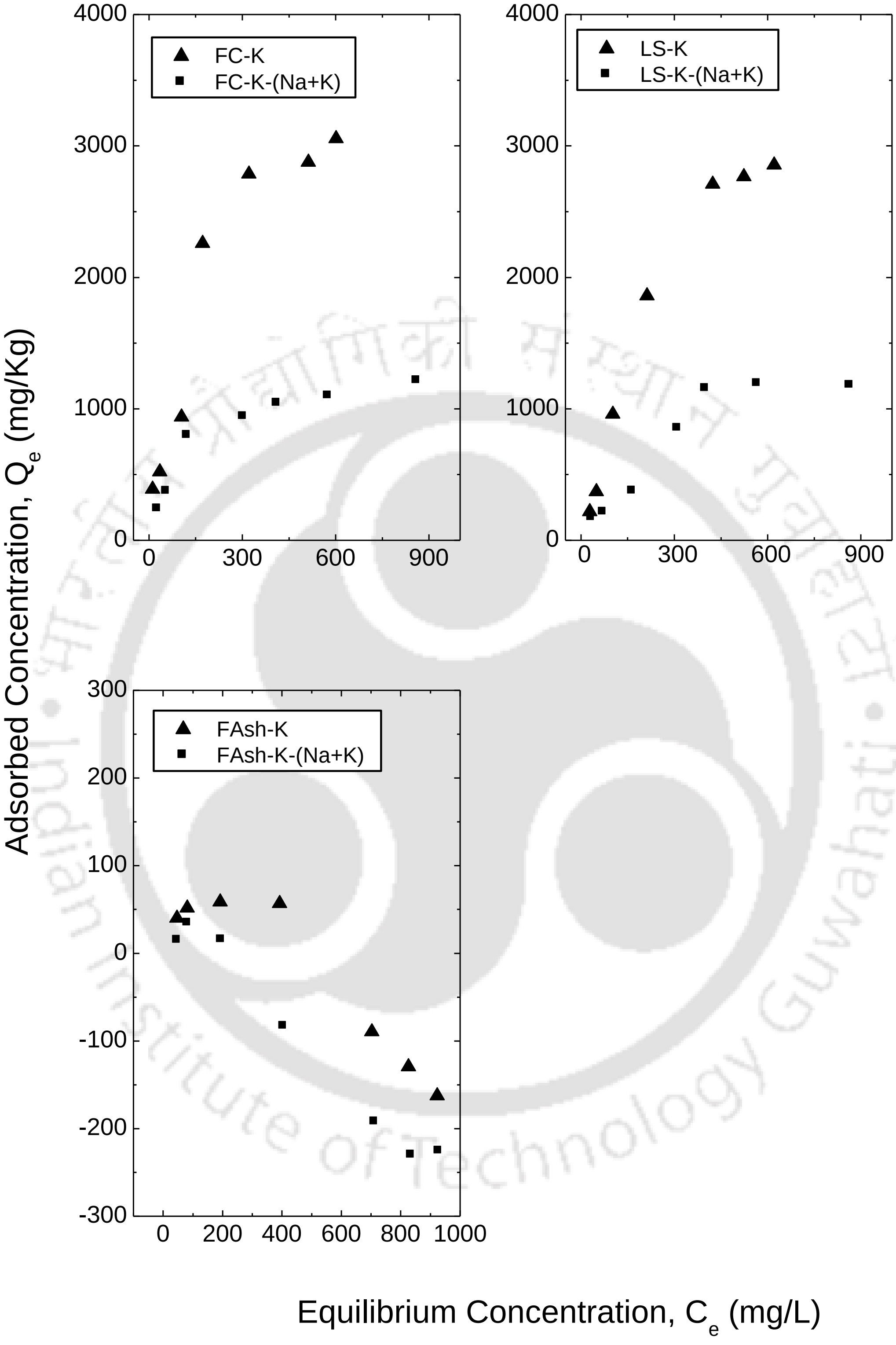


Fig.6.5b Comparison of retention characteristics of K^+ on 3 soils corresponding to single and binary (Na+K) solution

6.2.4 Batch test results for NH_4^+ and K^+ in binary (NH_4+K) solution

NH_4^+ and K^+ are major plant nutrients and the soil retention behaviour are individually reported in literature (Dala, 1975, Carski and Sparks, 1987) and K^+ retention (Marschner,1995, Rezaei and Naeini, 2009). However, the presence of each other influence soil retention and subsequently the nutrient availability to plants has not been documented in detail. In this study, NH_4^+ and K^+ ions retention on soils from multiple (NH_4+K) chloride solution has been quantified for seven different soils. NH_4^+ retention is reported to be higher in acidic solutions (pH <6.0) than in basic solutions (pH 7.5) for vermiculite soil (Shen et al., 1997). Therefore, an initial pH of 6 is considered in this study.

The simultaneous retention of K^+ and NH_4^+ on soils is depicted in Fig. 6.6a, b. It can be observed from the figures that at lower concentration the NH_4^+ and K^+ ion competed equally in all the soils. However, after a certain range of concentration unique for each soil, NH_4^+ retention was found to be marginally higher than K^+. There are studies reported where it is demonstrated it is demonstrated that there was a preference of NH_4^+ than K^+ in soils (Bower, 1950; Nommik, 1957; Nielsen, 1972). Studies by Shen et al., (1997) and Chung and Zasoski, (1994) stated a clear preference for K^+ than NH_4^+. They also reported that the concentration of NH_4^+ in the soil solution has a strong and direct impact on the distribution of K^+ between the soil solution and the exchange complex. Studies conducted by Kithome et al (1998) and Rezaei and Naeini, (2009) documented that NH_4^+ ions behaves similar to K^+. This can be attributed to the fact that NH_4^+ and K^+ are both univalent cations with relatively low hydration energies, have comparable ionic radius (2.8A^0) and crystal ionic radii of 0.133nm and 0.143nm for K^+ and NH_4^+ respectively. Thus, it is expected to compete for the same exchangeable and non-exchangeable sites of soil particles thereby leading to strong interactions between them in the soil. In addition, both the ions are held by the same non-exchangeable sites in the interlayers and edges of interlayers of the 2:1 clay minerals. The results obtained in this study also justify this finding since the variation of retention is minimal. IBent and FBent resulted in a better performance for both K^+ and $NH4^+$ retention and was related to the high SSA. In FAsh it was observed that there was a net release of K^+ for entire concentration range whereas NH_4^+ exhibited retention. Table 6.4 and 6.5 shows the fitting parameters for Langmuir and Freundlich models. According to the results both the models gave satisfactory fitting retention data for K^+ and NH_4^+ for soils. Maximum retention capacity Q_m of K^+ varied from 2747.32 mg/Kg to 17462.26 mg/Kg in the presence of competing NH_4^+ ions. Simultaneously the Q_m value of NH_4^+ varied from 677.714 to

25515.10. The K_F value varied from 11.39 L/Kg to 433.89 L/Kg for $NH4^+$ ions and 51.88L/Kg to 861.12L/Kg for K^+ ions.

6.2.5 Comparison of NH_4^+ and K^+ corresponding to single and binary solution (NH_4+K)

It can be observed from Figs 6.7a, b, 6.8a,b that soils retained more ions in single system compared to (NH_4+K) binary system and each of the ion has a definite influence on the other. As can be seen from the figure, for FBent there was not much affect of $NH4^+$ on K^+ retention for the entire range of concentration. For soils IBent, FC, LS and Kao there was negligible effect of multiple contaminants in the lower range of concentration. For soils like RS there is appreciable difference between single and multiple retention for K^+. For FAsh K^+ is released more in the binary case. As seen from Figs. 6.8a and 6.8b, it can be observed that the presence K^+ has influence on the NH_4^+ retention for soils IBent, RS, FC, LS and FAsh. For soils FBent and Kao this effect is marginal. Similar findings were observed in the literature where K^+ and NH_4^+ are attracted by the same exchange sites with similar affinity and also the presence of competition among one another could affect K^+ and NH_4^+ retention and release (Cooney et al.,1999; Weatherley and Miladinovic, 2004; Hankins et al., 2004; Mezaei and Naeini, 2009).Thus we can conclude that the source of NH_4^+ availability to plants and its transformations within the soil, influence K^+ availability and vice versa.

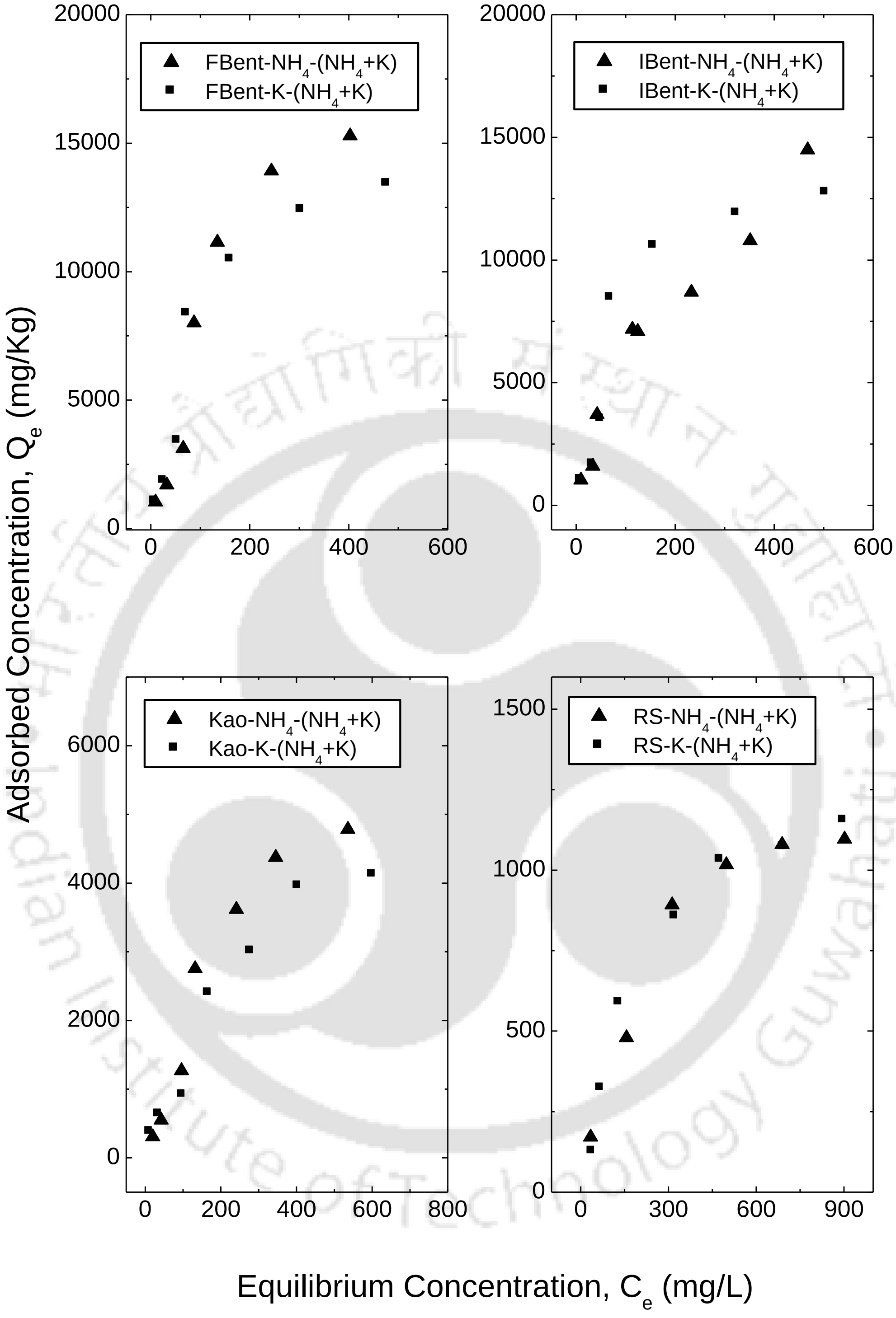


Fig. 6.6a Comparison of retention characteristics of NH_4^+ and K^+ on 4 soils from binary (NH_4+K) solution

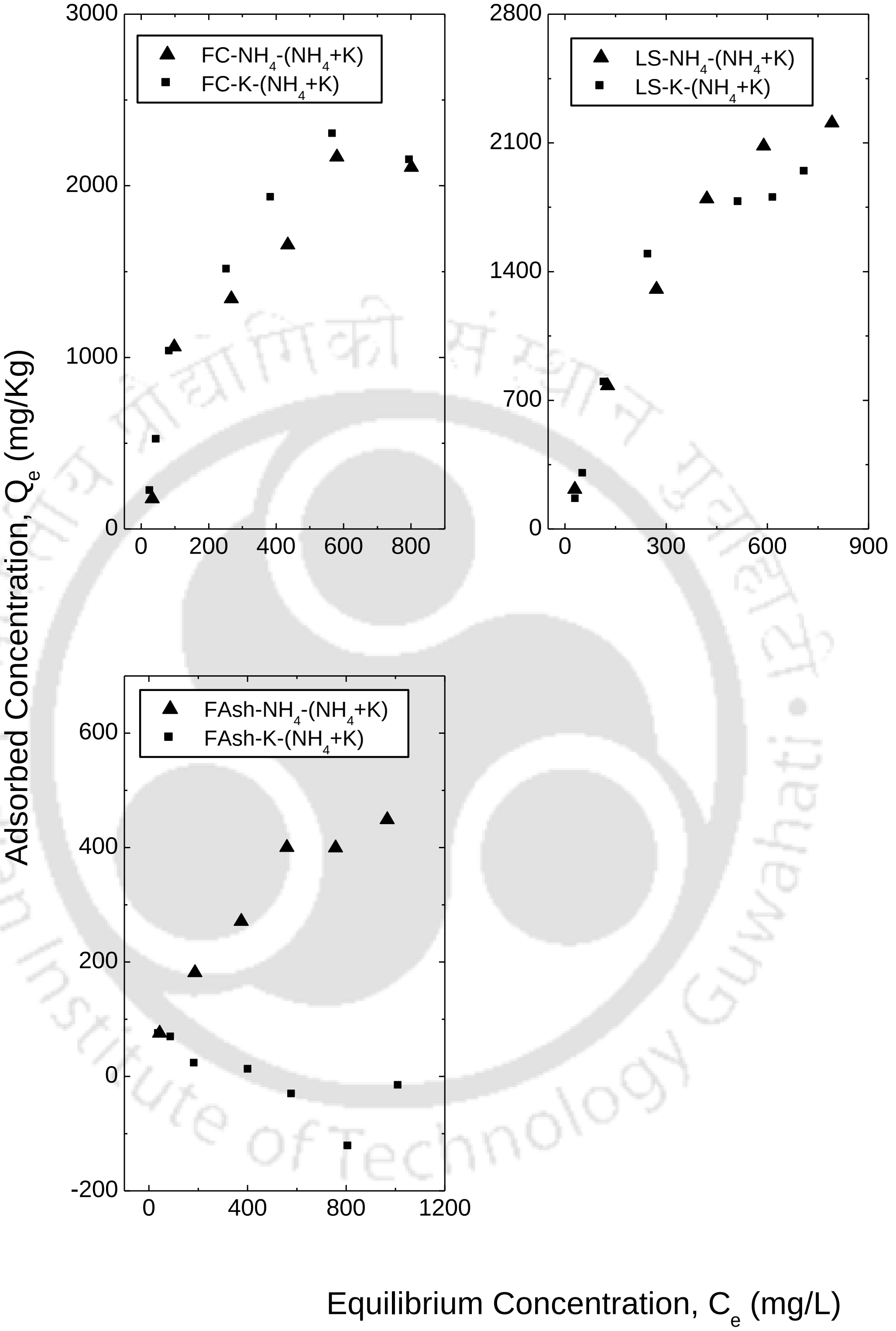


Fig.6.6b Comparison of retention characteristics of NH_4^+ and K^+ on 3 soils from binary (NH_4+K) solution

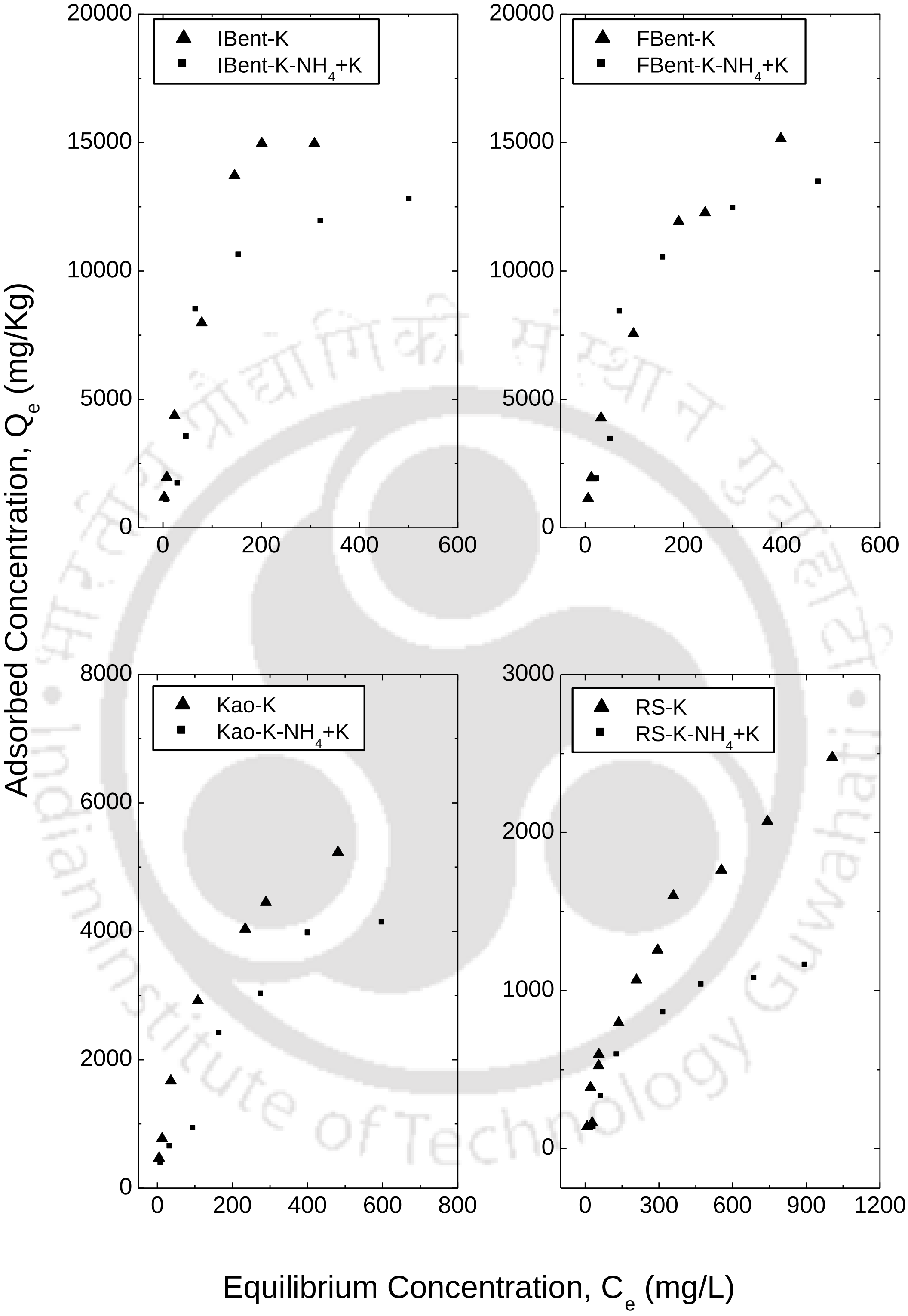


Fig.6.7a Comparison of retention characteristics of K^+ on 4 soils corresponding to single and binary (NH_4+K) solution

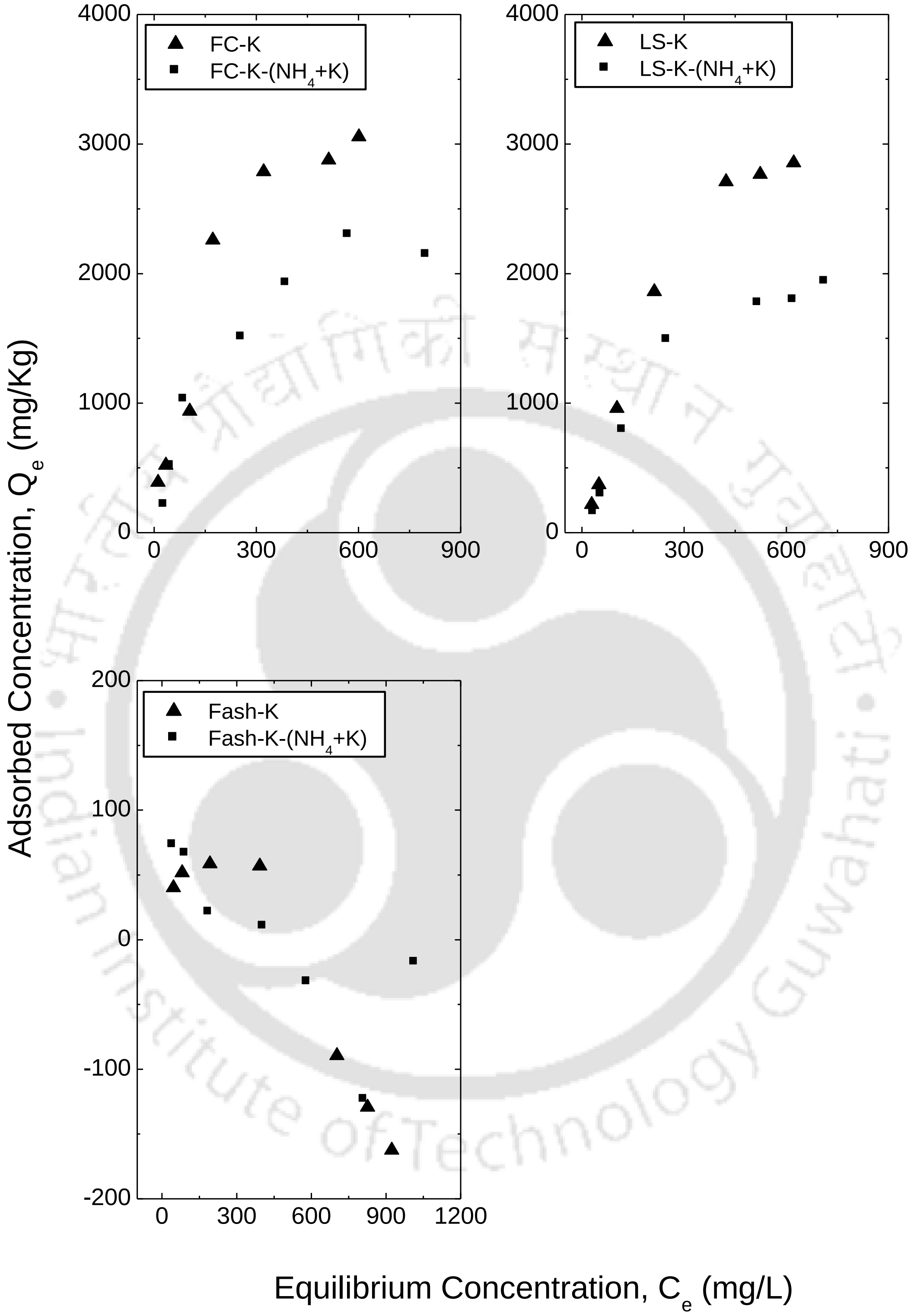


Fig.6.7b Comparison of retention characteristics of K^+ on 3 soils corresponding to single and binary (NH_4+K) solution

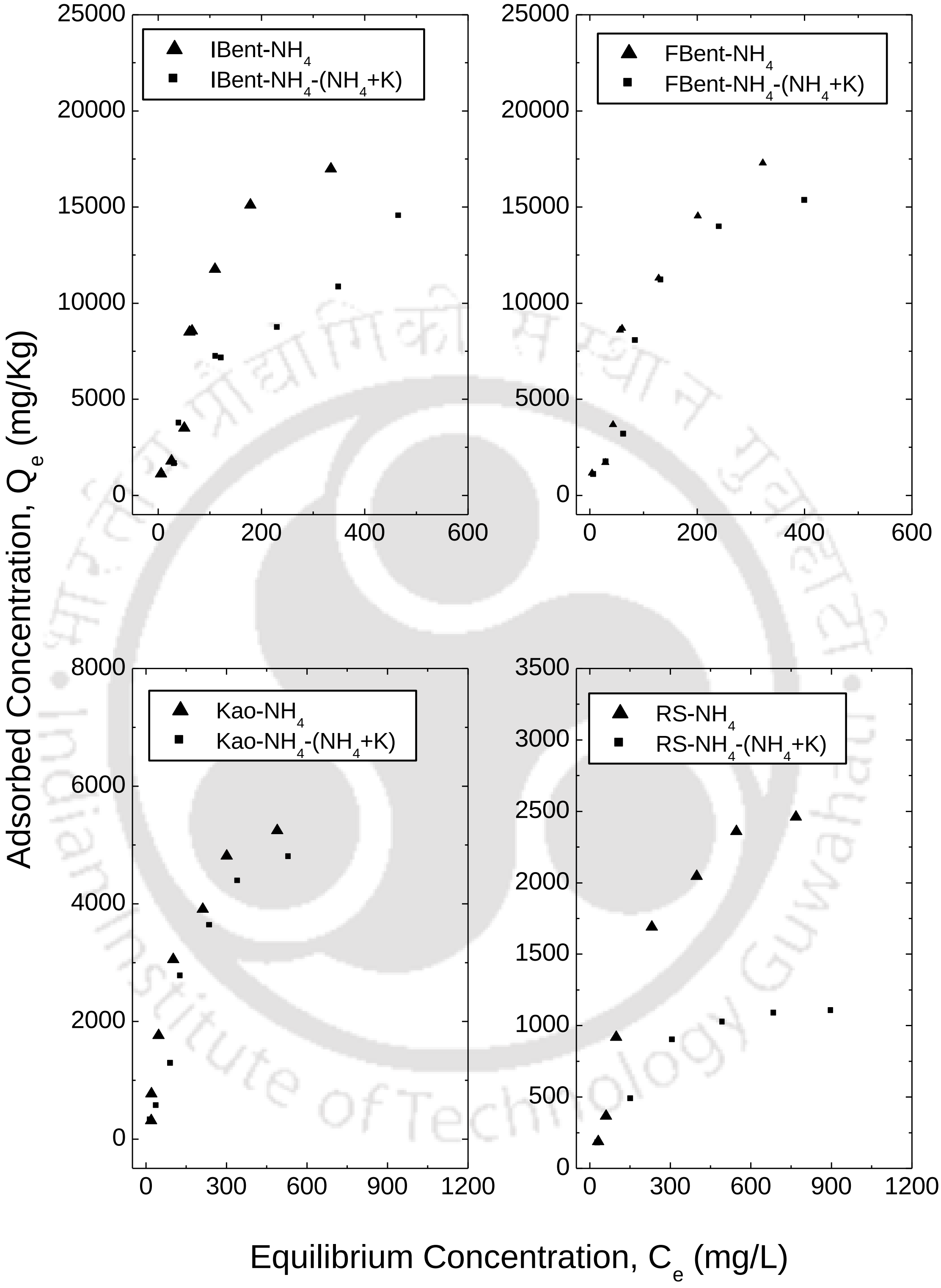


Fig.6.8a Comparison of retention characteristics of NH_4^+ on four soils corresponding to single and binary (NH_4+K) solution

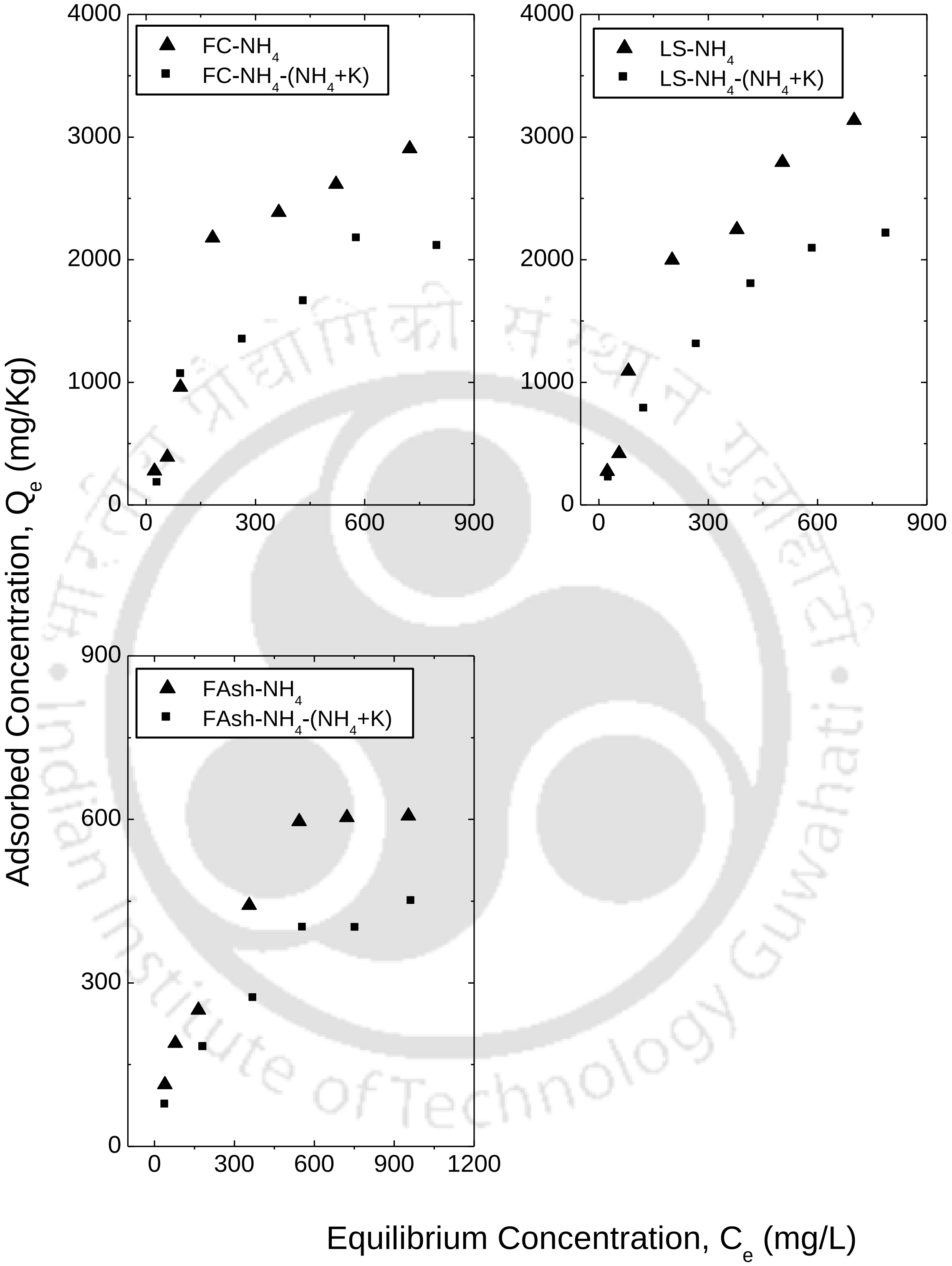


Fig.6.8b Comparison of retention characteristics of NH_4^+ on three soils corresponding to single and binary (NH_4+K) solution

Table 6.4 Retention isotherm parameters for NH4^{+} from (NH4+K) solution

Soil	Parameters NH$_4$ - (NH$_4$+K)						Best Fit
	Freundlich			Langmuir			
	K$_F$(L/Kg)	N	R^2	K$_L$(L/mg)	Q$_m$(mg/K	R^2	
IBent	365.76	0.59	0.987	0.0039	20413.32	0.95	Freundlich
FBent	433.89	0.61	0.89	0.0043	25515.11	0.93	Langmuir
RS	53.92	0.46	0.93	0.0045	1454.37	0.98	Langmuir
FC	91.04	0.48	0.92	0.0043	2759.22	0.96	Langmuir
Kao	96.18	0.64	0.92	0.0029	8275.58	0.96	Langmuir
LS	51.91	0.57	0.97	0.0023	3504.32	0.99	Freundlich
FAsh	11.39	0.54	0.9	0.0021	677.714	0.97	Langmuir

Table 6.5 Retention isotherm parameters for K^{+} from (NH4+K) solution

Soil	Parameters K-(NH$_4$+K)						Best Fit
	Freundlich			Langmuir			
	K$_F$(L/Kg)	N	R^2	K$_L$(L/mg)	Q$_m$(mg/Kg)	R^2	
IBent	861.12	0.45	0.83	0.009	16199.81	0.91	Langmuir
FBent	774.59	0.48	0.88	0.0081	17462.26	0.94	Langmuir
RS	53.93	0.46	0.93	0.0045	1454.38	0.98	Langmuir
FC	108.43	0.47	0.92	0.0052	2839.11	0.97	Langmuir
Kao	87.22	0.62	0.94	0.0025	7177.08	0.96	Langmuir
LS	51.88	0.56	0.92	0.0034	2747.32	0.97	Langmuir
FAsh	-	-	-	-	-	-	-

6.2.6 Batch test results for Na^{+}, K^{+} and Ca^{+2} in tertiary (Na+K+Ca) chloride solution

Solutions of different concentrations were prepared by mixing equivalent amount of K^{+}, Na^{+} and Ca^{+2} chloride salts in deionised water to obtain range of concentrations varying from 10 mg/l to 1200 mg/l. Owing to the release trend of Na^{+} in single and binary system its retention is not considered in tertiary system. The simultaneous retention of K^{+} and Ca^{+2} on soils from Na+K+Ca solution is depicted in Figs.6.9 a, b. It can be observed from the figures that at low concentration the Ca^{+2} and K^{+} ion competed equally. From the results it could be seen that the retention isotherm of K^{+} and Ca^{+2} exhibited a S-shape for soils FC and LS and L shaped curves for soils IBent, Fbent, Kao and RS. It was also observed that the affinity of soil for K^{+} is greater than Ca^{+2} for IBent, FBent and Kao. For RS and FC competition was equal. For LS Ca $^{+2}$ retention was more than K^+. It can also be seen that for FAsh Ca^{+2} and K^+ release took place.

Ionic selectivity is dependent on both intrinsic ion properties and exchanger characteristics. The complex nature of the soil solid phase makes it difficult to understand the reasons responsible for the preferential retention of K^+. This can be mainly attributed to the following facts. The non-hydrated atom K^+ has the largest radius (r=0.133 nm). Also in mineral structures the number of oxygen atoms in coordination bonding are large (8 or 12) which eventually makes the strength of each K-O bond relatively weak (Sparks and Huang, 1985).The hydration energy of K^+ is 142.5 kJ ion $^{-1}$, indicating that the ability of K^+ to cause soil swelling is small (Helfferich, 1962). The polarization effect of K^+ is also larger than Ca^{+2} and thus is preferred in ion exchange reactions (Sparks, 1987). Similar observations were found by research conducted by Shainberg and Kemper (1963), Goulding (1983) regarding the condition that favour K^+ preferential retention. Liang et al., (1992) in his study stated that this tendency could not be changed by factors such as the pH, the concentration of the cations, the dielectric constant of solvent, the accompanying anions and the iron oxide content etc., suggesting that this difference in affinity is caused by the difference in the nature of the two cations. Haghnia and Pratt, (1988) have demonstrated in their study that there exists retention preference for K^+ as compared with of Ca^{+2} in soils and it depends apparently on the nature of the exchangeable complex.

Also another important finding by Parfitt, 1992 stated that the retention of K^+ is preferred to Ca^{+2} and Na^+ when soils contain much more exchangeable Ca^{+2} and Na^+ than exchangeable K^+. This preference decreases as more K^+ is added to the soil. Furthermore, the electrostatic repulsion itself is more intense for divalent ions such as Ca^{+2} than for monovalent ones. Research conducted by Fanning et al.,1989 have stated that K^+ status and distribution in soils is almost entirely governed by soil mineralogy This applies not only to the dominant mineral species present in the clay and silt fraction of the soil, but also associated minerals of importance as well. Many other investigators have also shown higher selectivity for K^+ over Ca $^{+2}$ in kaolinite and kaolinitic soils (Levy et al., 1988; Levy and Hillel, 1968; Udo, 1978). Similar findings were noted from our study where soils havings smectite and Kaolinite sorbed more than Ca^{+2}. In FAsh it was observed that there was a net release happening throughout the range for both K^+ and Ca^{+2} and hence no isotherm could be quantified.

Ferris and Jepson (1975); Goulding and Talibudeen (1980); Levy et al (1988) have ascribed the preferential retention of K^+ to Ca^{+2} in soils to the presence of 2:1 clay minerals. 2:1 clay minerals has two zones planar surface charges which has regular exchange sites with lower K^+ selectivity and wedge shaped zones or frayed edge sites that show high affinity for K^+ (Beckett and Nafady 1967; Saha et al., 2001). Since K^+ loose their hydration shell more easily than the strongly hydrated Ca^{+2} ions they enter the wedge zones preferentially to Ca^{+2} thus resulting in more retention. Eventually, when the wedge zones become more saturated with K^+ ions, the selectivity is then determined by the planar surface sites which have relatively lower affinity for K^+. Thus, the K^+ selectivity decreases as K^+ saturation increases. (Goulding and Talibudeen 1984; Jardine and Sparks 1984). Studies have reported that since the electrostatic repulsion is more intense for divalent ions such as Ca^{+2} than for monovalent K^+ the preferential retention of the divalent cation Ca^{+2} decreases compared to K^+. The various fitting parameters of the retention isotherms for all the soils along with the goodness of fit (R^2) are listed in table. 6.6 for K^+ and table 6.7 for Ca^{+2} in (Na+K+Ca) tertiary solution.

6.2.7 Comparison of K^+ and Ca^{+2} corresponding to single, binary, and tertiary (Na+K+Ca) solution

An effort was made to compare the retention results of single of both K^+ and Ca^{+2} corresponding to single and multiple solution and thereby understand the influence of the latter on soil-contaminant interaction. The retention of K^+ and Ca^{+2} ions increased with increase of concentration in both single and multiple ions. It can be noted from the experimental results that Ca^{+2} was the major competitor of K^+ for the exchangeable sites of the different soils and thus the retention of K^+ ions depends on the competitive retention of Ca^{+2}. Bolt (1967) has stated that considering the electrostatic retention of cations, it is commonly observed that some cationic species are preferentially adsorbed by the soil solid phase. For K^+ and Ca^{+2} there is a decrease in retention when multiple ions are present. This reduction is quantified and discussed in detail in the section 6.5. From Fig 6.10a,b the retention of K^+ is less in tertiary as compared to binary for soils IBent, FBent, LS and FC. The difference in binary and tertiary is minimal for Kao and RS for K^+. It can be demonstrated from the figures 6.11a,b that there is a considerable decrease in retention for Ca^{+2} between single and tertiary system. It can be noted that there is a change in the shape of Ca^{+2} isotherm in single and tertiary where it reaches saturation quickly. The difference was more apparent for soils Kao, LS and FC. For FAsh the release was found to be higher and there was more scatter in the results.

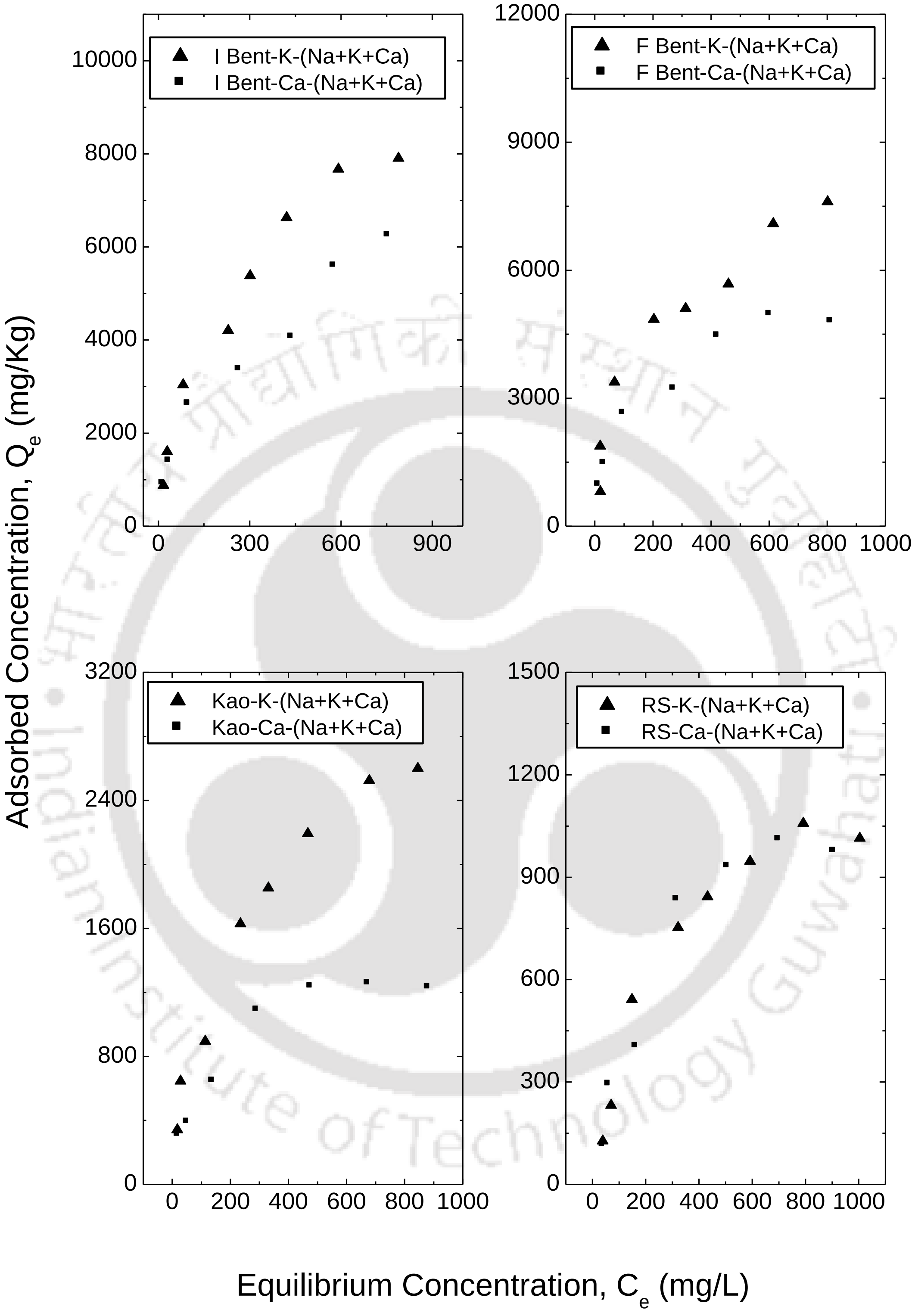


Fig.6.9a Comparison of retention characteristics of K^+ and Ca^{+2} on 4 soils from tertiary (Na+K+Ca) solution

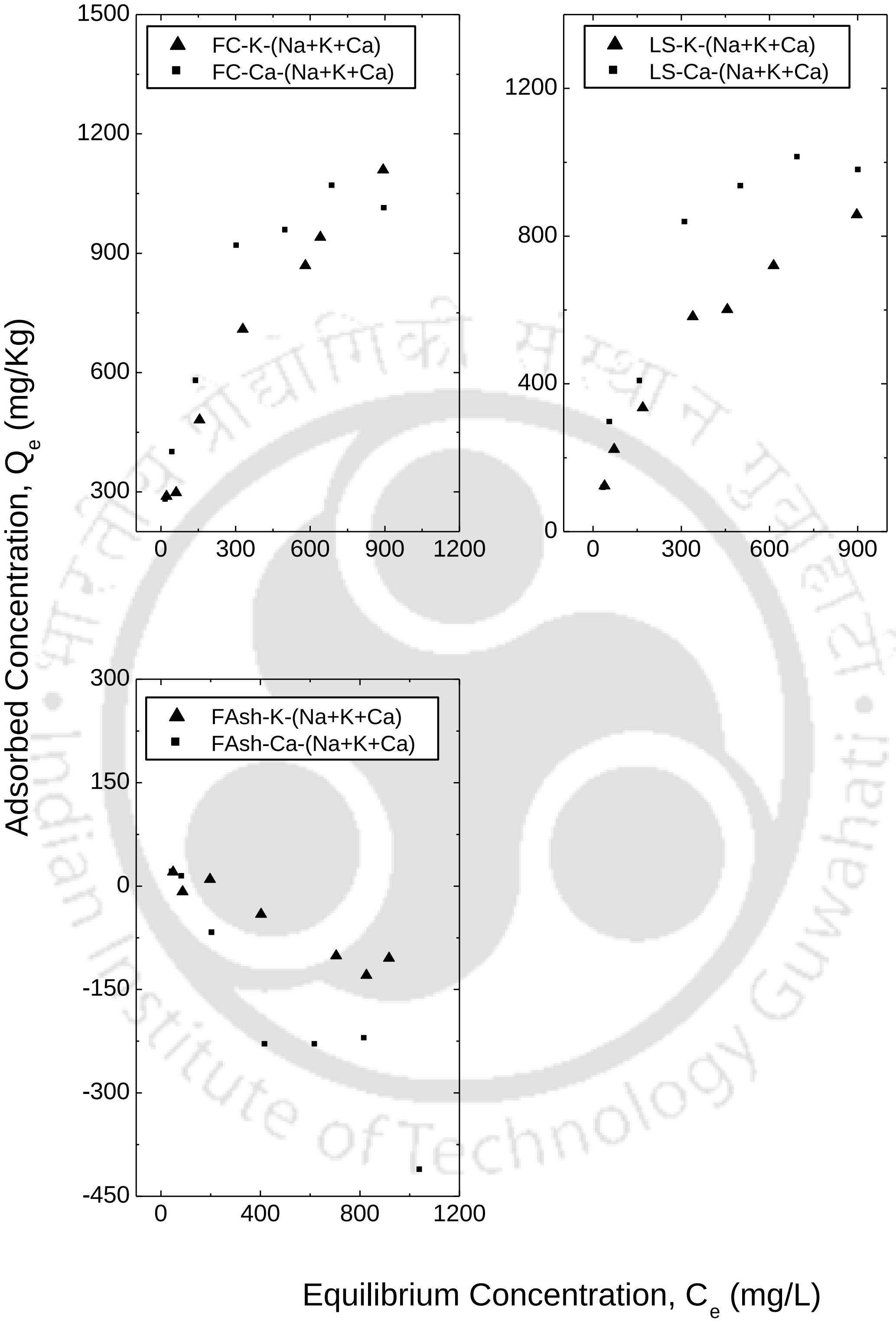


Fig.6.9b Comparison of retention characteristics of K^+ and Ca^{+2} on 3 soils from tertiary (Na+K+Ca) solution

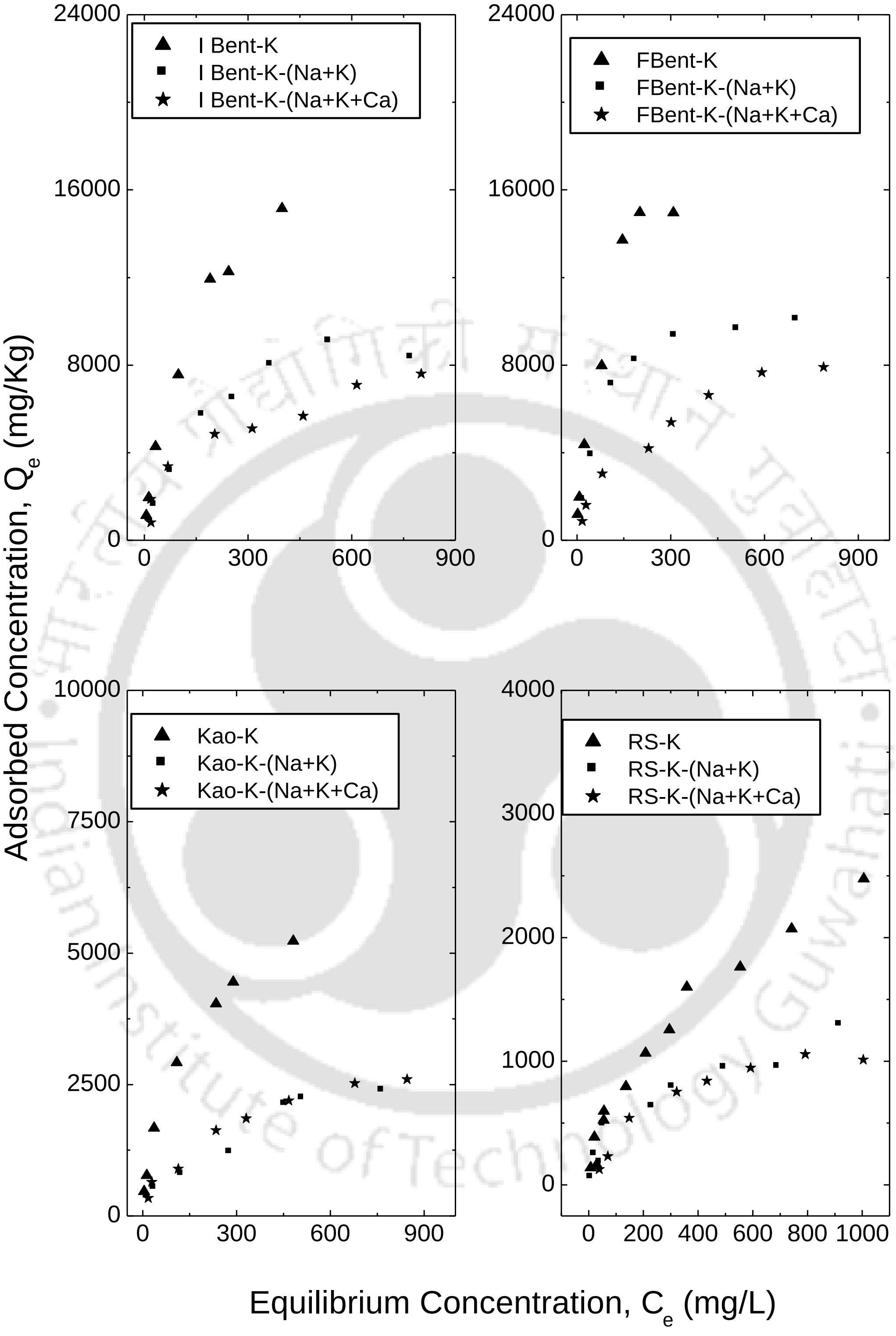


Fig.6.10a Comparison of retention characteristics of K^+ on 4 soils corresponding to single, binary and tertiary (Na+K+Ca) solution

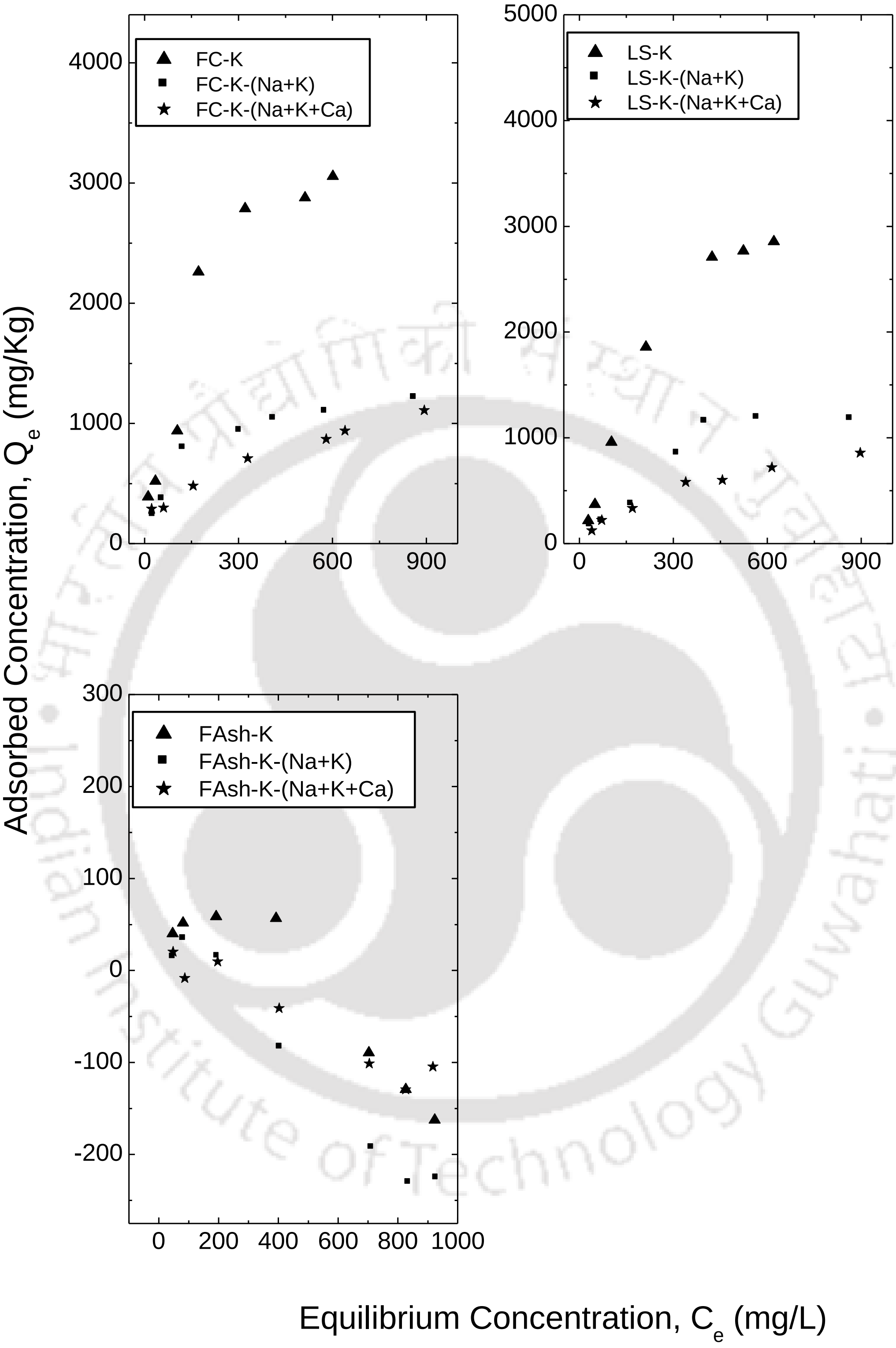


Fig.6.10b Comparison of retention characteristics of K^+ on 3 soils corresponding to single, binary and tertiary (Na+K+Ca) solution

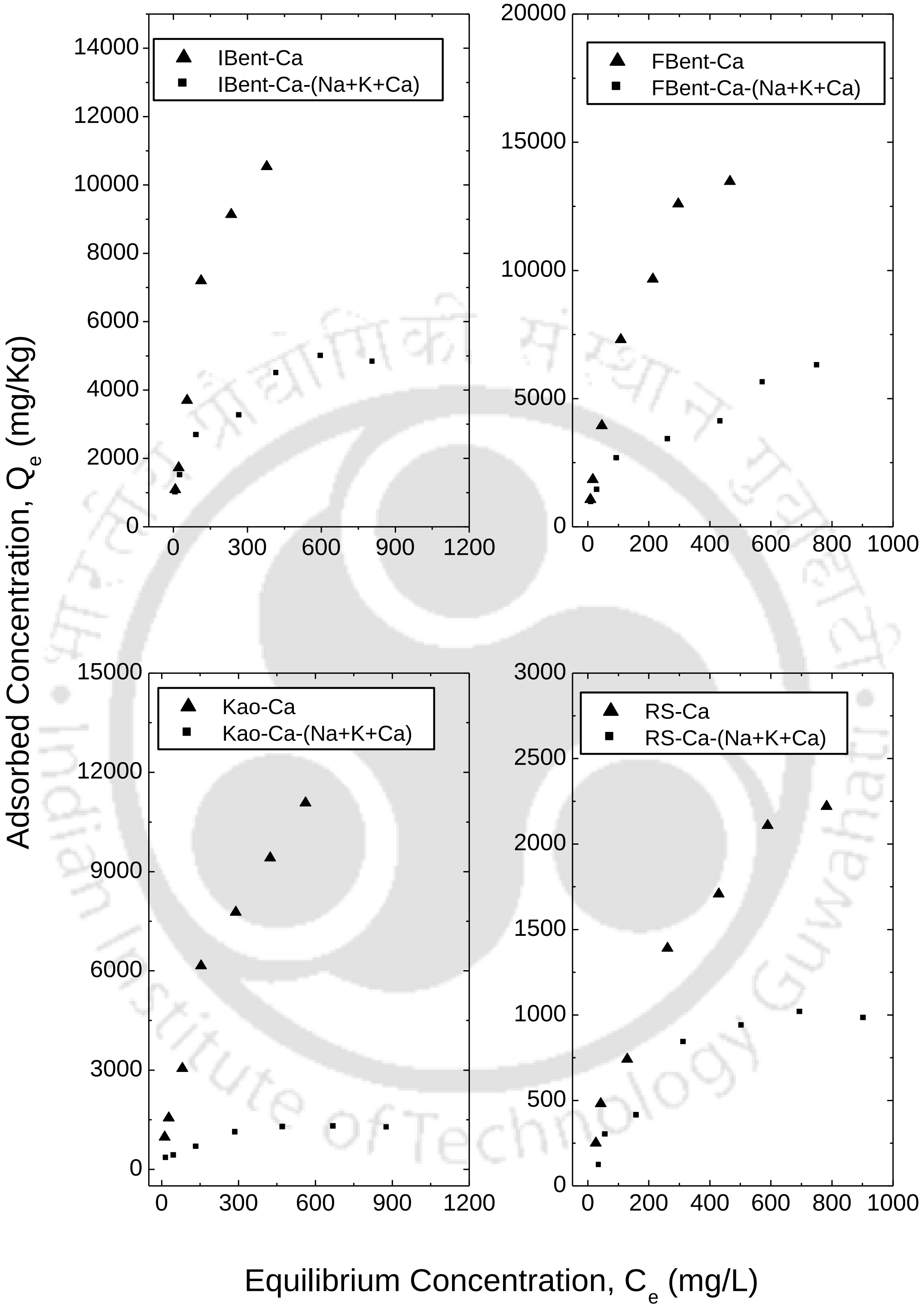


Fig.6.11a Comparison of retention characteristics of Ca^{+2} on 4 soils corresponding to single and tertiary (Na+K+Ca) solution

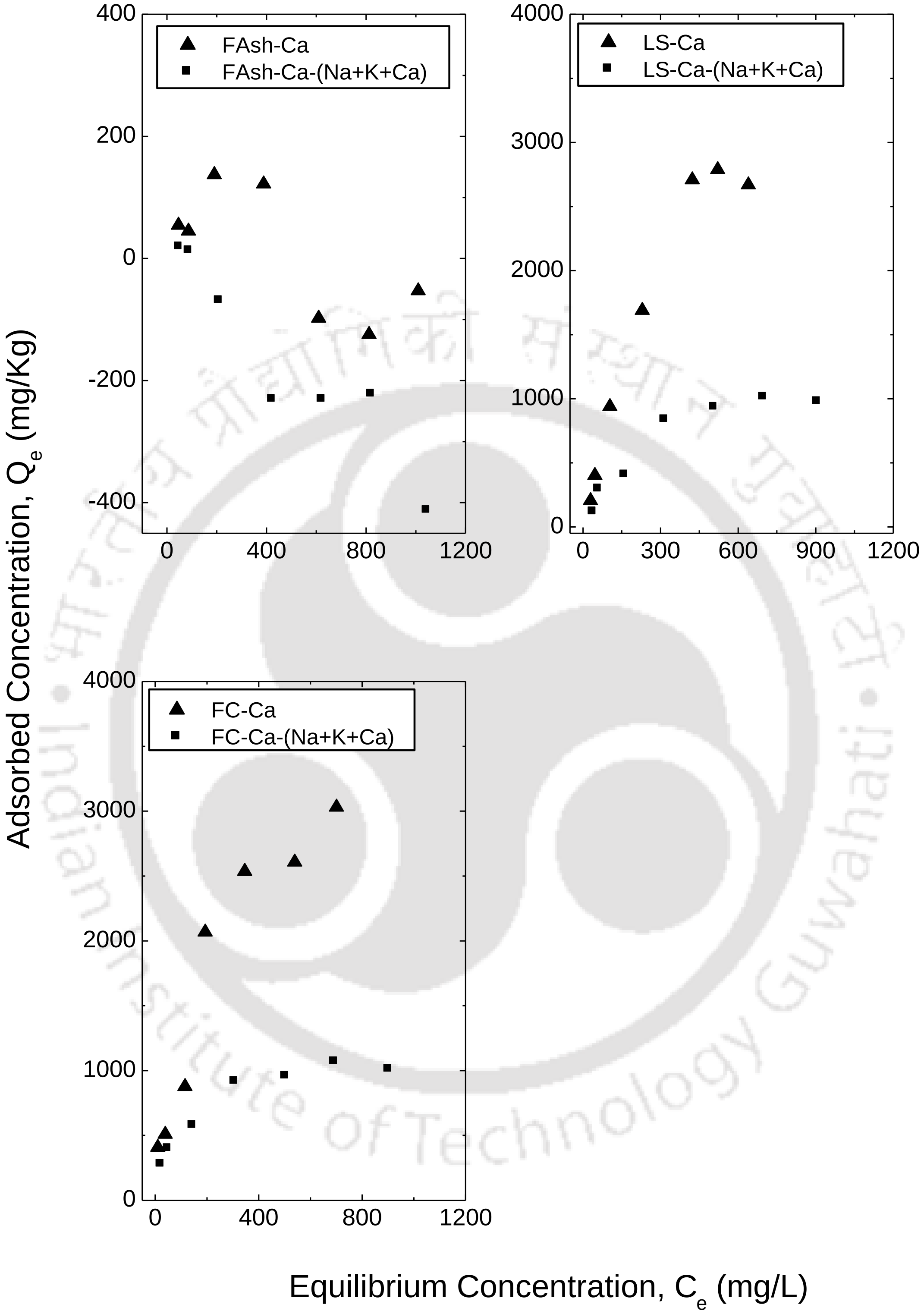


Fig.6.11b Comparison of retention characteristics of Ca^{+2} on 3 soils corresponding to single and tertiary (Na+K+Ca) solution

Table.6.6 Retention isotherm parameters for K^+ from (Na+K+Ca) solution

Soil	Parameters K-(Na+K+Ca)						Best Fit
	Freundlich			Langmuir			
	K_F(L/kg)	N	R^2	K_L(L/mg)	Q_m(mg/Kg)	R^2	
IBent	525.93	0.40	0.96	0.00857	7950.82	0.93	Freundlich
FBent	324.83	0.48	0.98	0.0039	10477.74	0.97	Freundlich
RS	46.889	0.46	0.93	0.00375	1384.54	0.98	Langmuir
FC	55.385	0.43	0.98	0.00424	1298.79	0.92	Freundlich
Kao	121.71	0.46	0.97	0.00393	3387.43	0.97	Freundlich
LS	21.83	0.54	0.98	0.00251	1204.39	0.98	Langmuir
FAsh	-	-	-	-	-	-	-

Table.6.7 Retention isotherm parameters for Ca^{+2} from (Na+K+Ca) solution

Soil	Parameters Ca-(Na+K+Ca)						Best Fit
	Freundlich			Langmuir			
	K_F(L/kg	N	R^2	K_L(L/mg)	Q_m(mg/K)	R^2	
IBent	464.314	0.36	0.96	0.01	5373.69	0.94	Freundlich
FBent	242.26	0.48	0.97	0.0040	7579.83	0.92	Freundlich
RS	41.389	0.48	0.90	0.0037	1365.97	0.95	Langmuir
FC	115.64	0.33	0.93	0.0094	1169.67	0.96	Langmuir
Kao	116.33	0.36	0.92	0.0074	1497.15	0.96	Freundlich
LS	41.37	0.48	0.90	0.0037	1365.96	0.95	Langmuir
FAsh	-	-	-	-	-	-	-

6.3 Batch test results for heavy metals

The retention of heavy metals is important in any waste management project. Its retention may get influenced by the presence of other heavy metals and also common ions (Covelo et al., 2004b; Gomes et al., 2001; Jalali and Moharrami 2007; Serrano et al., 2005; Sparks 1995). Such influence need to be systematically investigated. The interaction of single ion with soils may not adequately portray the retention behaviours of heavy metal in the presence of multiple ions. It is also important to conduct this type of study with various soils, as the composition of the soil matrix may result in unexpected interaction behaviour (Serrano et al., 2005)

6.3.1. Batch test results for Ni^{+2} and Cu^{+2} in binary (Ni+Cu) solution

Simultaneous Ni^{+2} and Cu^{+2} solution were made by mixing equal amount of Ni^{+2} and Cu^{+2} nitrate salts in deionized water. The retention characteristics of Ni^{+2} and Cu^{+2} in binary

(Ni+Cu) solution were plotted as shown in Fig.6.12a,b. From the figures, it can be noted that Cu^{+2} show higher retention than Ni^{+2} for all soils. For FAsh, comparable retention was observed for Ni^{+2} and Cu^{+2}. The isotherm parameters along with the goodness of fit is presented in tables 6.8 and 6.9. The retention selectivity sequence of the heavy metals was derived based on K_F and K_L and Q_m values. The Q_m values of all these seven soils showed a wide range of properties ranged from 1310.43 to 28417 mg/Kg for Cu^{+2} and from 1304.87 to 11034.71 mg/Kg for Ni^{+2}. These results show that the soils differ markedly in their Q_m values. Apparently, the large variation of Q_m values in the soils are related to the soil specific properties. It was observed that IBent and FBent, rich in smectite showed high retention of Ni^{+2} and Cu^{+2}. The results obtained in this study are in agreement with those reported by Elliott et al., (1986), Usman (2008) and Veeresh et al., (2003b), which indicates that Cu^{+2} retention is much greater than Ni^{+2} retention. This preferential retention is particularly followed according to the metal sequence as cited in Table 2.1. It was observed that as the initial concentration increased, Cu^{+2} was a strong competitor in occupying most of the retention sites than Ni^{+2}.

6.3.2 Comparison of Ni^{+2} and Cu^{+2} corresponding to single and binary (Cu+Ni) solution

Fig. 6.13a,b and Fig. 6.14a,b shows the comparison of Ni^{+2} and Cu^{+2} corresponding to single and binary system. The magnitude of these competitive effects was different for each metal. It can be noted from 6.13a,b that Cu^{+2} significantly influence the retention capacity of Ni^{+2} for all soils as compared to single ion system. From Fig 6.14a, b it can be noted that for the low range of concentration Ni^{+2} did not have a significant influence on the retention of Cu^{+2}. This can be attributed to the fact that Ni^{+2} is more affected by the electrostatic interactions with the surface exchange sites, while Cu^{+2} is more affected by covalent binding to mineral surfaces (McBride, 1994). Such ideas are in agreement with the findings of Matos et al., (1996); Fontes et al., (2000); Gomes et al., (2001); Fontes and Gomes (2003). Thus at low metal concentrations, effects of competition were not significant for Cu^{+2}. This seems to concur with the work of Saha et al., (2002), who reported no evidence of metal competition at low concentrations. Saha et al., (2002) explained that at low metal concentrations metals are mainly retained onto specific retention sites. At higher metal concentration soil lose its ability to bind heavy metals as retention sites overlap, thereby becoming less specific for a particular metal. This reduces metal retention. Thus the effect of competition in reducing the retention of metals followed the order $Cu^{+2} > Ni^{+2}$. In addition, different soil behaved differently which is likely to have been the result of differences in the nature of the dominant sorbing surfaces for each metal. Alloway (1995) explained that specific retention is related to the hydrolysis of heavy metal ions. The metals thus can form hydroxyl complexes are specifically adsorbed more (Thompson and Goyne 2012). Therefore, the hydrolysis constant, pK values of metal hydrolysis product determine the retention behaviour of the metals, with specific retention decreasing with increasing pK. Thus, the order of increasing pK values: Cu(7.7) < Ni(9.9) offers an explanation for the preferential retention of Cu^{+2} to Ni^{+2}.

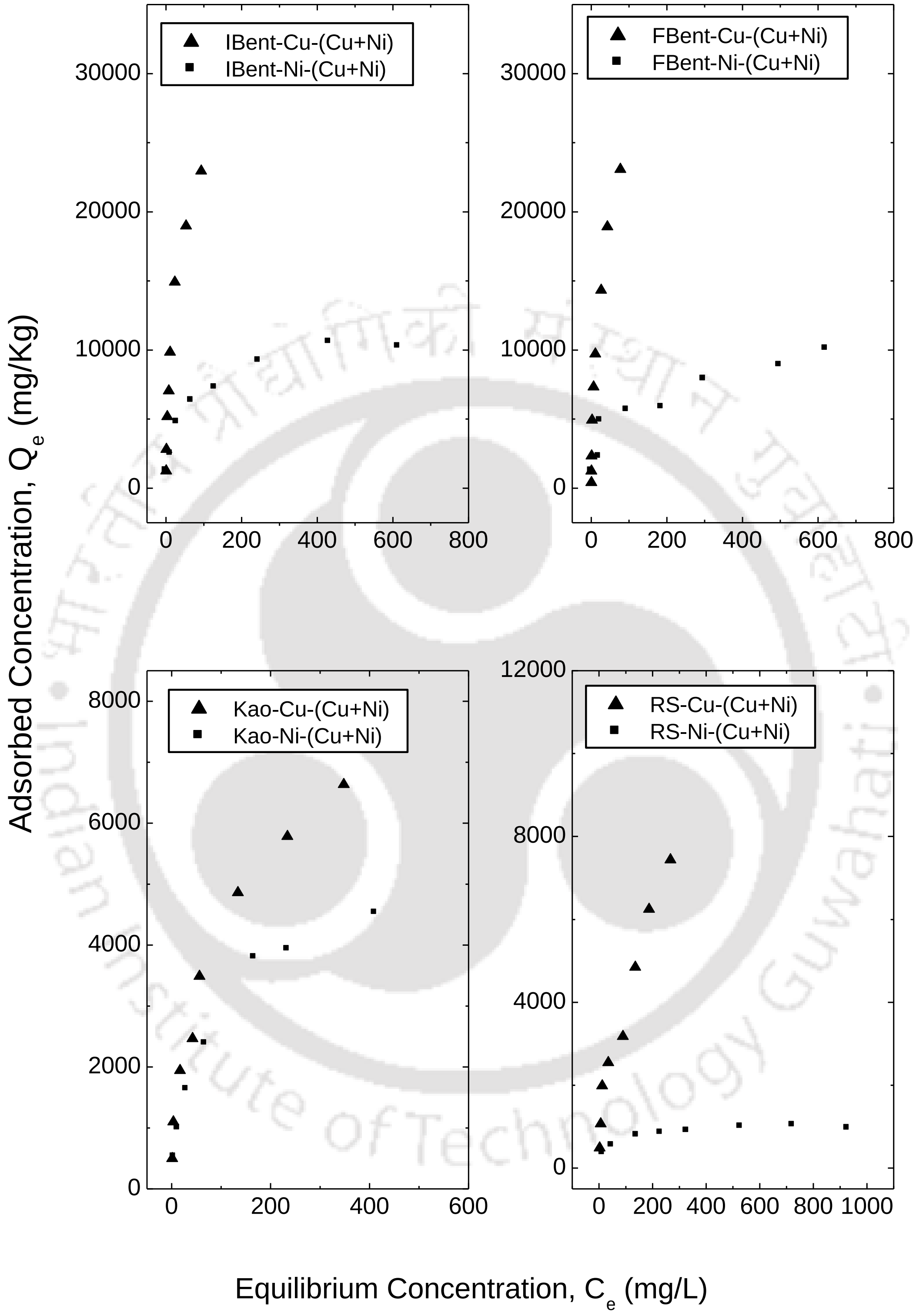


Fig. 6.12a Comparison of retention characteristics of Cu^{+2} and Ni^{+2} on 4 soils from binary (Cu+Ni) solution

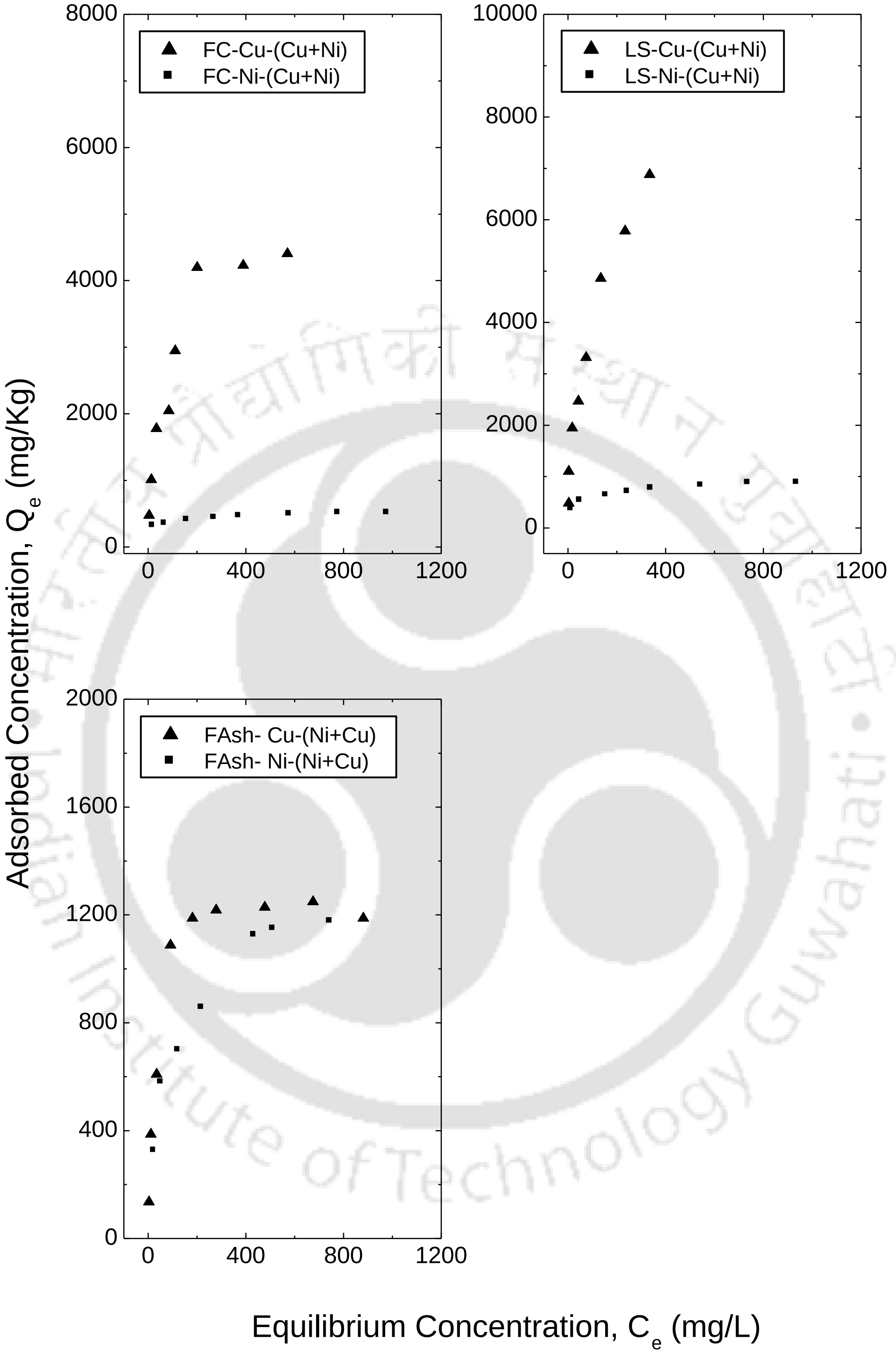


Fig.6.12b Comparison of retention characteristics of Cu^{+2} and Ni^{+2} on 3 soils from binary (Cu+Ni) solution

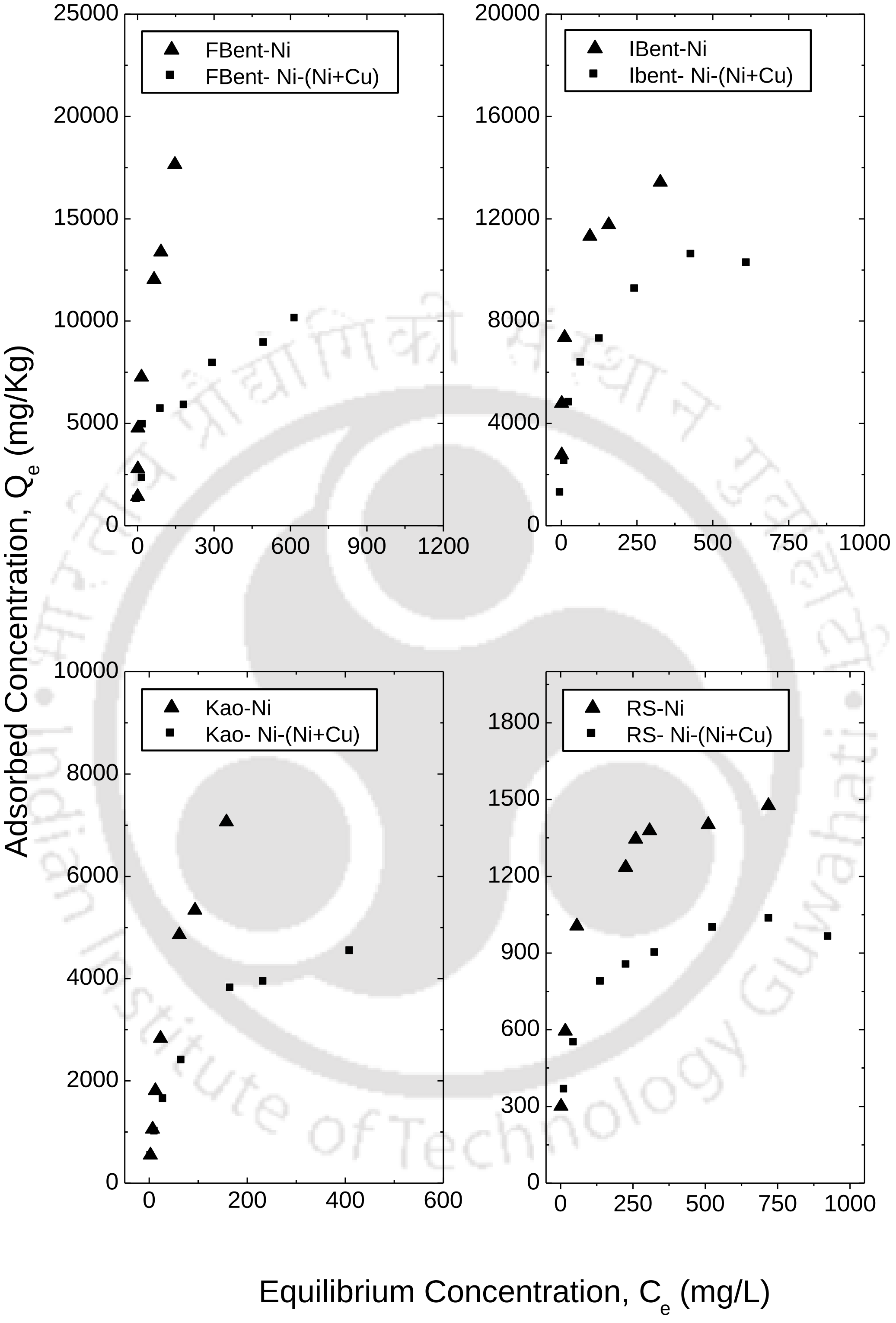


Fig.6.13a Comparison of retention characteristics of Ni^{+2} on 4 soils corresponding to single and binary (Cu+Ni) solution

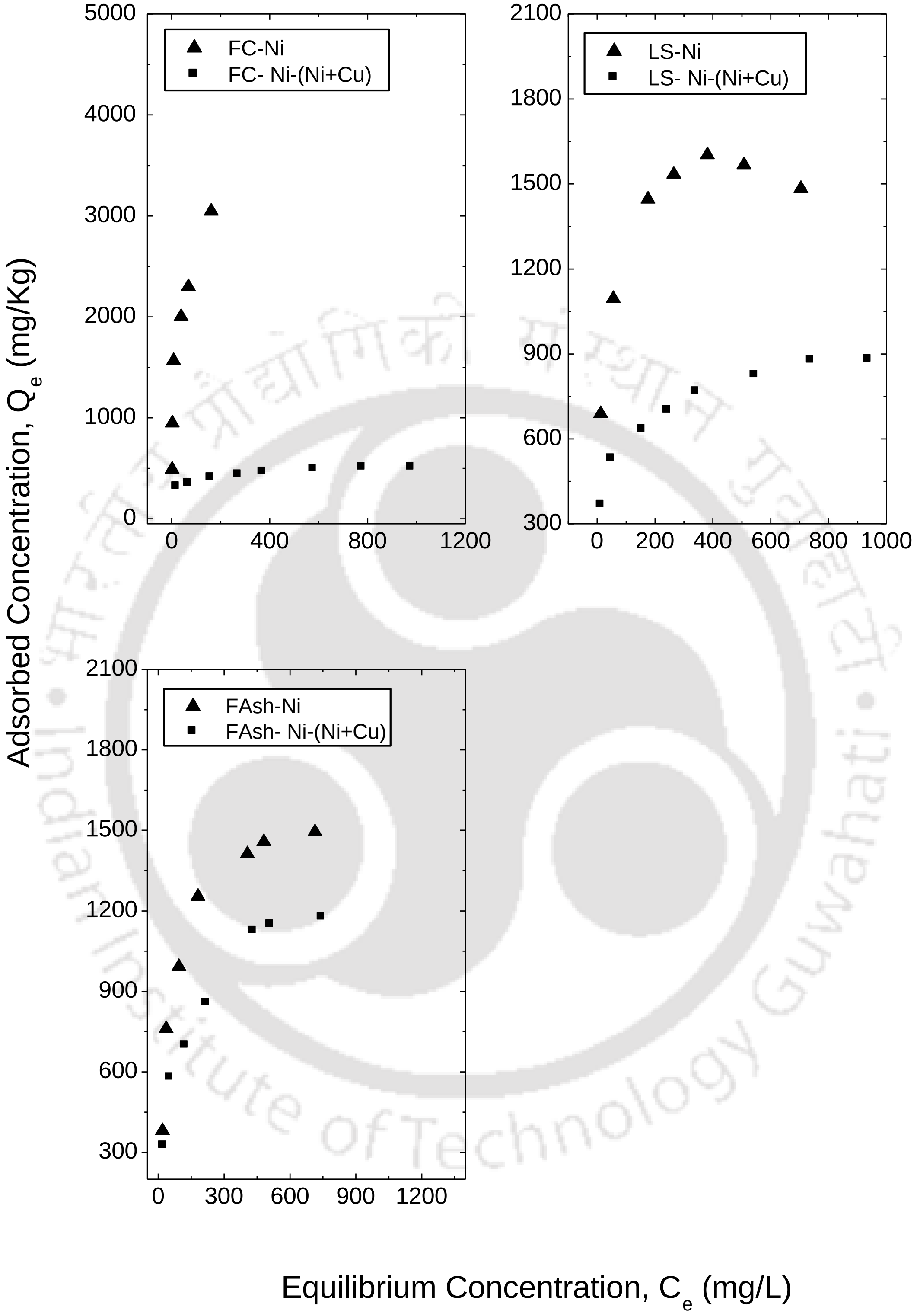


Fig.6.13b Comparison of retention characteristics of Ni^{+2} on 3 soils corresponding to single and binary (Cu+Ni) solution

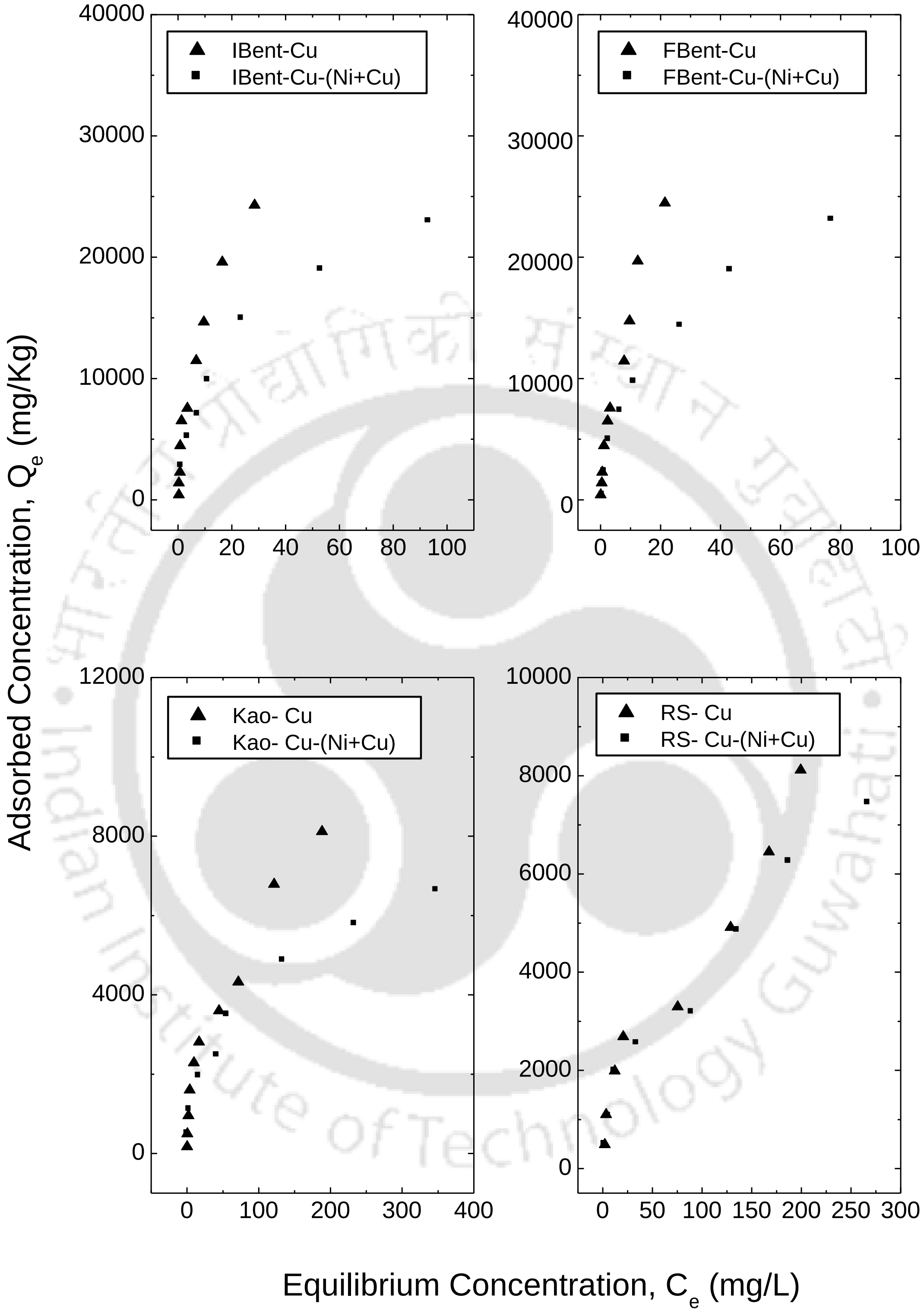


Fig.6.14a Comparison of retention characteristics of Cu^{+2} on 4 soils corresponding to single and binary (Cu+Ni) solution

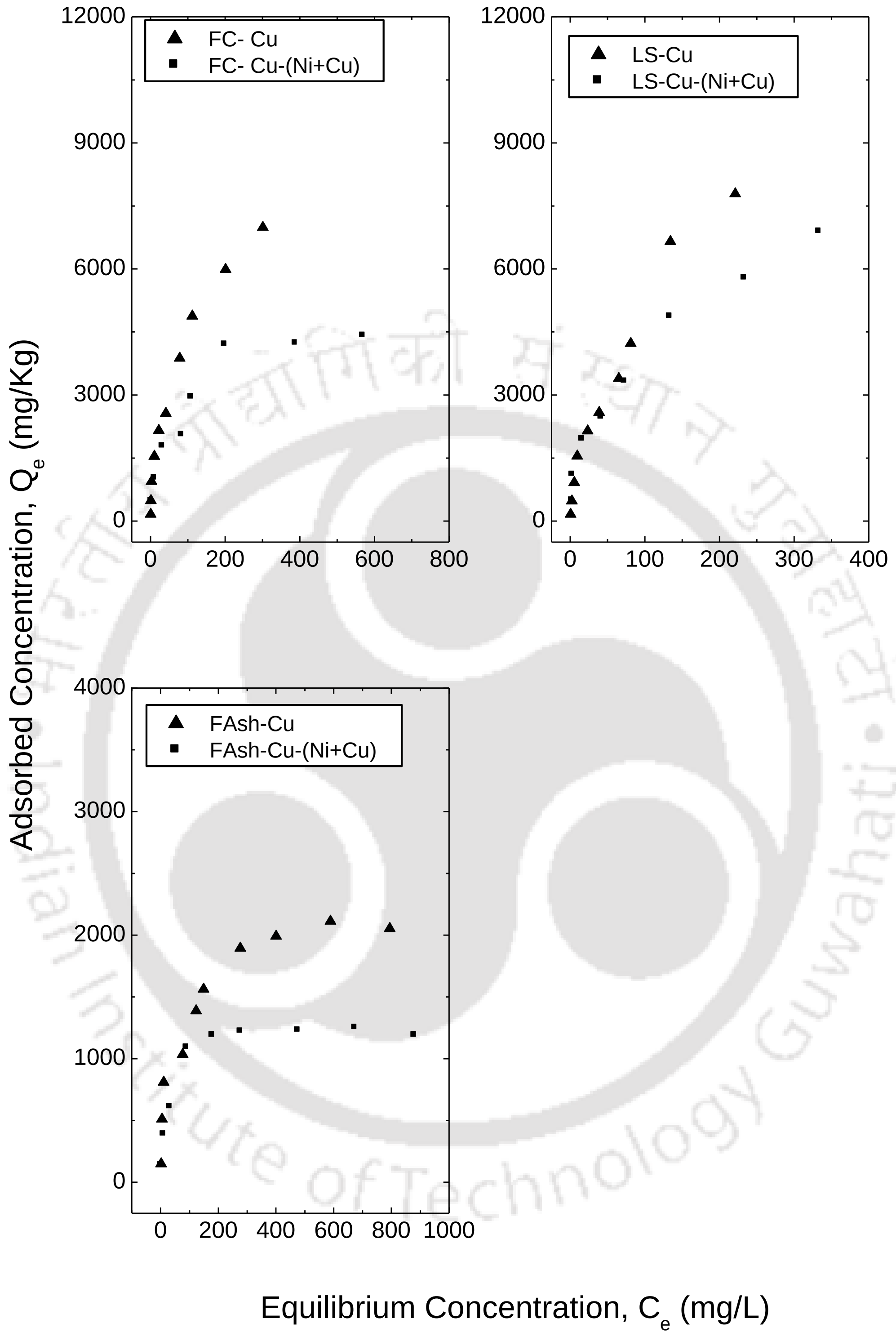


Fig.6.14b Comparison of retention characteristics of Soils in Cu^{+2} on 3 soils corresponding to single and binary (Cu+Ni) solution

Table.6.8 Retention isotherm parameters for Cu^{+2} from (Ni+Cu) solution

Soil	**Parameters Cu-(Ni+Cu)**						**Best Fit**
	Freundlich			**Langmuir**			
	K_F(L/Kg)	**N**	**R^2**	**K_L(L/mg)**	**Q_m(mg/Kg)**	**R^2**	
IBent	3108.59	0.45	0.97	0.0525	26836.04	0.99	Langmuir
FBent	2630.68	0.51	0.98	0.047	28417.66	0.98	Freundlich
RS	351.62	0.54	0.97	0.006	11406.61	0.92	Freundlich
FC	501.50	0.36	0.92	0.0132	5083.17	0.94	Langmuir
Kao	618.56	0.41	0.98	0.0144	7646.74	0.96	Freundlich
LS	483.47	0.46	0.99	0.0105	8422.42	0.96	Freundlich
FA	296.31	0.23	0.81	0.0348	1310.43	0.97	Langmuir

Table.6.9 Retention isotherm parameters for Ni^{+2} from (Ni+Cu) solution

Soil	**Parameters Ni-(Ni+Cu)**						**Best Fit**
	Freundlich			**Langmuir**			
	K_F(L/Kg)	**N**	**R^2**	**K_L(L/mg)**	**Q_m(mg/Kg)**	**R^2**	
IBent	1733.21	0.291	0.96	0.022	11034.71	0.96	Langmuir
FBent	1291.82	0.314	0.93	0.0195	9554.26	0.85	Freundlich
RS	253.35	0.211	0.92	0.0271	1023.19	0.96	Langmuir
FC	208.14	0.13	0.98	0.0683	485.00	0.76	Freundlich
Kao	420.22	0.40	0.97	0.015	5171.85	0.99	Langmuir
LS	234.10	0.19	0.98	0.036	847.25	0.88	Freundlich
FA	144.98	0.33	0.96	0.0116	1304.87	0.96	Langmuir

6.3.3 Batch test results for $Cu^{+2}$and Pb^{+2} in binary (Pb+Cu) solution

Simultaneous retention of Pb^{+2} and Cu^{+2} on soils were conducted by mixing equivalent amount of lead and copper nitrate solutions. The data obtained after conducting batch tests for Cu^{+2} and Pb^{+2} from binary (Cu+Pb) solution is presented in Fig.6.15a,b. It can be observed from the figures that for all the soils at the initial range of concentration both Cu^{+2} and Pb^{+2} showed comparable retention. For low equilibrium concentration of competitive isotherms all competing ions were retained, whereas for higher equilibrium concentrations isotherms showed more affinity for Pb^{+2} than Cu^{+2}. The metal retention capacities followed the sequence $Pb^{+2} > Cu^{+2}$ in binary systems for all soils except RS and FC explaining their higher affinity to the former. For soil RS, it can be seen that both Pb^{+2} and Cu^{+2} competed equally for C_e around 120 mg/L. However, as concentration increased the repression effect of retention was observed to be more for Pb^{+2} as compared to Cu^{+2}. Similar results were reported by Usman (2008), who studied the competitive retention of Pb^{+2} and Cu^{+2} onto Egyptian smectitic soils.

The observed affinity in the retention of Pb^{+2} and Cu^{+2} could be attributed to the difference in their behavior based of their covalent indices. Pb^{+2} is classified as a class b ion, while Cu^{+2} is classified as borderline ions. On the basis of this argument, it is possible to explain clearly the competition effects observed in the present study. Since Pb^{+2} belongs to a different class of ions (class b), other cations do not exert any effect on its retention. Iqbal and Edyvean (2004) and Paradello and Barral (2012) reported that maximum retention capacity of composts for Pb^{+2} was about twice of Cu^{+2}. This affinity of Pb^{+2} can also be demonstrated with the order of electronegativity (2.33 Pb^{+2} >1.90 Cu^{+2}), hydrolysis constant (pK 8.6 Pb^{+2} > pK 7.9 Cu^{+2}) and ionic radii (1.20 Å Pb^{+2} > 0.72 Å Cu^{+2}). Thus the results affirms that the metal ion electronegativity, hydrolysis constant, and ionic radius may influence the order of preference of metal binding onto soil and were consistent with previous studies in the literatures. Nevertheless, these results cannot be generalised as there are reversed trends depicted by soils RS and FC.

Another important observation to be noted from Table 6.10 and 6.11 (retention parameters) is that the K_F for Pb^{+2} is 792.79 L/Kg as compared to 220.192 L/Kg of Cu^{+2} for soil RS. However, the Q_m value was less for Pb^{+2} as compared to Cu^{+2}. Similar observation could be noted from soil Kao from Fig.6.15a where it is quite evident that Cu^{+2} exhibited lower retention than Pb^{+2}. However, K_F value of Cu^{+2} was higher than Pb^{+2}. It is clear that the experimental observation is not reflected by mathematical quantification. This contradictory finding raises an important question whether the isotherms fails at higher concentration (or where the saturation curve is achieved). Therefore, it is indispensable to highlight that such Freundlich isotherm parameters could be misleading for the prediction of fate of contaminants. Freundlich isotherm is often criticised for lacking a fundamental thermodynamics basis since it does not reduce to Henry's law at low concentration (Porter and Mckay 2001).

6.3.4 Comparison of Pb^{+2} and Cu^{+2} corresponding to single and binary solution (Pb+Cu)

Fig.6.16a, b and Fig.6.17a,b represented the retention behavior of Pb^{+2} and Cu^{+2} onto both single and binary metal solution. As expected, the retention for Pb^{+2} and Cu^{+2} was greater from single solution for all the soils. The results confirmed that the presence of Pb^{+2} and Cu^{+2} had evident competitive effect on the retention characteristics of each other. The inhibitory effect of Cu^{+2} in the presence of Pb^{+2} was more pronounced in case of FAsh (Fig

6.17b). The study also highlights that Pb^{+2} could compete with Cu^{+2} and other metals in multiple metal combination for binding sites on soil. Such a trend is similar to Fontes et al., (2000) which indicated that competition has a very small effect on lead retention. As can be seen from the figures the competition was evident at higher range of concentration, which was unique for Cu^{+2} and Pb^{+2} and also depends on the soil type.

In a similar trend with Cu^{+2}, the values of Q_m for Pb^{+2} was lower for binary solution as compared to the single solution for all the soils. Chotpantarat et al., (2011) observed that retention capacities of metals in binary system are lower than that of single metal system. Qin et al., (2006) observed that total retention of both Pb^{+2} and Cu^{+2} on peat in binary system was higher than their respective single solute system. They concluded that total retention capacity of metals in multi-component systems increased, but individual metal retention will decrease due to metal interaction and competition for retention sites.

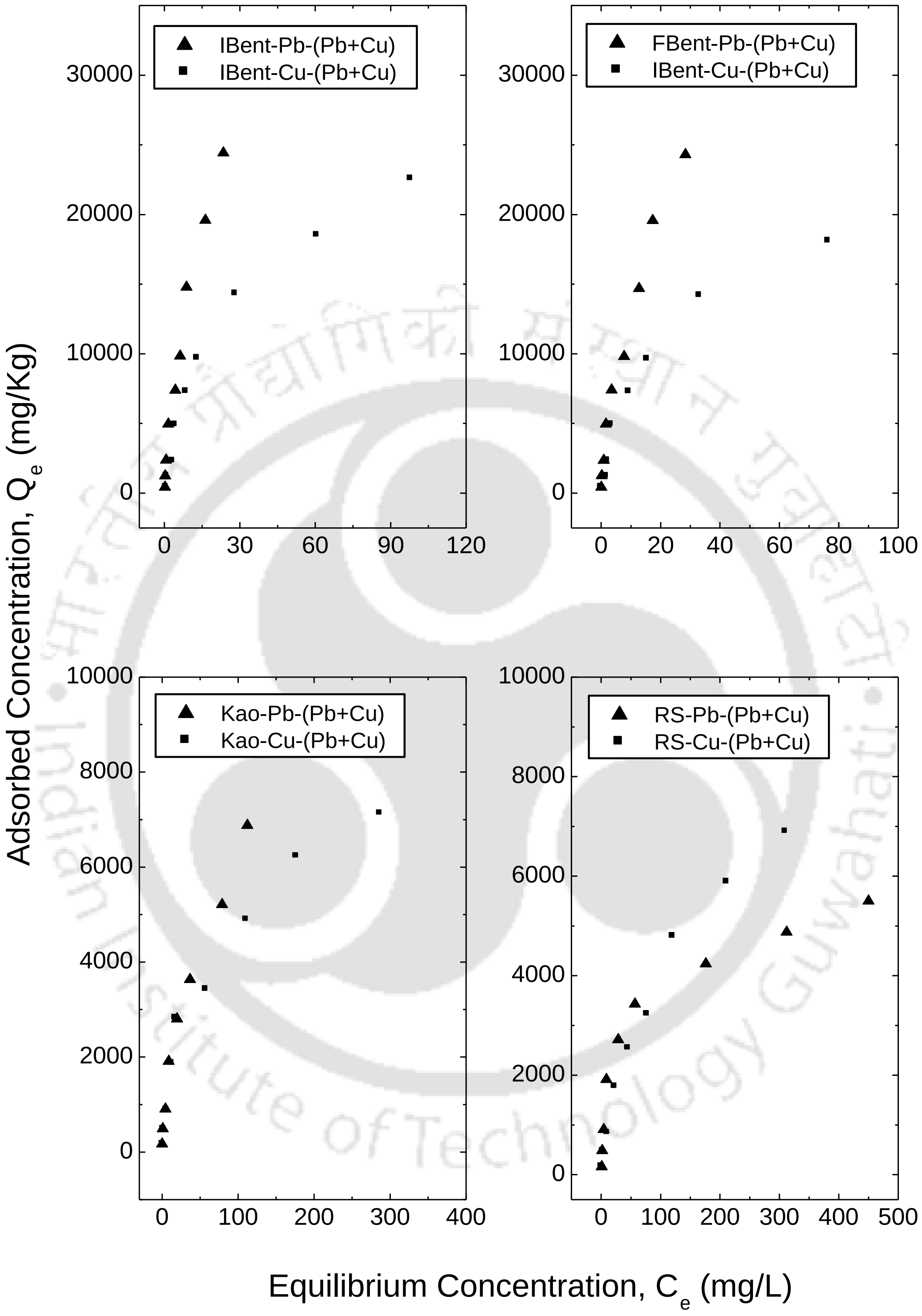


Fig. 6.15a Comparison of retention characteristics of Cu^{+2}and Pb^{+2} on 4 soils from binary (Pb+Cu) solution

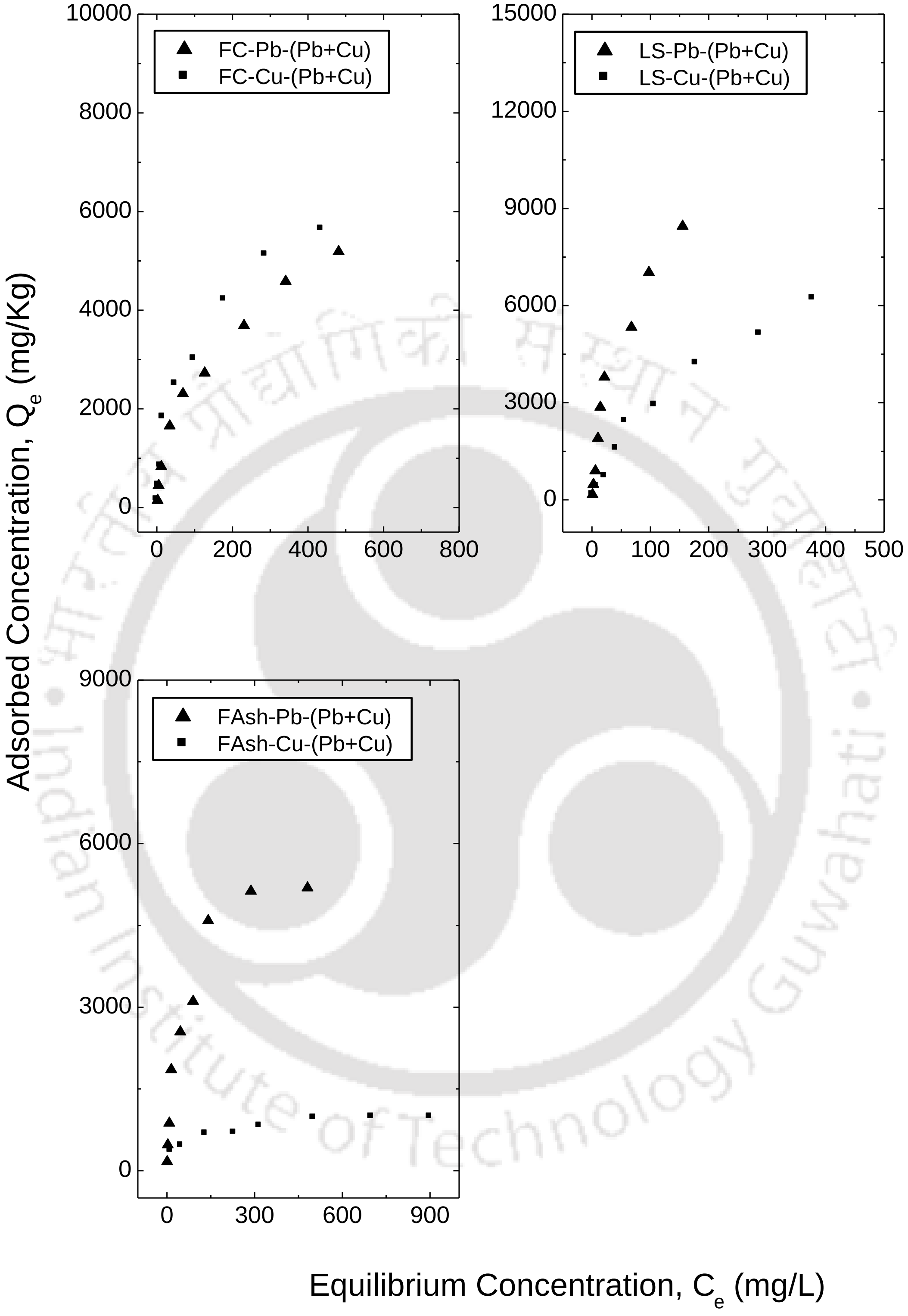


Fig. 6.15b Comparison of retention characteristics of soils in $Cu^{+2}$and Pb^{+2} on 3 soils corresponding to binary (Pb+Cu) solution

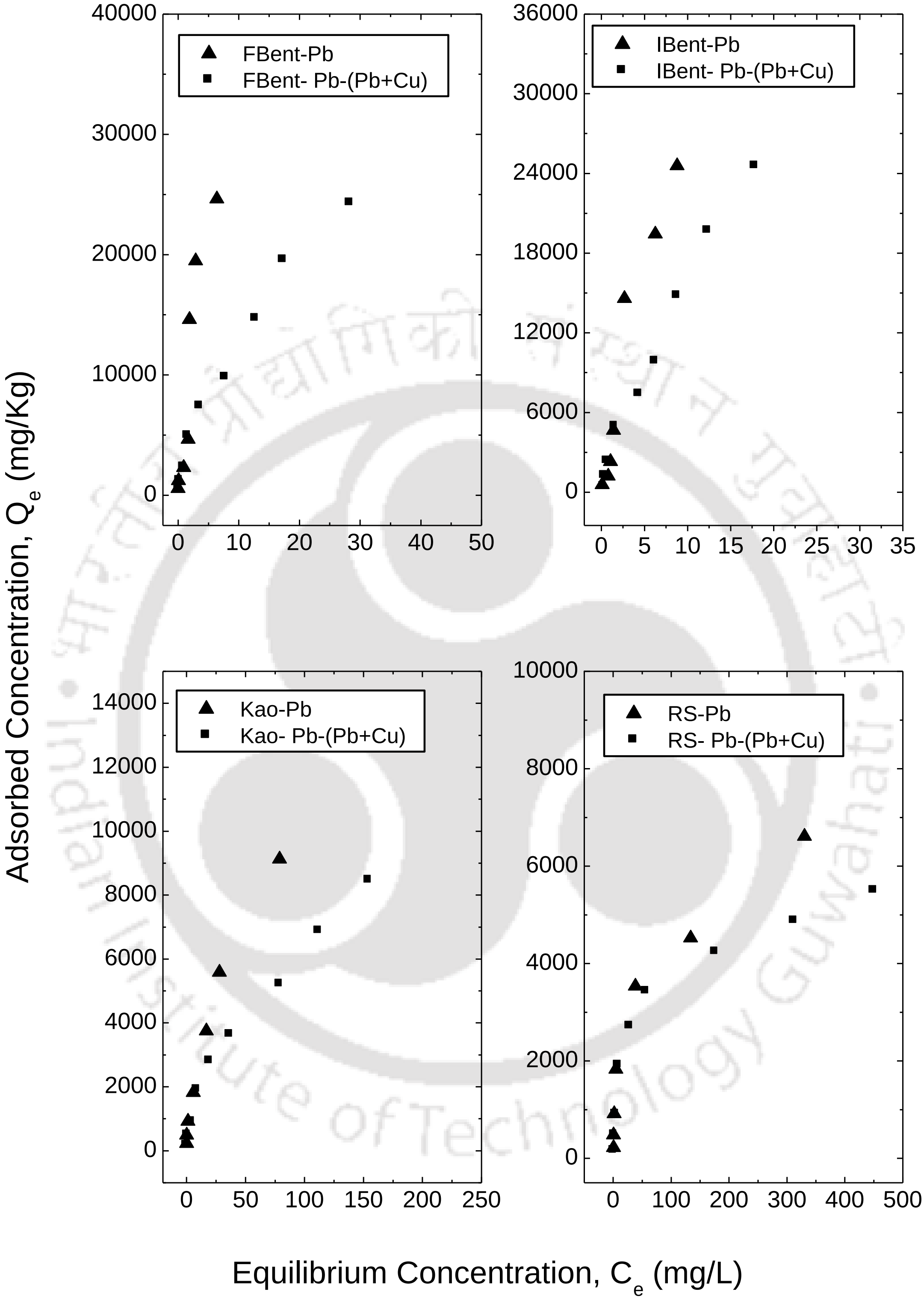


Fig. 6.16a Comparison of retention characteristics of Pb^{+2} on 4 soils corresponding to single and binary (Pb+Cu) solution

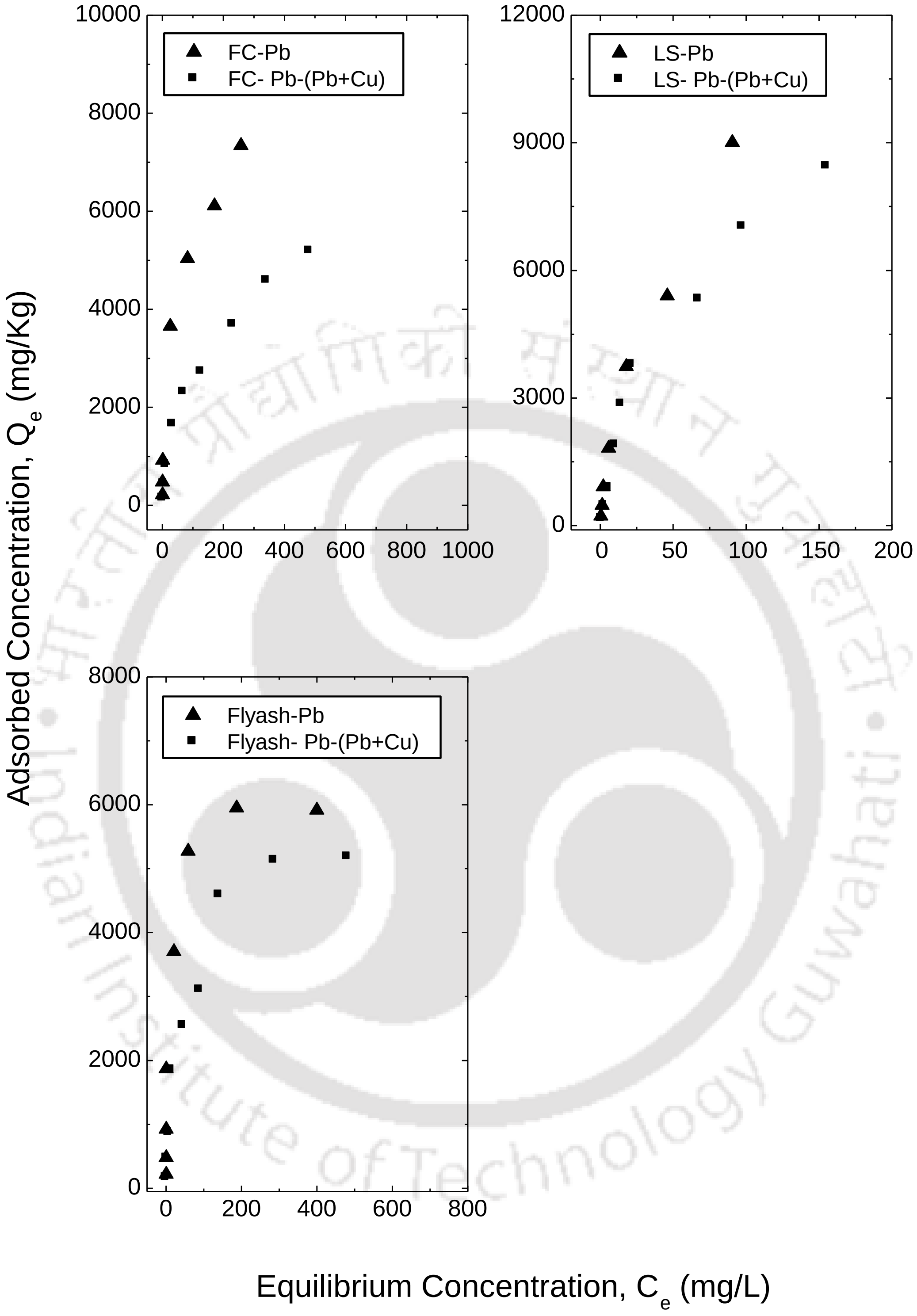


Fig. 6.16b Comparison of retention characteristics of Pb^{+2} on 3 soils corresponding to single and binary (Pb+Cu) solution

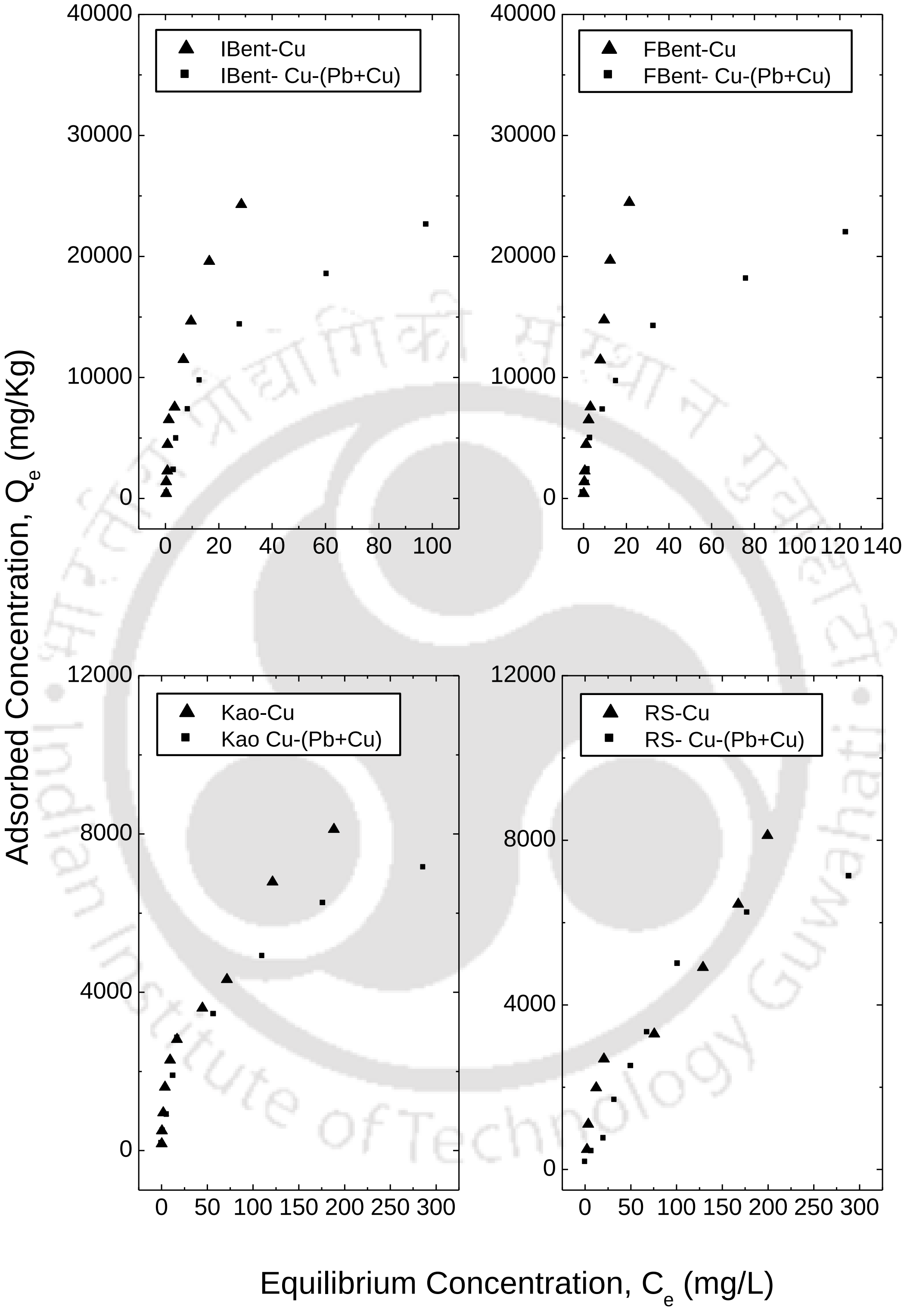


Fig. 6.17a Comparison of retention characteristics Cu^{+2} on 4 soils corresponding to single and binary (Pb+Cu) solution

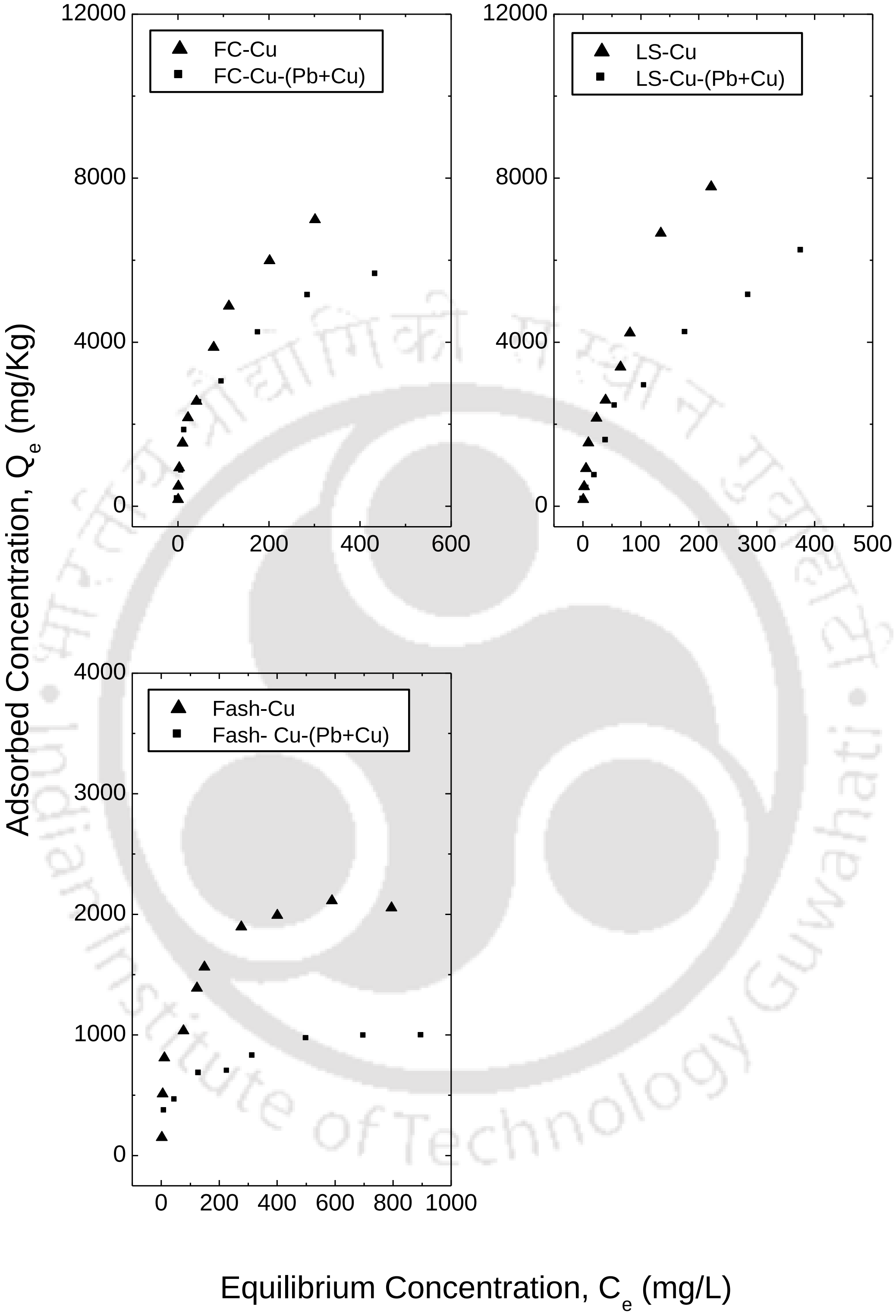


Fig. 6.17b Comparison of retention characteristics Cu $^{+2}$ on 3 soils corresponding to single and binary (Pb+Cu) solution

Table.6.10 Retention isotherm parameters for Cu^{+2} from (Pb+Cu) solution

Soil	Parameters Cu-(Pb+Cu)						Best Fit
	Freundlich			Langmuir			
	K_F(L/Kg)	N	R^2	K_L(L/mg)	Q_m(mg/Kg)	R^2	
IBent	2259.28	0.51	0.97	0.0387	27610.59	0.99	Langmuir
FBent	2494.37	0.46	0.97	0.04168	25017.49	0.98	Langmuir
RS	220.19	0.63	0.95	0.0057	11906.84	0.98	Langmuir
FC	431.04	0.43	0.98	0.0128	6365.68	0.97	Freundlich
Kao	549.19	0.46	0.97	0.0179	8058.33	0.96	Freundlich
LS	176.31	0.60	0.98	0.00482	9257.96	0.98	Langmuir
FA	186.87	0.25	0.96	0.01849	1006.66	0.87	Freundlich

Table 6.11 Retention isotherm parameters for Pb^{+2} from (Pb+Cu) solution

Soil	Parameters Pb-(Pb+Cu)						Best Fit
	Freundlich			Langmuir			
	K_F(L/Kg)	N	R^2	K_L(L/mg)	Q_m(mg/Kg)	R^2	
IBent	3209.35	0.65	0.99	0.0534	43275.41	0.99	Freundlich
FBent	3125.90	0.61	0.99	0.048	41475.94	0.98	Freundlich
RS	792.79	0.32	0.96	0.042	5255.18	0.97	Langmuir
FC	273.37	0.48	0.99	0.0078	6231.62	0.98	Freundlich
Kao	481.72	0.56	0.99	0.0129	11875.69	0.97	Freundlich
LS	593.12	0.53	0.99	0.0221	10344.79	0.98	Freundlich
FA	632.15	0.36	0.94	0.021	5780.20	0.97	Langmuir

6.3.5 Batch tests results for Cu^{+2} and Zn^{+2} in binary (Cu+Zn) solution

Simultaneous Cu^{+2} and Zn^{+2} retention were conducted by mixing equal amount of Cu^{+2} and Zn^{+2} nitrate salts in deionized water. The data obtained after conducting batch tests were compared as shown in Figs.6.18a,b. It can be noted from the figures that the curves are highly non linear and depict strong affinities at lower concentration for both Cu^{+2} and Zn^{+2}. The competitive behavior of (Cu+Zn) binary system showed that for the soils except for FAsh, Cu^{+2} sorbed higher than Zn^{+2}, explaining their higher affinity to the former. The various fitting parameters of the isotherms Langmuir and Freundlich long with goodness of fir are listed in Table 6.12 for Cu^{+2} and 6.13 for Zn^{+2}. Both the isotherms gave a satisfactory fitting. But in majority of the cases Langmuir isotherm gave the best fit for both Cu^{+2} and Zn^{+2}.

Findings by Mesquita (1998) reported that in acid soils Cu^{+2} is retained mainly on specific sites while Zn^{+2} is retained on non specific sites. Also the retention of Cu^{+2} begins at lower pH than Zn^{+2}. It was observed that Cu^{+2} and Zn^{+2} retention increased when concentration of the added cation increased. In most of the cases Cu^{+2} performed better than Zn^{+2}. This result may be related to their ionic radii and chemical properties. The electronegativity values are 1.46 and 1.75 for Cu^{+2} and Zn^{+2}, respectively, and their respective radii of 0.098 and 0.069 nm. The average electric dipole polarizabilities of Cu^{+2} and Zn^{+2} atoms are 7.2 and 6.8×10^{-24} cm^3, respectively (Liu et al., 2006). Metal ions with low electronegativity, high polarizability and large ionic size are called “soft” ions (Sparks, 1995) and they aid in the retention process.

6.3.6 Comparison of Cu^{+2} and Zn^{+2} corresponding to single and binary (Cu+Zn) solution

Fig 6.19a,b and 6.20a,b shows the comparison of Cu^{+2} and Zn^{+2} with respect to single and binary solutions, respectively. It can be noted that the metal retention from binary solution were reduced as compared to the single solution for both heavy metals. These results confirmed that the competition effect of metal ions for retention sites. Similar evidence that Cu^{+2} and Zn^{+2} retention are depressed by the mutual competition on to the retention sites are given by researchers (Christensen 1989; Mesquita and Vierae Silva, 1996; Mesquita 1998; Leitao et al., 2000; Fontes and Gomes, 2003). As evident from the figures the difference was more pronounced at the higher range of concentration. A low metal concentrations, effects of competition were not evident. This was further explained by Saha et al., (2002) that at low added metal concentrations metals are mainly adsorbed onto specific retention sites, while at higher metal inputs soils lose some of their ability to bind heavy metals as retention sites overlap. This makes the retention sites less specific for a particular metal. This in turn induces a reduction in metal retention. It can be further described from the experimental findings that the magnitude of the reduction was different for each of soil.

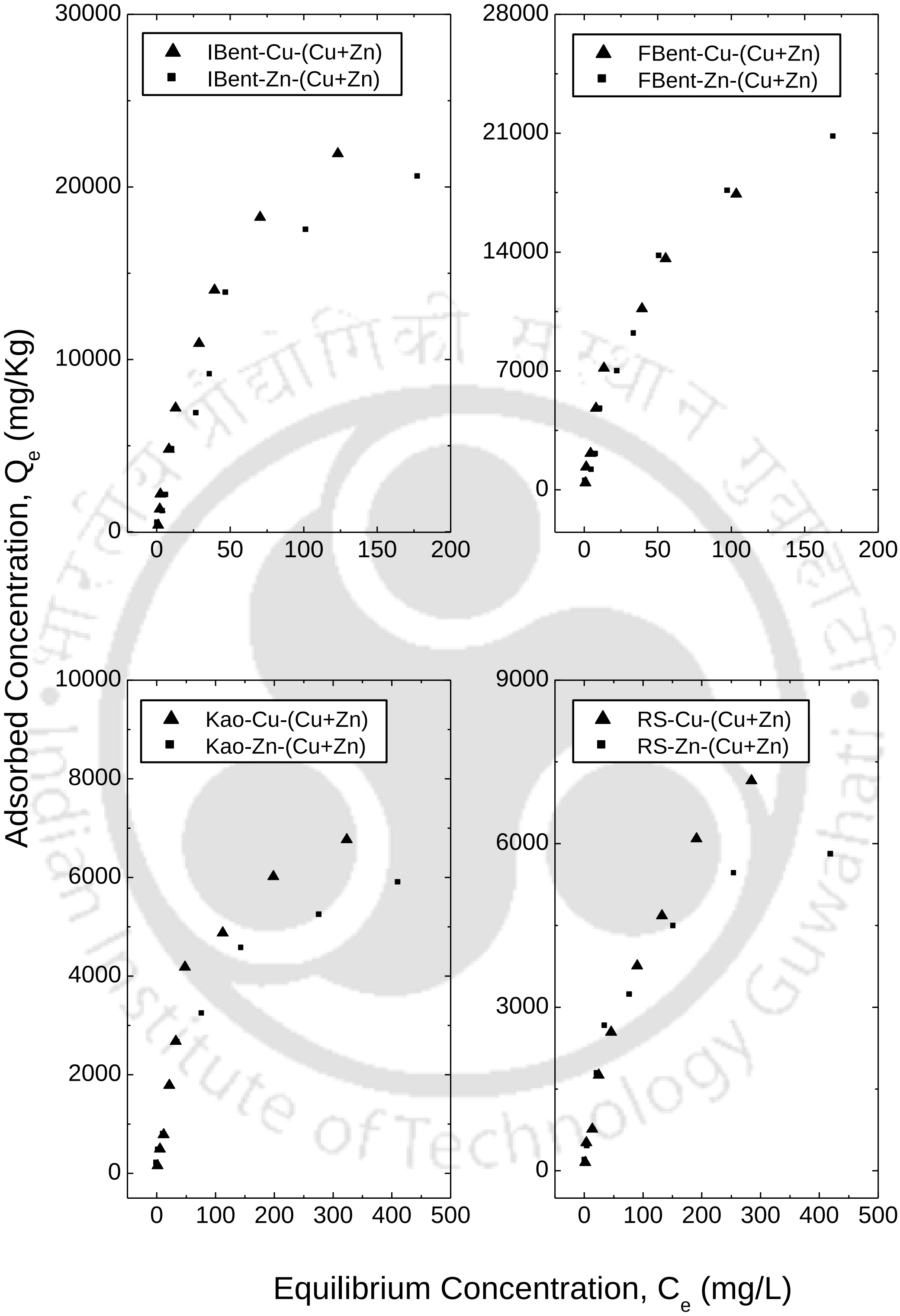


Fig. 6.18a Comparison of retention characteristics in Cu $^{+2}$ and Zn^{+2} on 4 soils corresponding to binary (Cu+Zn) solution

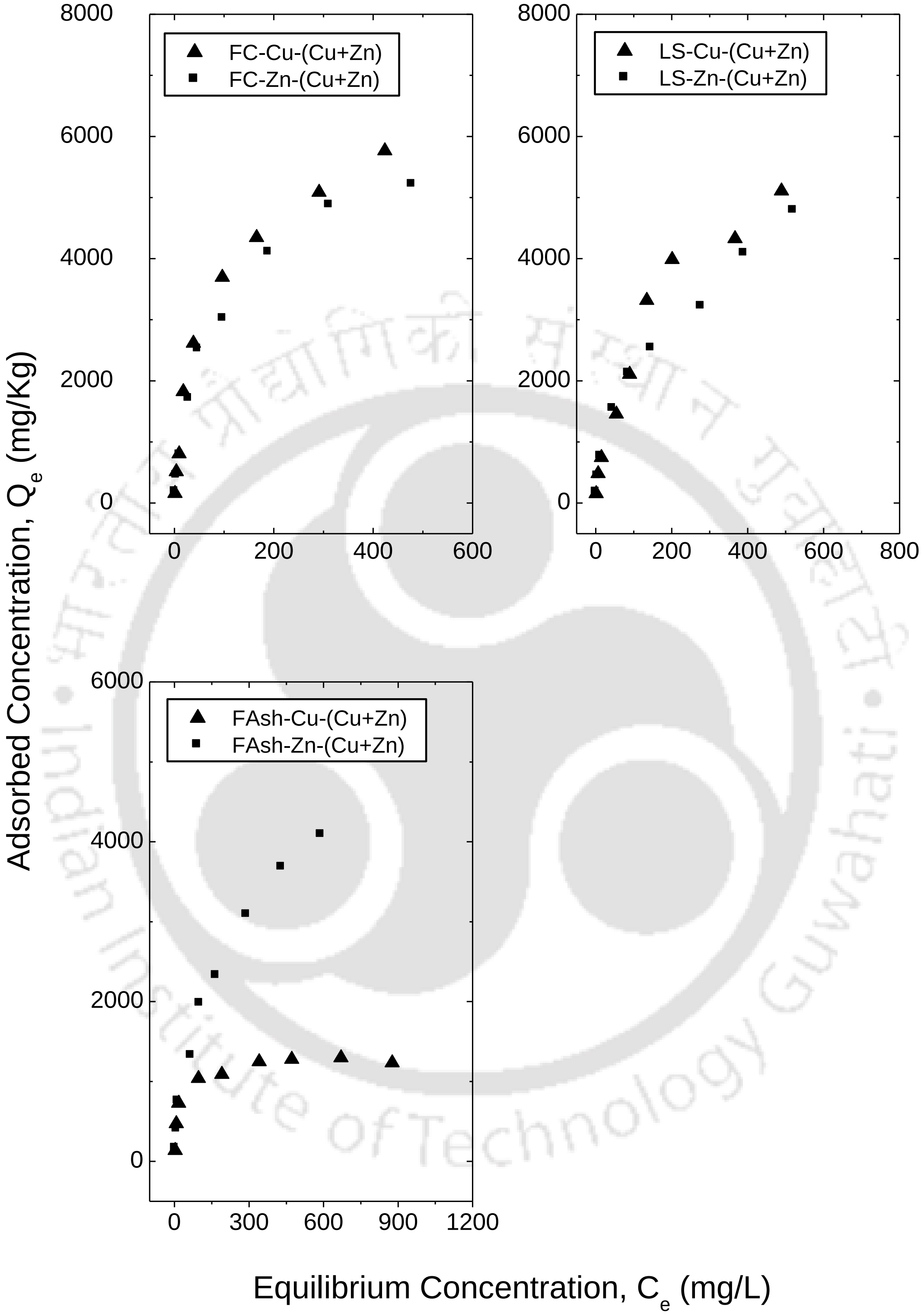


Fig. 6.18b Comparison of retention characteristics of Cu^{+2} and Zn^{+2} on 4 soils corresponding to binary (Cu+Zn) solution

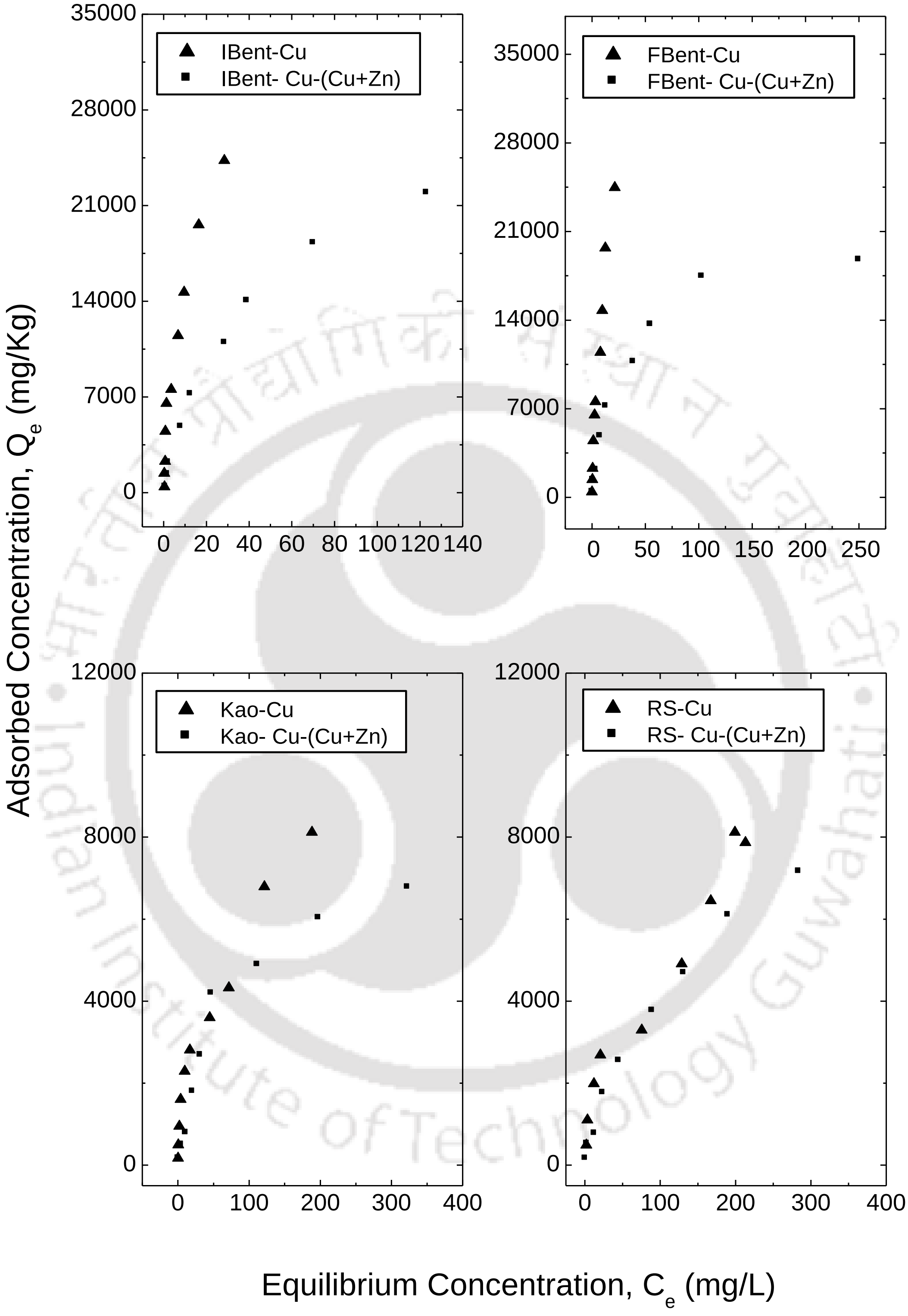


Fig.6.19a Comparison of retention characteristics of Cu^{+2} on 4 soils corresponding to single and binary (Cu+Zn) solution

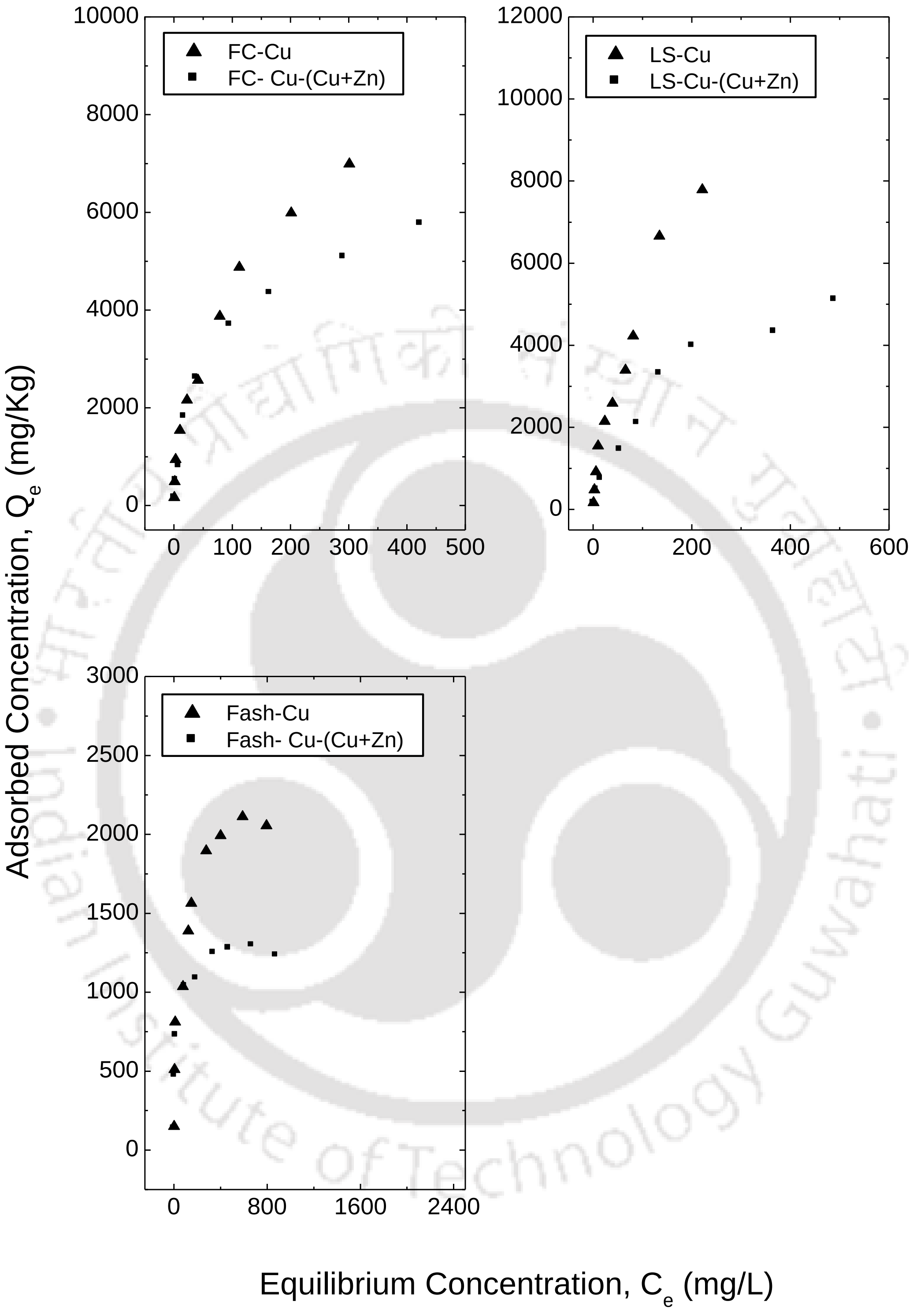


Fig.6.19b Comparison of retention Characteristics of Cu^{+2} on 3 soils corresponding to single and binary (Cu+Zn) solution

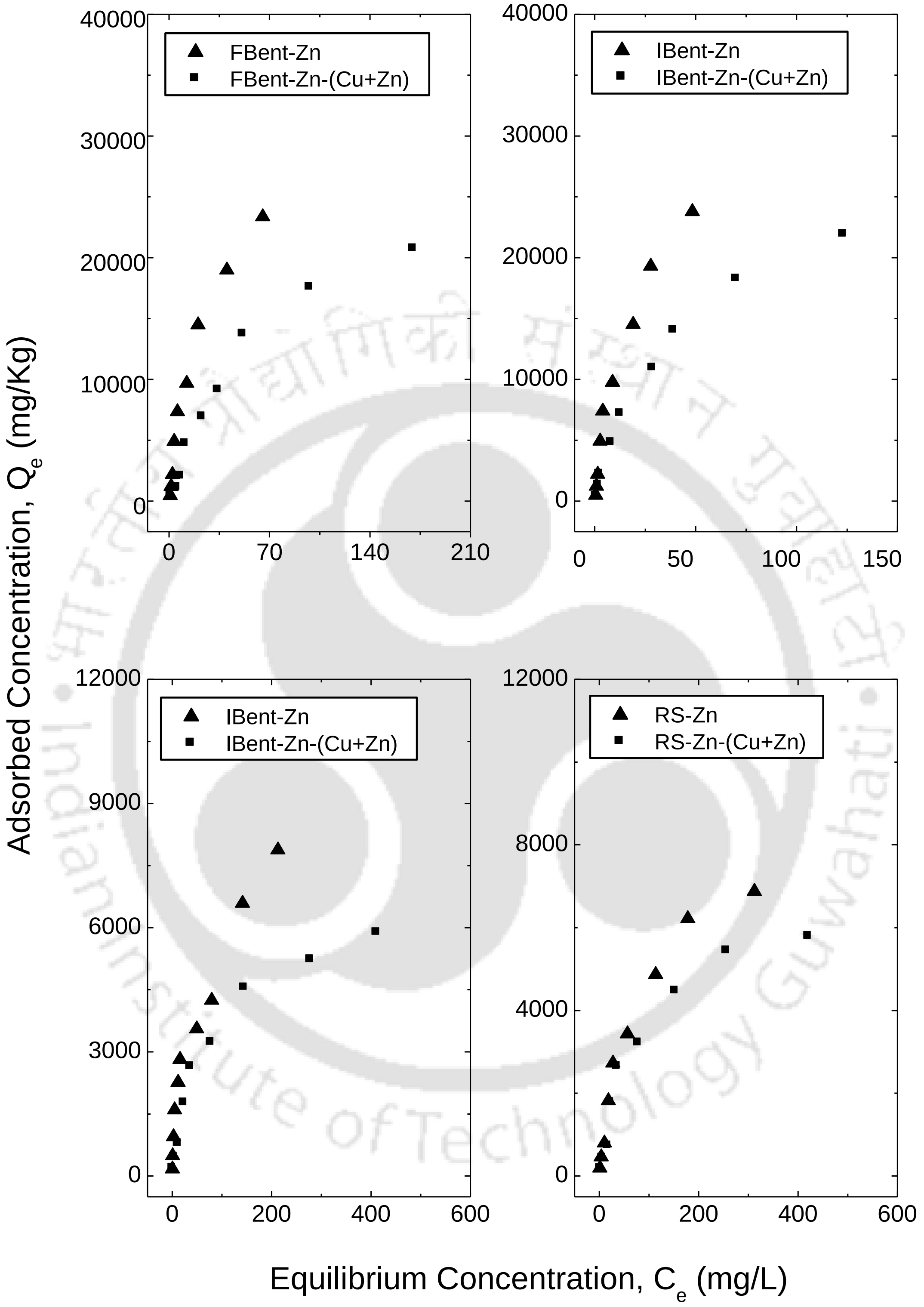


Fig. 6.20 a Comparison of retention Characteristics of Zn^{+2} on 4 soils corresponding to single and binary (Cu+Zn) solution

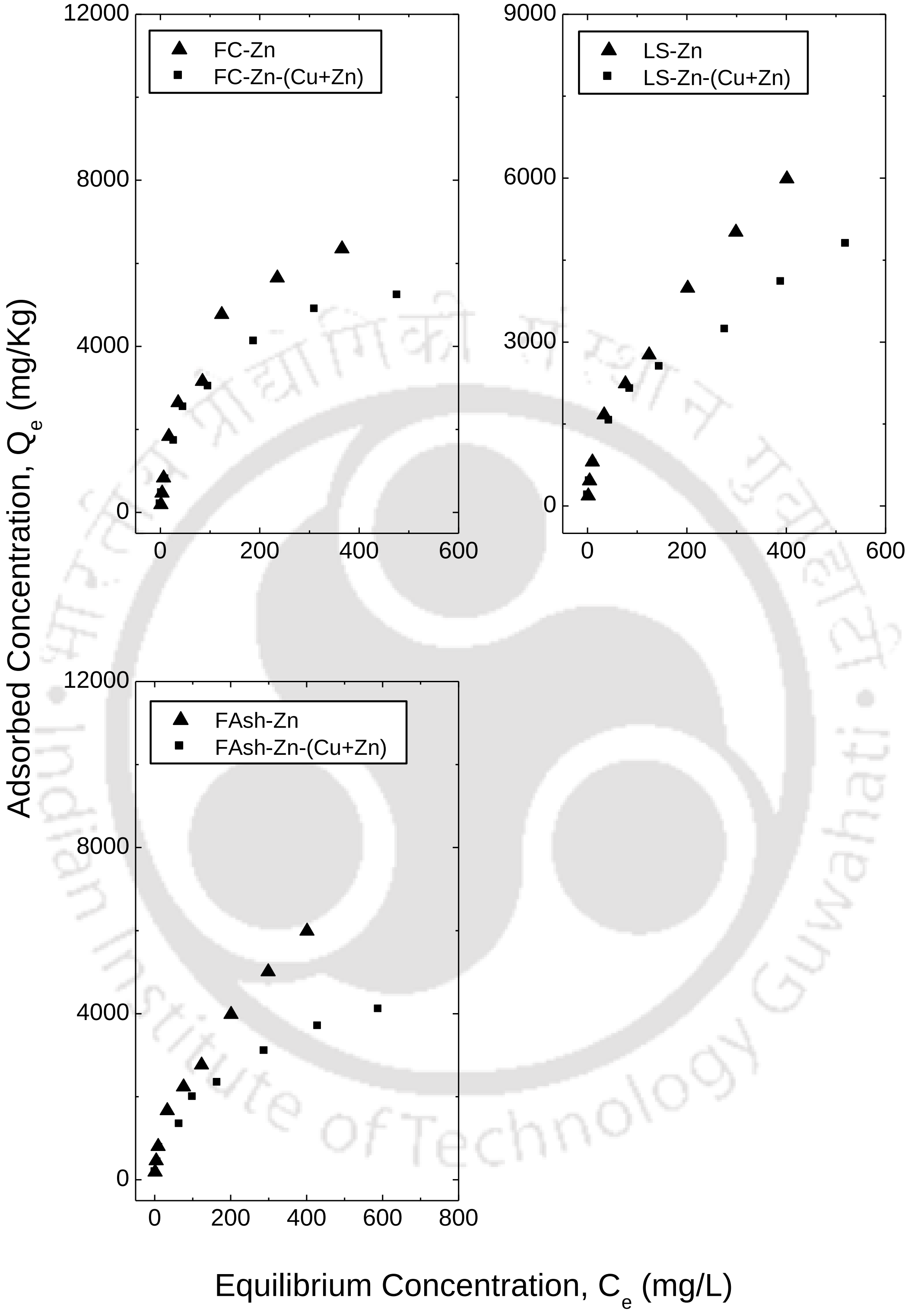


Fig 6.20b Comparison of retention characteristics of soils in Zn^{+2} on 3 soils corresponding to single and binary (Cu+Zn) solution

Table 6.12 Retention isotherm parameters for Cu^{+2} from (Cu+Zn) nitrate solution

Soil	**Parameters Cu-(Cu+Zn)**						**Best Fit**
	Freundlich			**Langmuir**			
	K_F (L/Kg)	**N**	**R^2**	**K_L(L/mg)**	**Q_m(mg/Kg)**	**R^2**	
IBent	1753.42	0.53	0.98	0.0227	29576.33	0.99	Freundlich
FBent	2385.72	0.39	0.93	0.0322	21374.37	0.99	Langmuir
RS	241.69	0.60	0.99	0.0052	11266.17	0.99	Langmuir
FC	523.66	0.40	0.97	0.018	6130.33	0.99	Langmuir
Kao	506.39	0.46	0.93	0.0156	8055.22	0.98	Langmuir
LS	248.06	0.49	0.96	0.0063	6622.83	0.98	Langmuir
FA	332.83	0.21	0.87	0.0647	1272.51	0.98	Langmuir

Table 6.13 Retention isotherm parameters for Zn^{+2} from (Cu+Zn) nitrate solution

Soil	**Parameters Zn-(Cu+Zn)**						**Best Fit**
	Freundlich			**Langmuir**			
	K_F(L/Kg)	**N**	**R^2**	**K_L(L/mg)**	**Q_m(mg/Kg)**	**R^2**	
IBent	1222.41	0.55	0.951	0.0135	30346.55	0.98	Langmuir
FBent	1134.27	0.58	0.956	0.0135	30344.71	0.98	Langmuir
RS	404.13	0.45	0.943	0.01234	6957.47	0.98	Langmuir
FC	422.26	0.42	0.972	0.01304	5949.461	0.99	Langmuir
Kao	457.76	0.43	0.963	0.01404	6716.79	0.99	Langmuir
LS	222.69	0.48	0.993	0.00626	5774.371	0.96	Freundlich
FA	184.41	0.49	0.991	0.00536	5245.04	0.98	Freundlich

6.3.7 Batch tests results for Cu^{+2}, Pb^{+2} and Ni^{+2} in tertiary (Pb+Cu+Ni) solution

The tertiary metal system were prepared by mixing equivalent amount of Cu^{+2}, Pb^{+2} and Ni^{+2} nitrate salts at varying concentrations for a range of 50 to 1000 mg/L approximately in deionized water. Data obtained after conducting batch tests were compared as shown in Figs. 6.21a, b. The various fittting parameters for Cu^{+2}, Pb^{+2} and Ni^{+2} in tertiary (Pb+Cu+Ni) solution is tabulated in Table 6.14 to 6.16 respectively. It could be observed from the Figs. 6.21a,b that in the tertiary combination, Pb^{+2} has the highest retention capacity over Cu^{+2} and Ni^{+2}. The retention capacity of soils in sorbing heavy metals from the different soils could be arranged in the following order: $Pb^{+2} \geq Cu^{+2} >> Ni^{+2}$ for most of the soils (IBent, FBent, Kao, LS and FAsh). It was observed that for soils FC for entire range Cu^{+2} retained better than Pb^{+2}. For RS though at lower range of initial concentration Pb^{+2} sorbed more, it was found to be reverse at higher range of initial concentration. The dominance of Pb^{+2} and

Cu^{+2} in the majority of affinity sequences is in agreement with its hydrolysis constant, reinforcing the role of specific binding mechanisms with high stability and binding energy (James and Healy, 1972) in the retention behaviour metals in soil. Additionally Pb^{+2} is preferentially sorbed over Cu^{+2} and Ni^{+2} onto the binding sites of most of the soils surface due to its high electronegativity, high softness value and with easy hydrolysation. The figures also illustrates that in the tertiary (Pb+Cu+Ni) solution the retention capacity of Ni^{+2} is greatly suppressed in the presence of Cu^{+2} and Pb^{+2}. For almost all the soils it was observed that at the initial range of concentration both Cu^{+2} and Pb^{+2} retained equally. It is understood that since Pb^{+2} and Cu^{+2} has strong attachments to the different soil layers both the ions tend to spread out on the surface. Such findings were also discussed by Stumn (1992). It can also be demonstrated from the figures that for low surface coverage (lowest equilibrium concentration of competitive isotherms) all Pb^{+2} than Cu^{+2} ions were retained, whereas for higher equilibrium concentrations soils showed more affinity for Pb^{+2} than Cu^{+2} in certain cases.

For FAsh it can be noted that Pb^{+2} occupied all the sites for the entire range of concentration leading to its high retention whearas Cu^{+2} and Ni^{+2} retention slowed down gradually until equilibrium is attained. FAsh having a very low SSA and CEC the sites on the surface are almost covered by metal ions $Pb^{+2.}$ and the remaining binding sites on the surface become more difficult to be filled by Cu^{+2} and Ni^{+2} due to the repulsive forces existing between the Pb^{+2} on FAsh surface and unbound metal ions Cu^{+2} and Ni^{+2}.

Fig.6.21a clearly depicts that for soil I Bent and FBent and for Cu^{+2} and Pb^{+2} the shape of the isotherm is a H type which reveals the soils total retention and its high affinity for the soil. The findings completely agree with Fontes et al. (2000) that competition has a very small effect on Pb^{+2} retention. It is apparent that the experimental data points of Pb^{+2}, Cu^{+2} and Ni^{+2} are in good agreement with Freundlich and Langmuir isotherm as evident from its high correlation value. The Q_m value is arranged as $Pb^{+2} > Cu^{+2} > Ni^{+2}$ for all soils except RS and FC where it followed the trend $Cu^{+2} > Pb^{+2} > Ni^{+2}$. With Ni^{+2} having the lowest Q_m value implies it is easily replaced by Pb^{+2} or Cu^{+2} due to its high dissociation constant and low affinity for soil surfaces. Therefore, Ni^{+2} may pose more threats to the ground water and plants more than Pb^{+2} and Cu^{+2}.

6.3.8 Comparison of Cu^{+2}, Ni^{+2} and Pb^{+2} corresponding to single, binary, and tertiary (Cu+Ni+Pb) solution

It can be demonstrated from the Figs 6.22a, b, 6.23a, b and 6.24a, b that compared to single-solution, the retention of metal ions for all the three metals Cu^{+2}, Ni^{+2} and Pb^{+2} decreased in the multiple ion solution, which can be attributed to the interference of metal ions with each other i.e., competitive reactions. The initial linear part of the isotherms was shorter when compared to single metal solution. Furthermore, Cu^{+2}, Pb^{+2} retention decreases from binary to tertiary solution in all the soils, but Ni^{+2} retention hardly changes under these conditions for soils RS, FC and LS (Fig 6.24a,b). In the tertiary systems, both Pb^{+2} and Cu^{+2} did not cause a significant decrease in Ni^{+2} retention as compared to the binary system. This might be because the occupation sites available for the retention of Ni^{+2} is comparable in binary and tertiary solution due to the competition from other ions. For soils IBent and FBent the retention curves of Pb^{+2} in the competitive systems took the form of nearly vertical lines, or H-type isotherms which indicates its high affinity for retention and that the sites are not yet fully occupied. These phenomenons usually occur by inner-sphere surface complexation or by significant van der Waals interactions in the retention process (Sposito, 1989). For other soils the L type isotherm shape is being observed indicating saturation being achieved at higher range of initial concentration. For Cu^{+2} it was observed that most of the soils followed the L type of curve resulting from the relatively high affinity of the soil particles for the metal at low surface coverage, an affinity that decreased as the surface became saturated (Echeverria et al., 1998; Sposito, 1989). For Ni^{+2} curves obtained for the competitive retention of Ni^{+2} for most soils revealed L type whearas FC revealed C type.

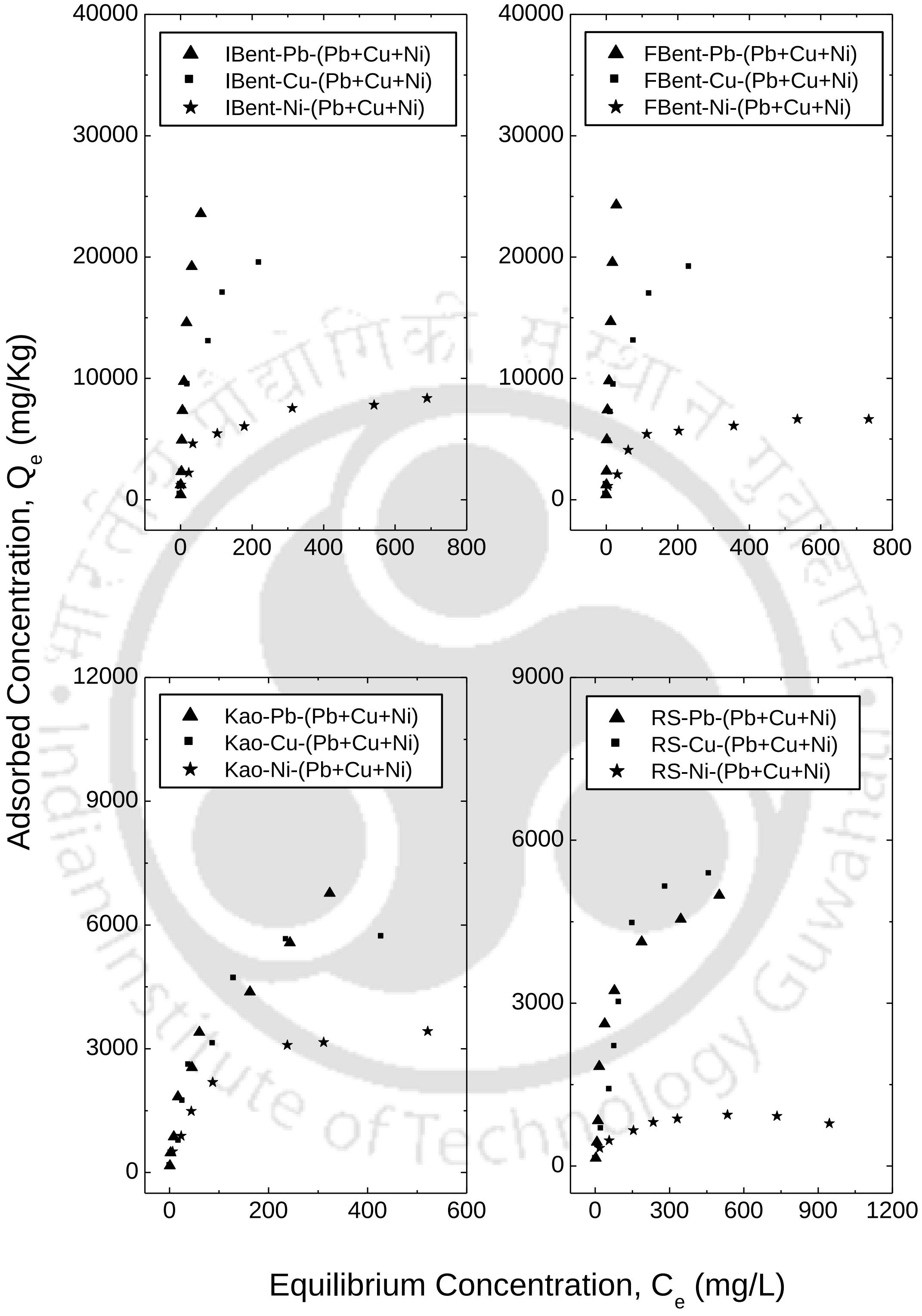


Fig 6.21a Comparison of retention characteristics of 4 Soils in Pb^{+2}, Cu^{+2} and Ni^{+2} corresponding to tertiary (Cu+Pb+Ni) solution

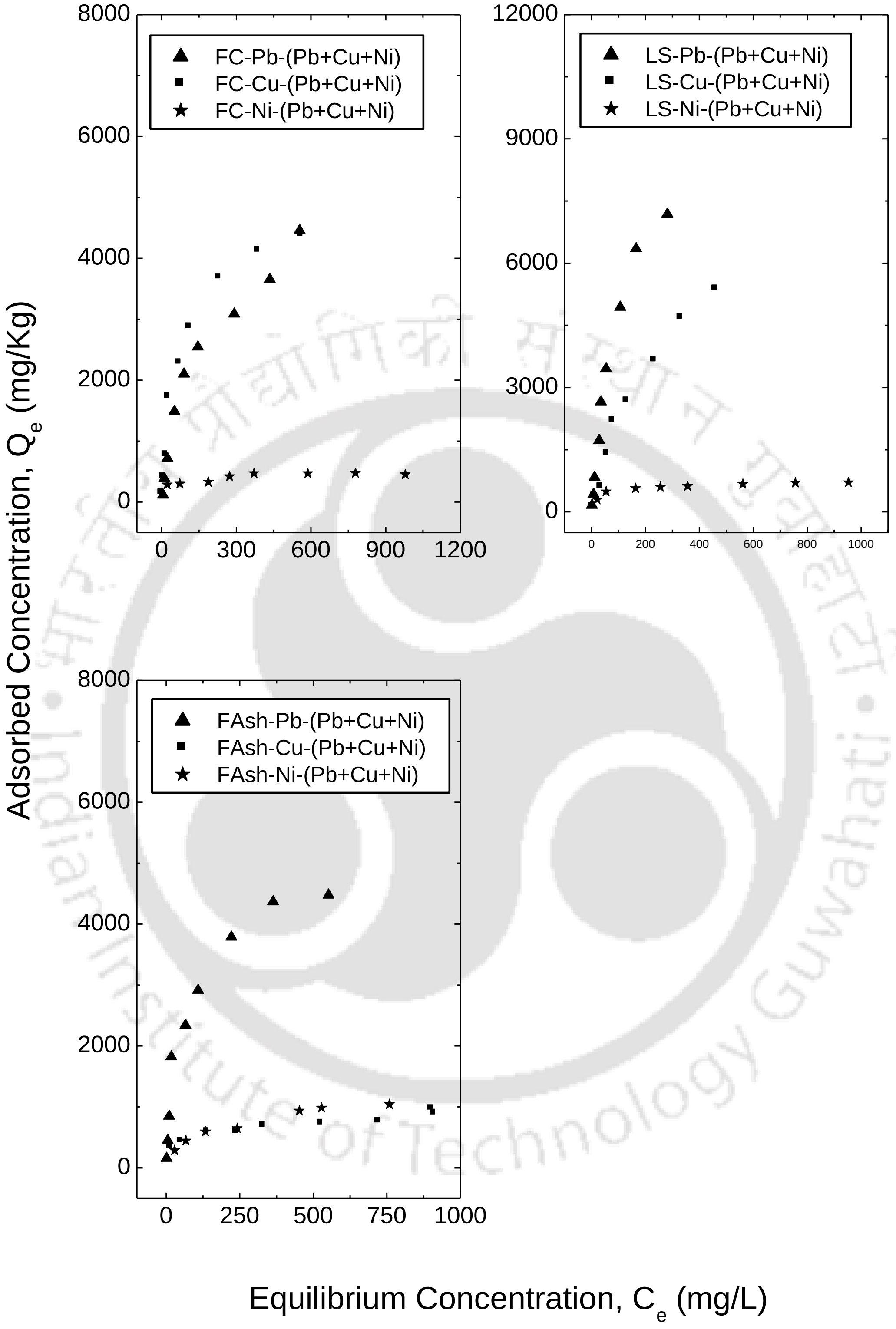


Fig 6.21b Comparison of retention characteristics of 4 Soils in Pb^{+2}, Cu^{+2} and Ni^{+2} corresponding to tertiary (Cu+Pb+Ni) solution

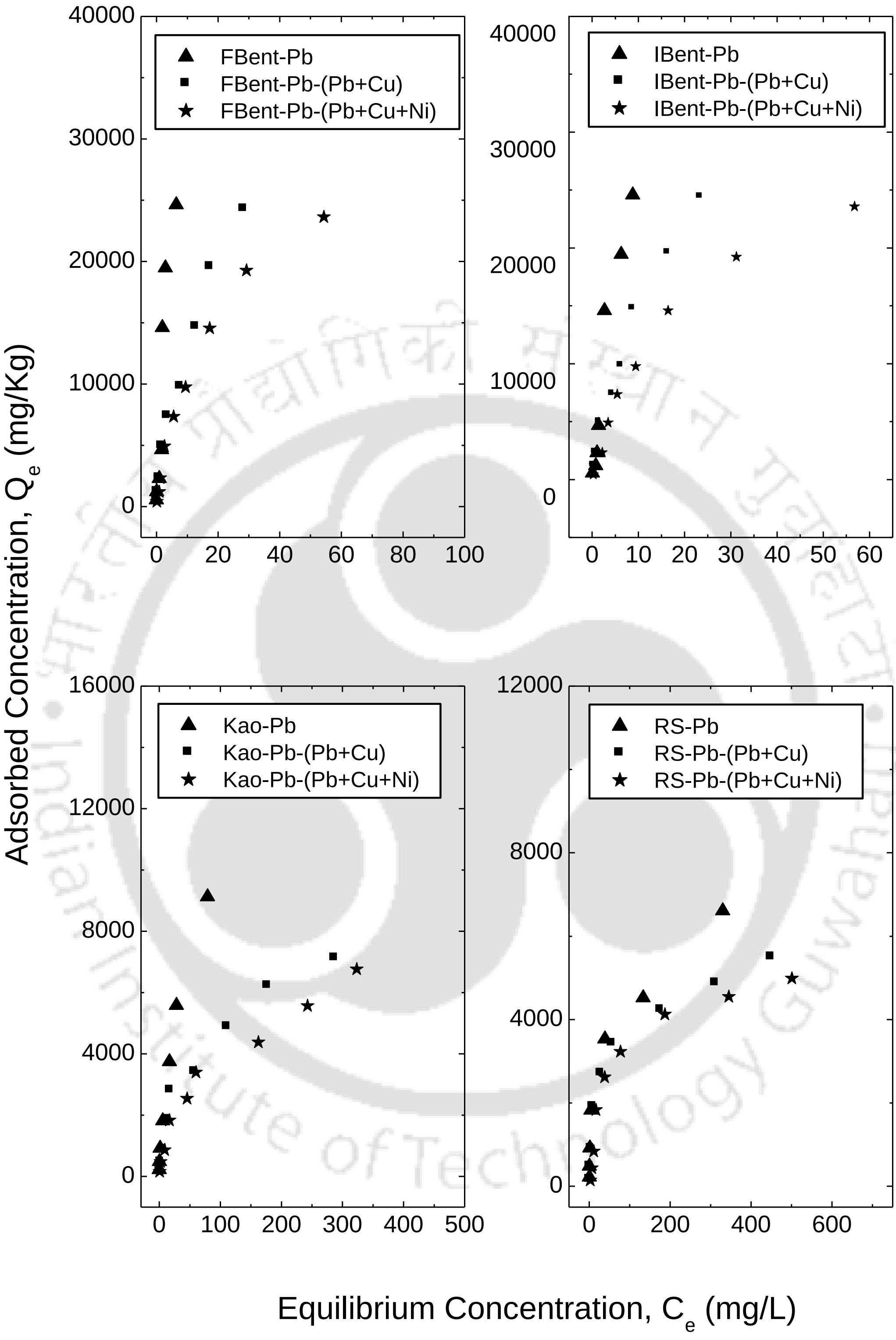


Fig.6.22a Comparison of retention characteristics of Pb^{+2} on 4 soils corresponding to single, binary and tertiary (Cu+Pb+Ni) solution

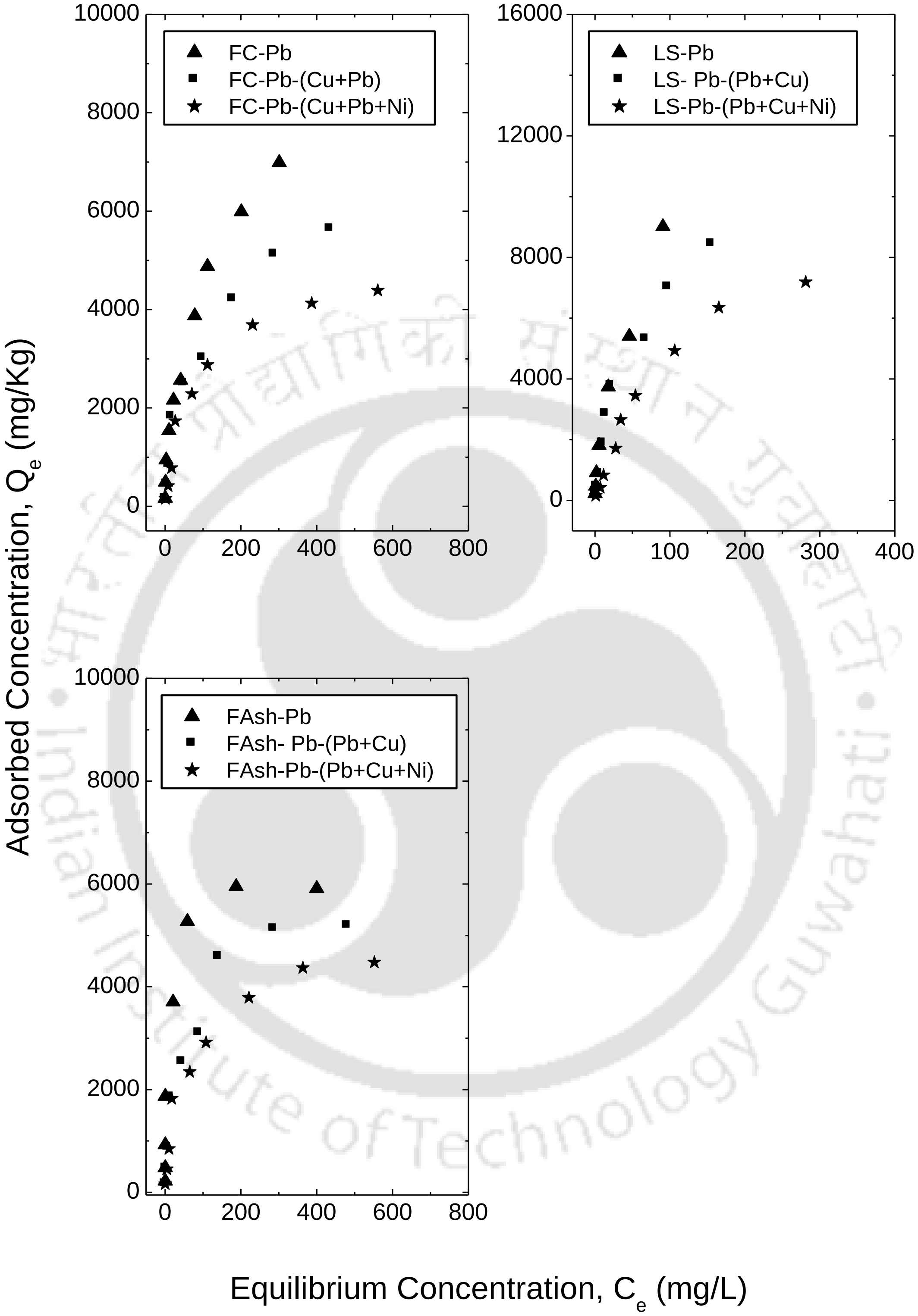


Fig 6.22b Comparison of retention characteristics of Pb^{+2} on 3 soils corresponding to single, binary and tertiary (Cu+Pb+Ni) solution

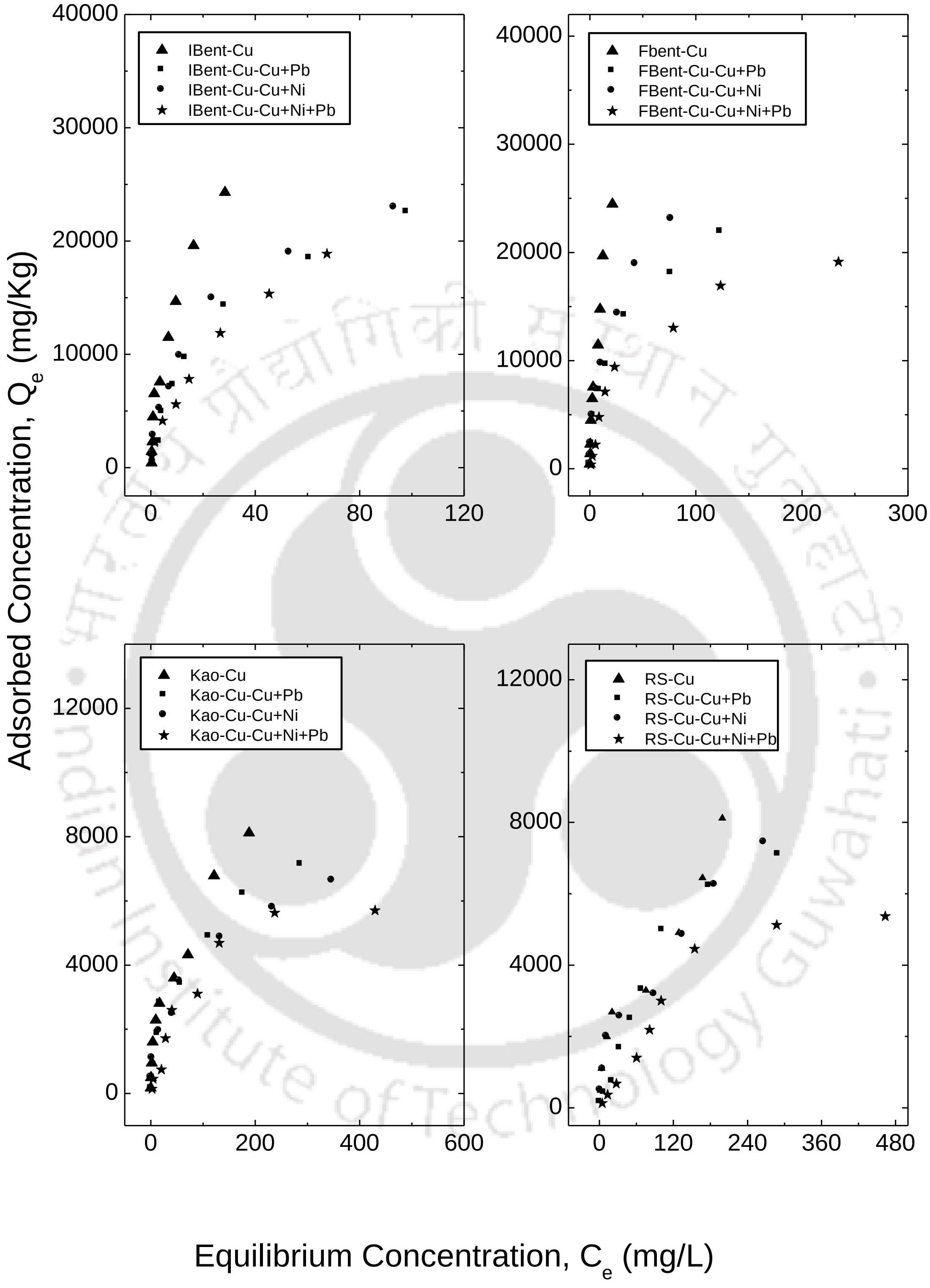


Fig 6.23a Comparison of retention characteristics of Cu^{+2} on 4 soils corresponding to single, binary and tertiary (Cu+Pb+Ni) solution

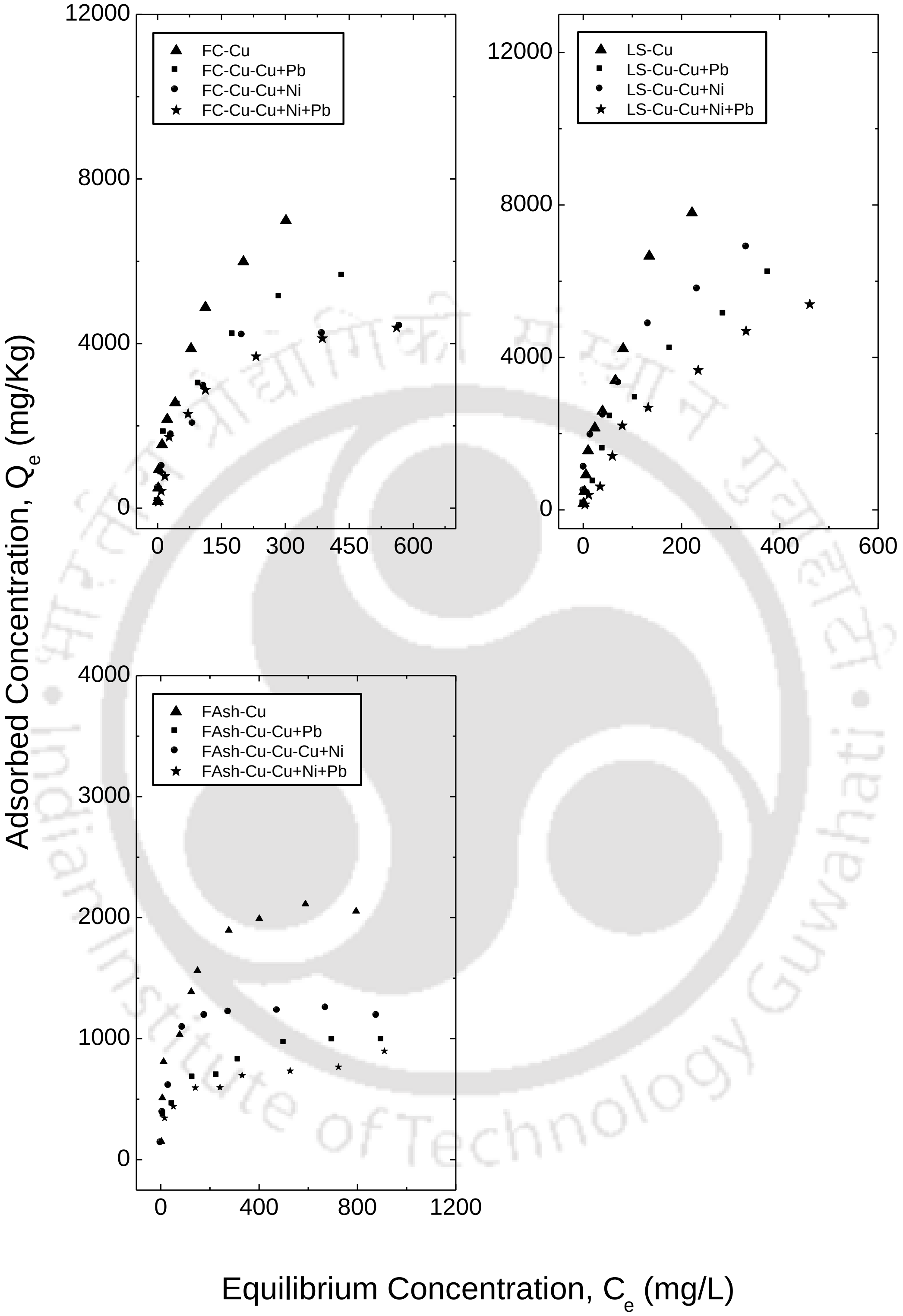


Fig 6.23b Comparison of retention characteristics of Cu^{+2} on 3 soils corresponding to single, binary and tertiary (Cu+Ni+Pb) solution

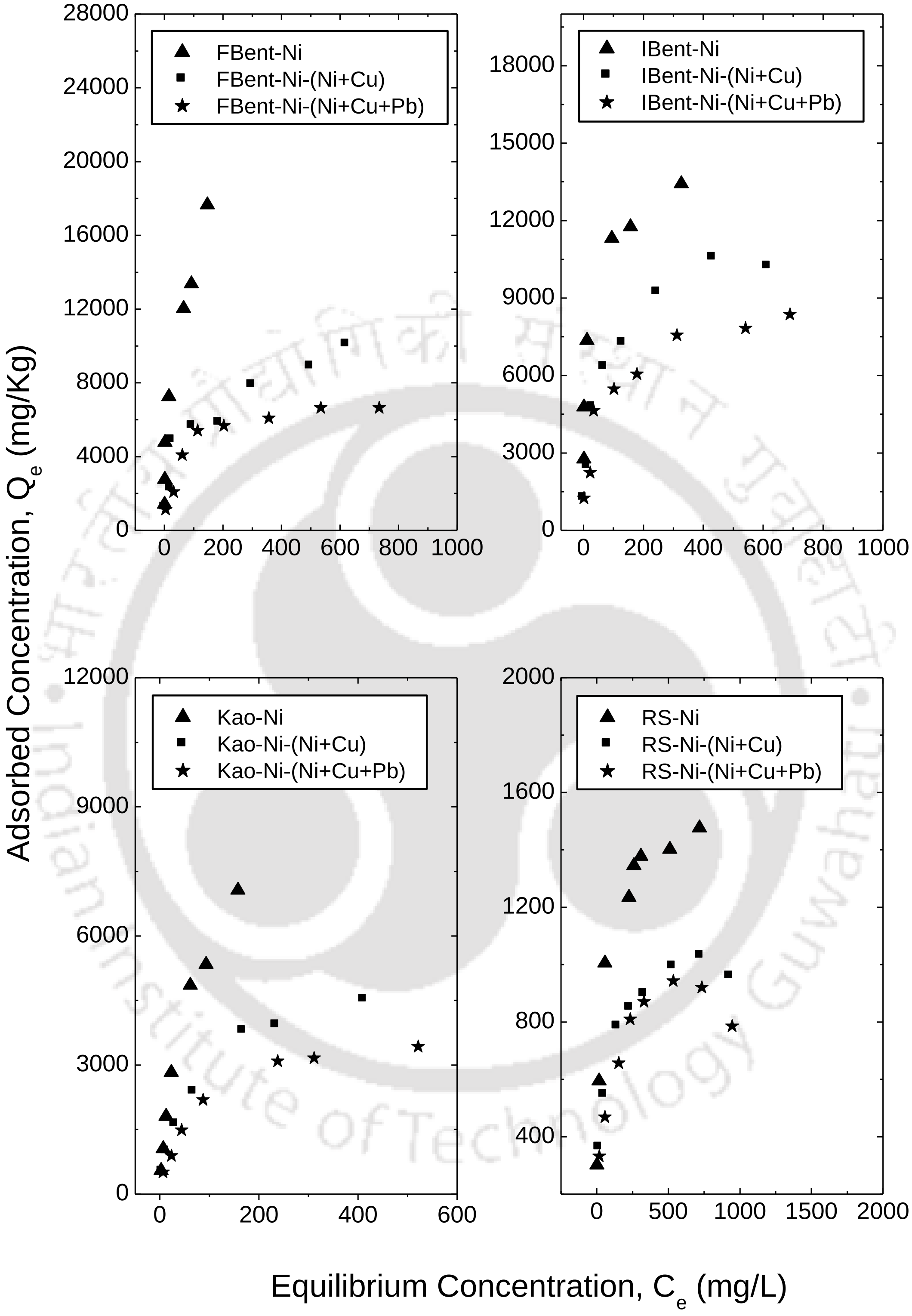


Fig 6.24a Comparison of retention characteristics of Ni^{+2} on 4 soils corresponding to single, binary and tertiary (Cu+Ni+Pb) solution

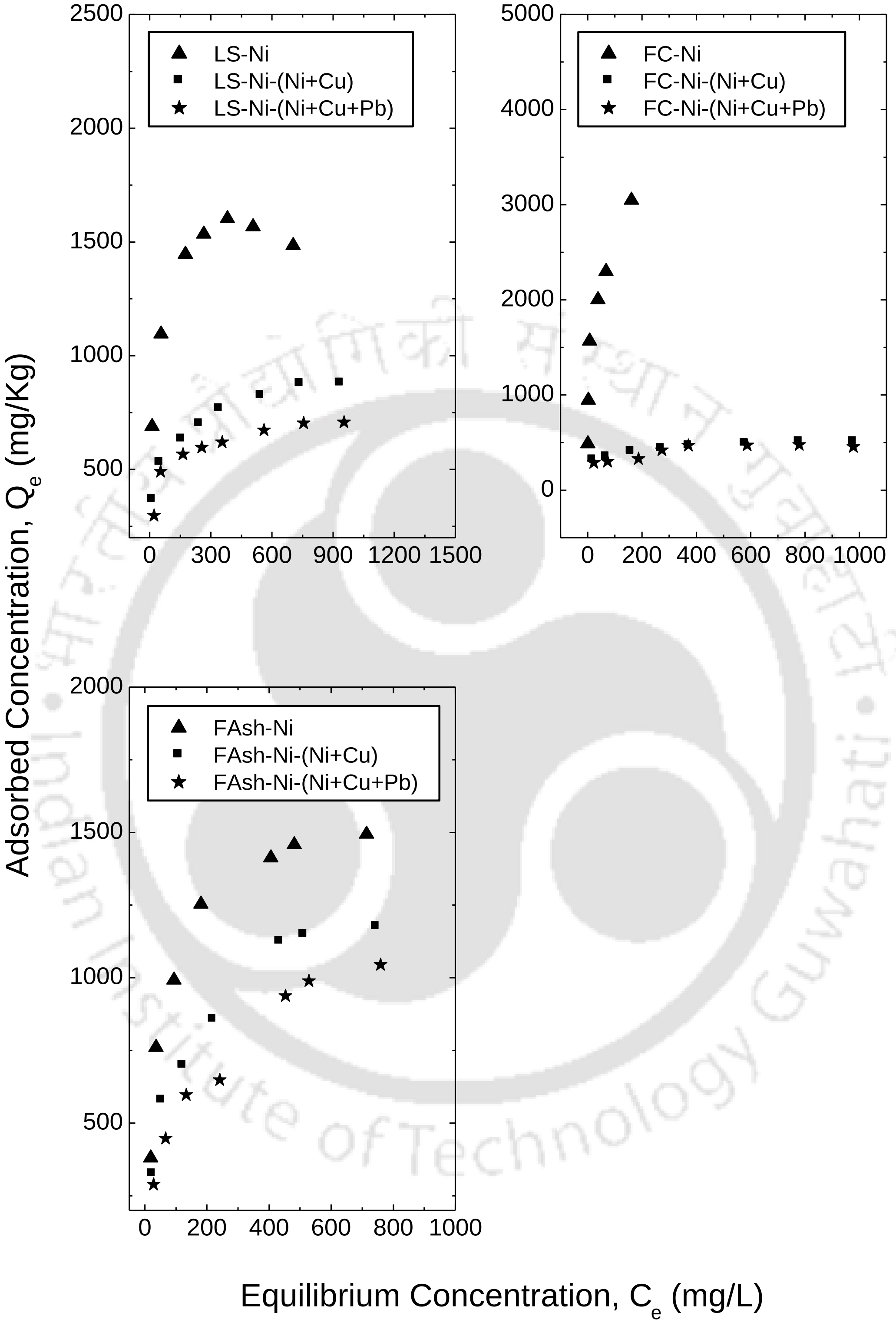


Fig. 6.24b Comparison of retention characteristics of Ni^{+2} on 3 soils corresponding to single, binary and tertiary (Cu+Ni+Pb) solution

Table 6.14 Retention isotherm parameters for Cu^{+2} from (Cu+Pb+Ni) solution

Soil	Parameters Cu-(Cu+Pb+Ni)						Best Fit
	Freundlich			Langmuir			
	K_F(L/Kg)	N	R^2	K_L(L/mg)	Q_m(mg/Kg)	R^2	
IBent	1943.52	0.44	0.95	0.03419	20754.55	0.97	Freundlich
FBent	1903.56	0.44	0.95	0.0415	21045.79	0.98	Freundlich
RS	196.81	0.56	0.90	0.0053	8126.64	0.96	Langmuir
FC	393.65	0.39	0.95	0.0137	4889.66	0.99	Langmuir
Kao	404.17	0.46	0.92	0.011	7337.52	0.97	Langmuir
LS	112.09	0.64	0.98	0.0033	8889.74	0.99	Langmuir
FAsh	184.91	0.22	0.97	0.0279	796.66	0.82	Freundlich

Table 6.15 Retention isotherm parameters for Pb^{+2} from (Cu+Pb+Ni) solution

Soil	Parameters Pb-(Cu+Pb+Ni)						Best Fit
	Freundlich			Langmuir			
	K_F(L/Kg)	N	R^2	K_L(L/mg)	Q_m(mg/Kg)	R^2	
IBent	2830.73	0.54	0.98	0.0499	31807.01	0.99	Langmuir
FBent	2928.69	0.53	0.98	0.051	31973.00	0.99	Langmuir
RS	556.30	0.36	0.92	0.023	5214.43	0.99	Langmuir
FC	193.23	0.49	0.97	0.0069	5130.51	0.98	Langmuir
Kao	415.56	0.48	0.99	0.0119	7731.15	0.97	Freundlich
LS	332.16	0.56	0.97	0.0089	10251.57	0.99	Langmuir
FAsh	499.53	0.36	0.96	0.0193	4767.43	0.97	Langmuir

Table 6.16 Retention isotherm parameters for Ni^{+2} from (Ni-Cu-Pb) solution

Soil	Parameters Ni-(Cu+Pb+Ni)						Best Fit
	Freundlich			Langmuir			
	K_F(L/Kg)	N	R^2	K_L(L/mg)	Q_m(mg/Kg)	R^2	
IBent	1434.43	0.27	0.94	0.022	8482.37	0.93	Freundlich
FBent	1205.46	0.27	0.89	0.0197	7177.82	0.97	Langmuir
RS	225.04	0.21	0.80	0.022	938.48	0.90	Langmuir
FC	166.21	0.16	0.83	0.0453	460.09	0.66	Freundlich
Kao	363.44	0.37	0.95	0.0144	3906.54	0.99	Langmuir
LS	215.09	0.18	0.92	0.0352	699.88	0.96	Langmuir
FAsh	89.54	0.38	0.98	0.0078	1189.82	0.95	Freundlich

6.3.9 Batch tests results for Cu^{+2} in quaternary (Cu+Ni+Pb+Zn) solution

Quaternary heavy metal solutions were made by mixing equivalent amount of Cu^{+2}, Ni^{+2}, Zn^{+2} and Pb^{+2} nitrate salts in deionized water for a range of concentration 50 and 1000 mg /L). These solutions were adjusted at pH 5. The retention characteristics of Cu^{+2} in quaternary solution is quantified by conducting batch test and the various fitting parameters along with the goodness of fit is given in table 6.17 for all soils. The Q_m values of the soils ranged from 692.89 mg/Kg to 20507.499 mg/Kg. and the K_F ranged from 173.8L/Kg to 1658.66 L/Kg. The large variation of Q_m and K_F values is attributed to the diverse soil considered in this study. Among these soils, soils having high initial pH and CEC values retained much higher amount of Cu^{+2} than those having low pH and CEC. Similar observation was also reported by Adhikari and Singh (2003); Serrano et al., (2005); Jalali and Moharrami (2007); and Usman (2008), where the retention of heavy metals was favoured by high pH, organic matter, CEC and clay content of soils.

6.3.10 Comparison of Cu^{+2} retention in single, binary, tertiary and quaternary (Cu+Ni+Pb+Zn) solution

Fig 6.25a, b illustrates the comparison of Cu^{+2} retention in single, binary, tertiary and quaternary system. It can be demonstrated from the figure that compared with the single Cu^{+2} contaminant solution, the retention of Cu^{+2} in multiple contaminant solution decreased progressively from binary to quaternary combination. This can be attributed to the interference of other metal ions during the retention process i.e., competitive reactions. It can be seen for soil IBent and FBent that the isotherm curve followed an H type isotherm for single contaminant solution. The shape of the curve changes to L type in the presence of multiple ions. For binary solution Cu^{+2} in the presence of Ni^{+2} gave the highest retention followed by Pb^{+2} and Zn^{+2} as evident from the isotherm curves for soils IBent, Fbent and RS. There was no drastic variation in the retention characteristic for Cu^{+2} in the presence of Zn^{+2} and the tertiary system for soil FBent and RS. In all these case quaternary multiple solution showed the least retention characteristics. For RS the shape of the isotherm curve changes from L type for binary to S type for tertiary and quaternary multiple solution. For soil Kao Cu^{+2} in the presence of Zn^{+2} showed higher retention characteristics followed by Pb^{+2} and Ni^{+2}. It was also observed that there is significant change in the retention behaviour for tertiary as compared to quaternary. The trends observed for Cu^{+2} retention of FC in binary solution of Zn^{+2} and Pb^{+2} are comparable. Cu^{+2} in presence of Ni^{+2} have similar retention characteristics as that of tertiary and quaternary towards the higher concentration. Soil LS exhibited L type in the single and binary solution followed by S type in the tertiary and C type in the quaternary system. For FAsh all single and multiple the retention curve reached indicating a plateau formation. The presence of multiple contaminants clearly inhibited the retention behaviour of Cu^{+2} in FAsh. The L type shape was exhibited by retention data for single and binary combination in the presence of Ni^{+2}, Zn^{+2}. Cu^{+2} in the presence of Pb^{+2}, tertiary and quaternary exhibited S type of curve. It can be noted that for all soils, the difference between single and competitive systems was more prominent for the higher range of concentration indicating ionic competition did not affect much its preferential binding to specific retention sites at low concentration.

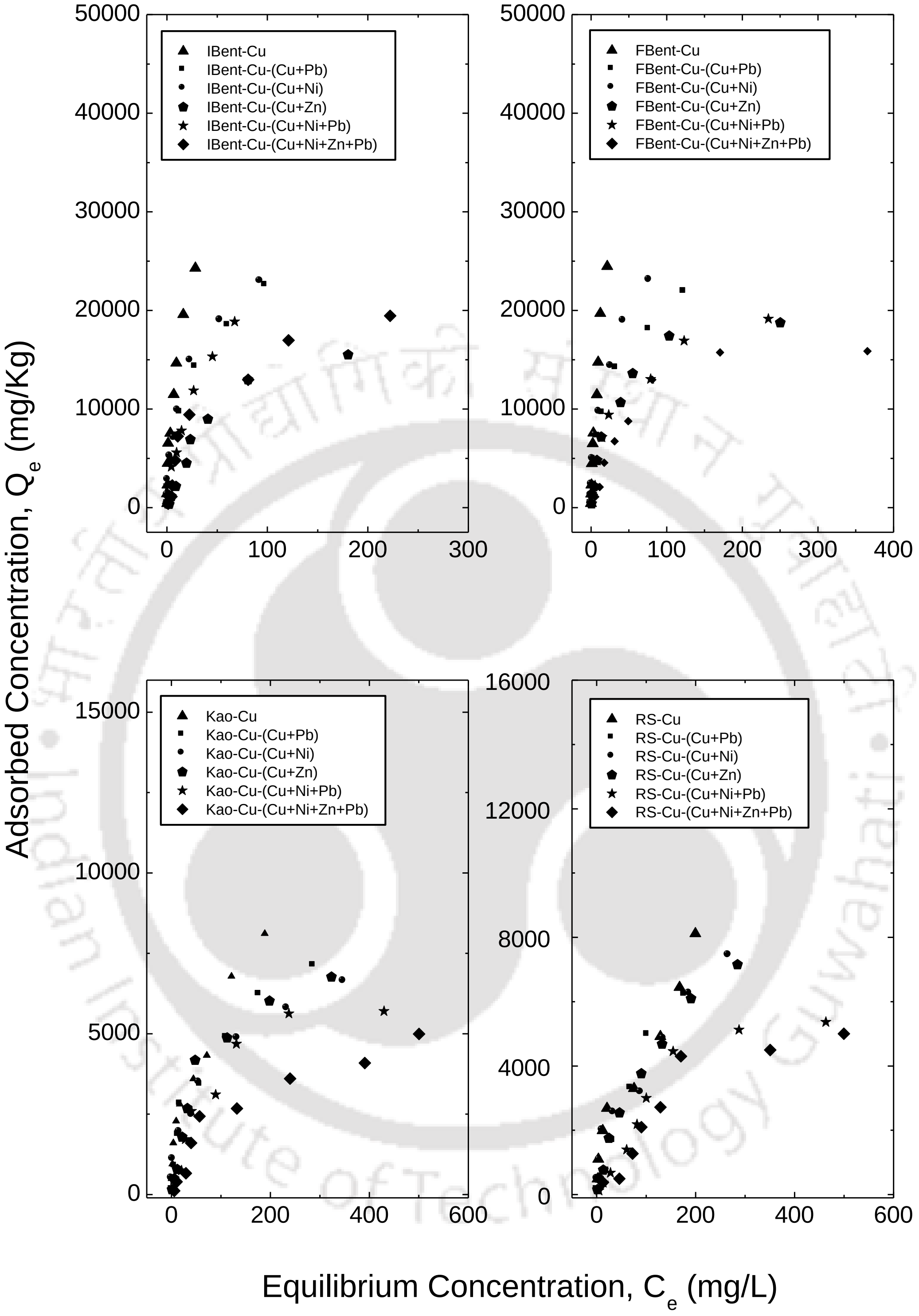


Fig. 6.25a Comparison of retention characteristics of Cu^{+2} on 4 soils corresponding to single, binary, tertiary and quaternary (Cu+Ni+Pb+Zn) solution

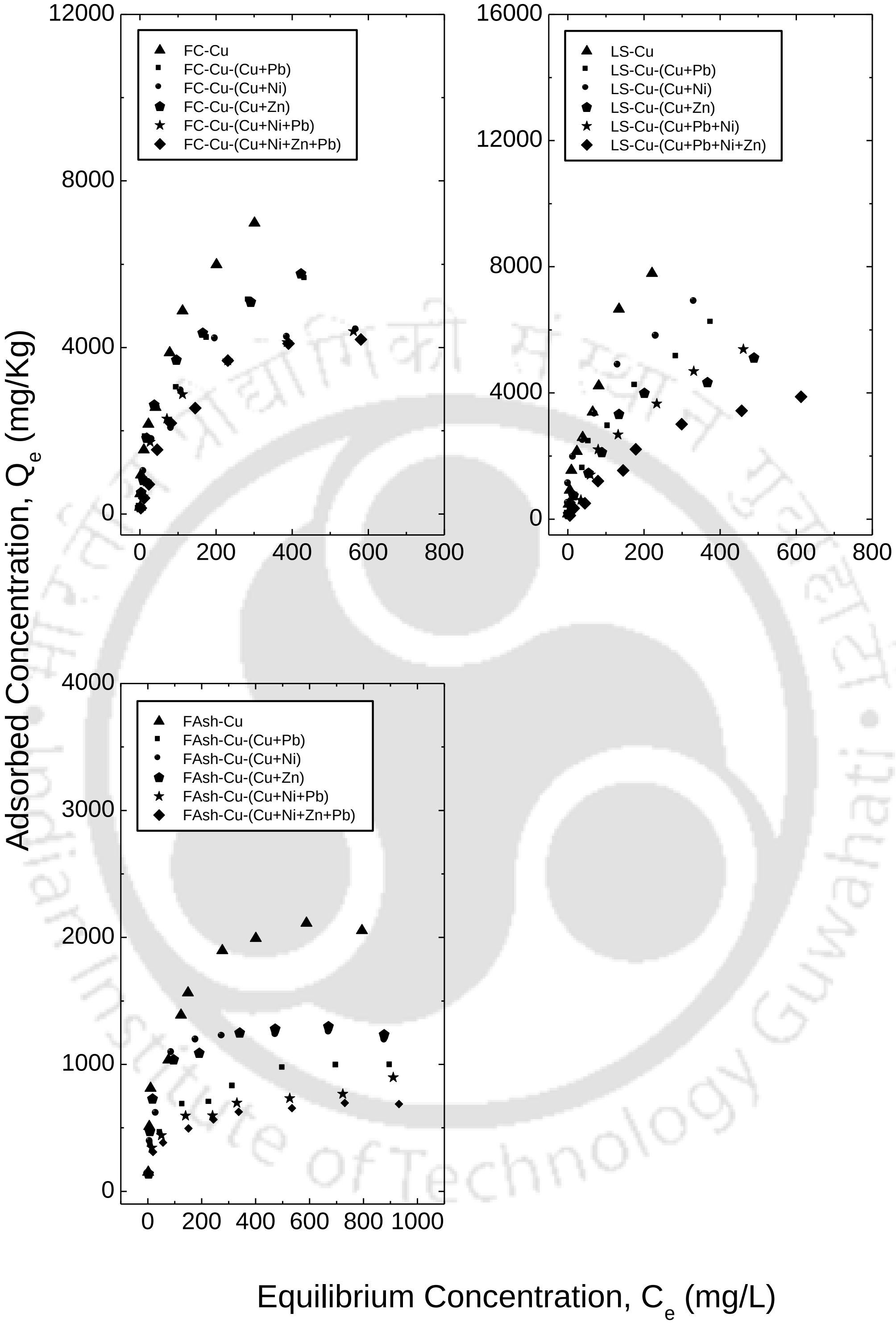


Fig. 6.25b Comparison of retention characteristics of Cu^{+2} on 3 soils corresponding to single, binary, tertiary and quaternary (Cu+Ni+Pb+Zn) solution

Table 6. 17 Retention isotherm parameters for Cu^{+2} from (Cu+Pb+Ni+Zn) quaternary solution

Soil	Parameters Cu-(Cu+Pb+Ni+Zn)						Best Fit
	Freundlich			Langmuir			
	K_F(L/Kg)	N	R^2	K_L(L/mg)	Q_m(mg/Kg)	R^2	
IBent	1448.72	0.45	0.93	0.0183	20507.50	0.99	Langmuir
FBent	1658.66	0.40	0.87	0.01758	19691.09	0.97	Langmuir
RS	151.49	0.58	0.86	0.00413	7771.63	0.91	Langmuir
FC	251.14	0.46	0.96	0.0075	5497.83	0.99	Langmuir
Kao	267.52	0.45	0.95	0.00824	5234.54	0.99	Langmuir
LS	82.66	0.61	0.97	0.0028	6205.58	0.99	Langmuir
FAsh	173.88	0.21	0.97	0.026	692.89	0.91	Freundlich

6.4 Affinity sequence

There have been a lot of anomalies and conflicting trends reported in the literature on metal affinity of soils. Gomes et al., (2001); McBride (1994); Serrano et al., (2005) have stated that metal characteristics such as the atomic weight, ionic radii, hydrolysis constant, electronegativity and softness sequences do not always explain metal bonding selectivity to heterogeneous soil systems. The main soil properties that influence the selectivity sequence of heavy metals are pH, organic matter content, the type and amount of clay as well as cation exchange capacity of soil (Adhikari and Singh 2003; Serrano et al., 2005; Usman 2008).

The order of selective affinity of soils for single metal and in competition are given in the table 6.18 a and b for common ions and heavy metals respectively. The affinity sequences are based on the experimental results obtained from the present study for different soil-contaminant interactions.

From Table 6.18a, it is clear that all soils exhibited varying affinity sequence for single contaminant (common ions) interactions. For multiple solutions, the affinity sequence based on most of the interaction results is similar for majority of the soils. FAsh exhibited negligible retention of common ions except for NH_4^+. Table 6.18b depicts that for heavy metal in single contaminant solution Pb^{+2} exhibited higher retention followed by Cu^{+2} , Zn^{+2} and Ni^{+2} the least in most of the cases. The trends are consistent for multiple interactions as well for majority of the cases.

Table 6.18a Affinity sequences of Na^+, K^+, NH_4^+ and Ca^{+2} based on the retention data for single and multiple contaminant solution

Soil	Single	Na+K	K+NH4	Na+K+Ca
IBent	K>Ca>NH_4>Na	K>Na	Comparable	K>Ca
FBent	K>NH_4>Ca>Na	K>Na	Comparable	K>Ca
RS	NH_4>Ca>K >Na	K>Na	Comparable	Comparable
FC	K>NH_4=Ca>>Na	K>Na	Comparable	Ca performed better at the lower range but at the higher range K sorbed more
Kao	Ca>K>NH_4>Na	K>Na	Comparable	K>Ca
LS	NH_4>K>Ca>Na	K>Na	Comparable	Ca>K
FAsh	NH_4>K	K>Na	NH_4>K	Both K and Ca desorbed. The release was more for Ca

Table 6.18b Affinity sequences of Pb^{+2}, Cu^{+2}, Ni^{+2}, and Zn^{+2} based on retention data for single and multiple contaminant solution

Soil	Single	Cu+Ni	Cu +Pb	Cu+Zn	Cu+Pb+Ni
IBent	Pb>Cu>Zn>>Ni	Cu>Ni	Pb>Cu	Cu>Zn	Pb>Cu>>Ni
FBent	Pb>Cu>Zn>Ni	Cu>Ni	Pb>Cu	Cu~Zn	Pb>Cu>>Ni
RS	Cu>Pb=Zn>>Ni	Cu>Ni	Cu>Pb	Cu>Zn	Cu>Pb>>Ni
FC	Pb>Cu>Zn>Ni	Cu>Ni	Cu>Pb	Cu>Zn	Cu≥Pb>>Ni
Kao	Pb>Cu>Ni>Zn	Cu>Ni	Pb>Cu	Cu>Zn	Pb≥Cu>Ni
LS	Pb>Cu>Zn>Ni	Cu>Ni	Pb>Cu	Cu>Zn	Pb>Cu>>Ni
FAsh	Pb>Zn>Cu>Ni	Cu>Ni	Pb>>Cu	Zn>Cu	Pb>Cu≥Ni

6.5 Percentage difference of isotherm parameters of soils obtained from multiple and single solutions

The percentage difference in isotherm parameters for common ions and heavy metal retention obtained from single and multiple solution comparison is listed in tables 6.19 to 6.26. The percentage difference is expressed as eqn. 6.1

$$\%\ \text{difference} = \frac{(\text{isotherm parameter})_{\text{single}} - (\text{isotherm parameter})_{\text{multiple}}}{(\text{isotherm parameter})_{\text{single}}} \text{X}100 \qquad (6.1)$$

As observed in table 6.19 a and b isotherm parameters based on multiple solution is in general less than single solution for K^+. From this tables it can also be noted that unexpected trends were exhibited for soils FBent and Kao in presence of NH_4^+ as K_F and Q_m was more (-ve value) for multiple solution as compared to single solution. On the contrary, multiple solution has lower retardation than single solution based on experimental trend.This unexpected trends is visible while comparing two sets of data that has different shape of the isotherm. This indicates the limitation of the mathematical model in representing the experimental data.

Table 6.20 shows the percentage difference of Freundlich and Langmuir parameters of multiple solution of NH_4^+ compared with single NH_4^+ solution. It was observed that N and K_L value was negative for most of the soils indicating higher values in multiple. It can also be noted that % difference of K_F and Q_m (except Kao) was positive indicating a decrease in retention. If N and K_L are used as indicator of retention then it is likely to portray a wrong understanding different from the actual experimental observation. Such irregularities are explicit by comparison performed in this study. Referring to an individual data set,such irregularities cannot be understood. Table 6.21 and table 6.22 have demonstrated that Ca^{+2} and Na^+ retention from (Na+K+Ca) and (Na+K) cohas resulted in less K_F and Q_m values for all the soils except for FC. Table.6.23a shows the percentage difference of Freundlich parameters of multiple solutions of Cu^{+2} with reference to single Cu^{+2} solution. From table 6.23a it can be apparently seen that competition reduced retention of Cu^{+2}, for almost all the soils though the magnitude of these effects was different for each soil-metals combination. The effect of competition in reducing the retention of metals followed the order quaternary>tertiary>binary. In single metal systems, K_F of Cu^{+2} was expected to be higher than in competitive systems according to experimental data. This was found to be reverse for soil LS for (Cu+Ni) combination and FC for (Cu+Zn) combination. It can be seen that % difference of K_F for Cu^{+2} single was less for all the soils in the presence of Ni^{+2} as compared to Zn^{+2} and Pb^{+2}. This suggests that Cu^{+2} became preferentially sorbed at the expense of other ions such as Ni^{+2}, Zn^{+2} and Pb^{+2}.As can be seen for soils RS, FC, LS and FAsh, the presence of Pb^{+2} increased the % difference of Cu^{+2} indicating high competitive effect. Also as seen from table 6.23b the comparative assessment of different soils and the different combinations indicated that except for the case FC quaternary the maximum retention capacity of all the soils decreased from single, binary, tertiary and quaternary.

Referring to tables 6.23b, 6.24, 6.25 and 6.26, it can be noted that in certain soils K_L value in competition was higher than that of single ion (Cu+Ni for RS, FC, LS, FAsh ;

Cu+Zn for FAsh, LS; Cu+Pb for FC, Kao; Cu+Ni+Pb for FC, FAsh and Cu+Ni+Pb+Zn for FAsh). Similar observation was noted by Ghasemi-Fasaei et al., (2012) and (2013) where K_L, derived from the Langmuir isotherm was higher for competitive condition as compared to single ions for Cd^{+2}. This observation was further confirmed by Vibhawari and Pandey (2010) where it was found that K_L parameter for Cd^{+2} retention in competition with Cu^{+2} was more than in single for clayey soil of India. On comparing the maximum retention capacity, Q_m it is obvious from the table 6.23b that the retention of Cu^{+2} decreased due to competition of cations. The % difference for all soil except FC increases from single to binary, tertiary and quaternary

Table 6.24 shows the % reduction of K_F and K_L values of Pb^{+2} in presence of Cu^{+2} and it was observed that reduction increases in multiple solution. For LS, K_L for Pb^{+2} was more in the presence of Cu^{+2}. The same is observed from table 6.25 where the Q_m value decreased for all soils in binary combination (Zn+Cu). The K_F value was found to be higher for LS and FAsh for multiple solutions which contradicts the experimental finding.

Fig 6.26 summarizes the % decrease in the maximum retention capacity Q_m for Cu^{+2} from multiple solution with respect to single ion solution. It can be observed from the figure that the % difference of Q_m are soil specific. For Cu^{+2} it can be noted that there is no significant variation in % of Q_m difference as observed for soil IBent and the % difference is less compared to the rest of the soil (<20%). For FBent the % difference followed the trend $Ni^{+2} < Pb^{+2} < Zn^{+2}$ in binary followed by tertiary and quaternary. For soil RS the variation of all binary was minimal while high variation was noted from binary to tertiary and quarternary. For FC, quaternary system had a low % difference than tertiary and binary (Cu-Cu+Ni) solution. For Kao there was a drastic variation observed for tertiary and quaternary system. Soil LS also behaved in the pattern binary < tertiary < quaternary. The % difference variation for FAsh was maximum among all soils. For Ni^{+2} the maximum % difference of Q_m was noted for RS. However, the difference between binary solutions was minimum for RS and maximum for IBent. Minimal change was observed RS and FC. For Pb^{+2} the % difference is more for LS and least for Kao.

Table 6.19a Percentage difference of Freundlich parameters of multiple solution of K^+ with reference to single K^+ solution

Soil	Na+K		NH_4+K		Na+K+Ca	
	K_F	N	K_F	N	K_F	N
IBent	13.45	20.62	17.14	7.42	49.40	17.48
FBent	18.36	17.75	-12.93	8.97	52.64	7.06
RS	7.87	15.58	9.68	14.66	21.47	14.29
FC	38.65	10.38	17.71	6.99	57.97	12.77
Kao	56.64	2.82	72.27	-33.84	61.30	-0.22
LS	41.83	11.18	0.26	12.13	58.03	14.49
FAsh	-	-	-	-	-	-

Table 6.19b Percentage difference of Langmuir parameters of multiple solution of K^+ with reference to single K^+ solution

Soil	Na+K		NH_4+K		Na+K+Ca	
	K_L	Q_m	K_L	Q_m	K_L	Q_m
IBent	12.04	41.78	16.67	21.24	20.65	61.35
FBent	10.14	45.68	-17.39	13.63	43.48	48.17
RS	-108.00	58.35	-80.00	55.44	-50.00	57.58
FC	2.13	52.49	-10.64	32.98	9.79	69.34
Kao	56.82	44.35	70.91	-14.82	55.34	45.81
LS	7.69	59.63	-30.77	42.93	3.46	74.98
FAsh	-	-	-	-	-	-

Table 6.20 Percentage differences of Freundlich and Langmuir parameters of multiple solution of NH_4^+ with reference to single NH_4^+ solution

Soil	K+NH_4		K+NH_4	
	K_F	N	K_L	Q_m
IBent	46.40801	-3.86643	36.07085	23.24847
FBent	30.93343	-4.80274	10.04184	2.985155
RS	11.34802	99.91399	-81.7814	55.56715
FC	8.807833	8.030593	-4.87805	30.17143
Kao	58.09655	-22.736	56.06061	-18.4941
LS	34.63451	-0.5291	31.15727	20.28097
FAsh	52.13884	-10.883	35.625	20.10822

Table 6.21 Percentage difference of Freundlich and Langmuir parameters of multiple solution of Ca^{+2} with reference to single Ca^{+2} solution

Soil	Na+K+Ca		Na+K+Ca	
	K_F	N	K_L	Q_m
IBent	16.8	31.8	-70.1	71.2
FBent	47.2	10.6	24.0	56.0
RS	26.1	13.8	-40.2	59.0
FC	-0.7	34.1	-142.9	71.6
Kao	56.1	38.6	-129.7	91.1
LS	16.9	24.1	-48.0	71.2

Table 6.22 Percentage difference of Freundlich and Langmuir parameters of multiple solution of Na^+ with reference to single Na^+ solution

Soil	Na+K		Na+K	
	K_F	N	K_L	Q_m
FC	15.65	-1.62	6.59	11.85
Kao	21.53	13.20	-39.09	41.95

Table.6.23a Percentage difference of Freundlich parameters of multiple solution of Cu^{+2} with reference to single Cu^{+2} solution

Soil	Cu+Ni		Cu+Zn		Cu+Pb		Cu+Ni+Pb		Cu+Ni+Pb+Zn	
	K_F	N	K_F	N	K_F	N	K_F	N	K_F	N
IBent	25.266	16.201	57.85	0.06	45.685	4.842	53.27	18.81	65.17	16.57
FBent	24.834	20.469	31.83	38.28	28.729	28.438	45.61	31.88	52.61	36.56
RS	8.034	2.342	36.78	-9.19	42.409	-12.97	48.52	-0.72	60.38	-3.96
FC	1.559	22.684	-2.79	13.20	15.392	6.710	22.73	14.94	50.70	-0.65
Kao	9.622	12.420	26.01	1.28	19.759	1.713	40.95	1.93	60.91	3.85
LS	-58.47	25.082	18.69	19.18	42.209	1.475	63.26	-4.43	72.91	0.33
FAsh	15.357	18.571	4.92	24.29	46.619	10.000	47.18	20.00	50.33	25.36

Table 6.23b Percentage difference of Langmuir parameters of multiple solutions of Cu^{+2} with reference to single Cu^{+2} solution

Soil	**Cu+Ni**		**Cu+Zn**		**Cu+Pb**		**Cu+Ni+Pb**		**Cu+Ni+Pb+Zn**	
	K_L	**Q_m**	**K_L**	**Q_m**	**K_L**	**Q_m**	**K_L**	**Q_m**	**K_L**	**Q_m**
IBent	44.74	17.02	76.11	8.55	59.26	14.63	64.01	35.82	80.73684	36.58
FBent	21.19	34.03	46.02	50.38	30.13	41.93	30.43	51.15	70.53	54.29
RS	-1.67	13.71	11.83	14.77	5.00	9.93	11.67	38.52	31.17	41.21
FC	-8.61	40.68	-47.54	28.36	-4.92	25.71	-12.3	42.94	38.52	35.84
Kao	14.78	22.75	7.80	18.62	-5.79	18.59	34.99	25.87	51.30	47.12
LS	-	36.74	1.56	50.26	24.69	30.46	48.44	33.23	56.25	53.39
FAsh	-	39.20	-207.6	40.95	11.95	53.29	-32.8	63.03	-23.81	67.85

Table 6.24 Percentage difference of Freundlich and Langmuir parameters of multiple solution of Pb^{+2} with reference to single Pb^{+2} solution

Soil	**Cu+Pb**		**Cu+Ni+Pb**		**Cu+Pb**		**Cu+Ni+Pb**	
	K_F	**N**	**K_F**	**N**	**K_L**	**Q_m**	**K_L**	**Q_m**
IBent	27.51	19.53	36.07	33.08	33.25	27.54	37.63	46.74
FBent	52.46	17.29	55.46	28.15	60.66	29.51	58.20	45.66
RS	7.63	8.52	35.18	-3.4	14.29	13.90	53.06	14.57
FC	67.47	-21.8	77.01	-25.7	74.84	18.70	77.74	33.06
Kao	39.96	-0.7	48.21	14.67	46.25	15.07	50.42	44.71
LS	0.21	11.35	44.11	6.68	-16.32	24.48	53.16	25.16
FAsh	55.19	-38.08	64.59	-38.8	84.09	2.36	85.38	19.46

Table 6.25 Percentage difference of Freundlich and Langmuir parameters of multiple solution of Ni^{+2} with reference to single Ni^{+2} solution

Soil	**Cu+Ni**		**Cu+Ni+Pb**		**Cu+Ni**		**Cu+Ni+Pb**	
	K_F	**N**	**K_F**	**N**	**K_L**	**Q_m**	**K_L**	**Q_m**
IBent	55.26	-31.67	63.08	-24.43	89.0	11.0	88.95	31.60
FBent	52.78	12.78	55.94	24.17	66.9	44.0	66.61	57.92
RS	29.77	5.80	37.61	5.36	38.4	29.8	50.00	35.60
FC	71.34	52.67	77.11	44.13	62.1	82.0	74.83	82.94
Kao	16.22	23.00	27.54	29.28	21.1	43.0	24.21	56.91
LS	56.82	-268.72	60.33	-233.33	31.7	47.1	33.21	56.34
FAsh	46.12	-20.22	66.73	-38.60	40.0	18.2	61.00	25.37

Table 6.26 Percentage difference of Freundlich and Langmuir parameters of Multiple solution of Zn^{+2} with reference to Zn^{+2} solution

Soil	`Cu+Zn			
	K_F	N	K_L	Q_m
IBent	55.31	1.76	74.24	6.02
FBent	50.49	-2.65	67.07	3.87
RS	14.20	5.00	8.89	18.04
FC	13.20	5.63	7.14	19.54
Kao	20.62	3.97	17.16	19.53
LS	-16.61	15.01	-53.66	37.75
FAsh	-1.29	8.57	-20.00	25.82

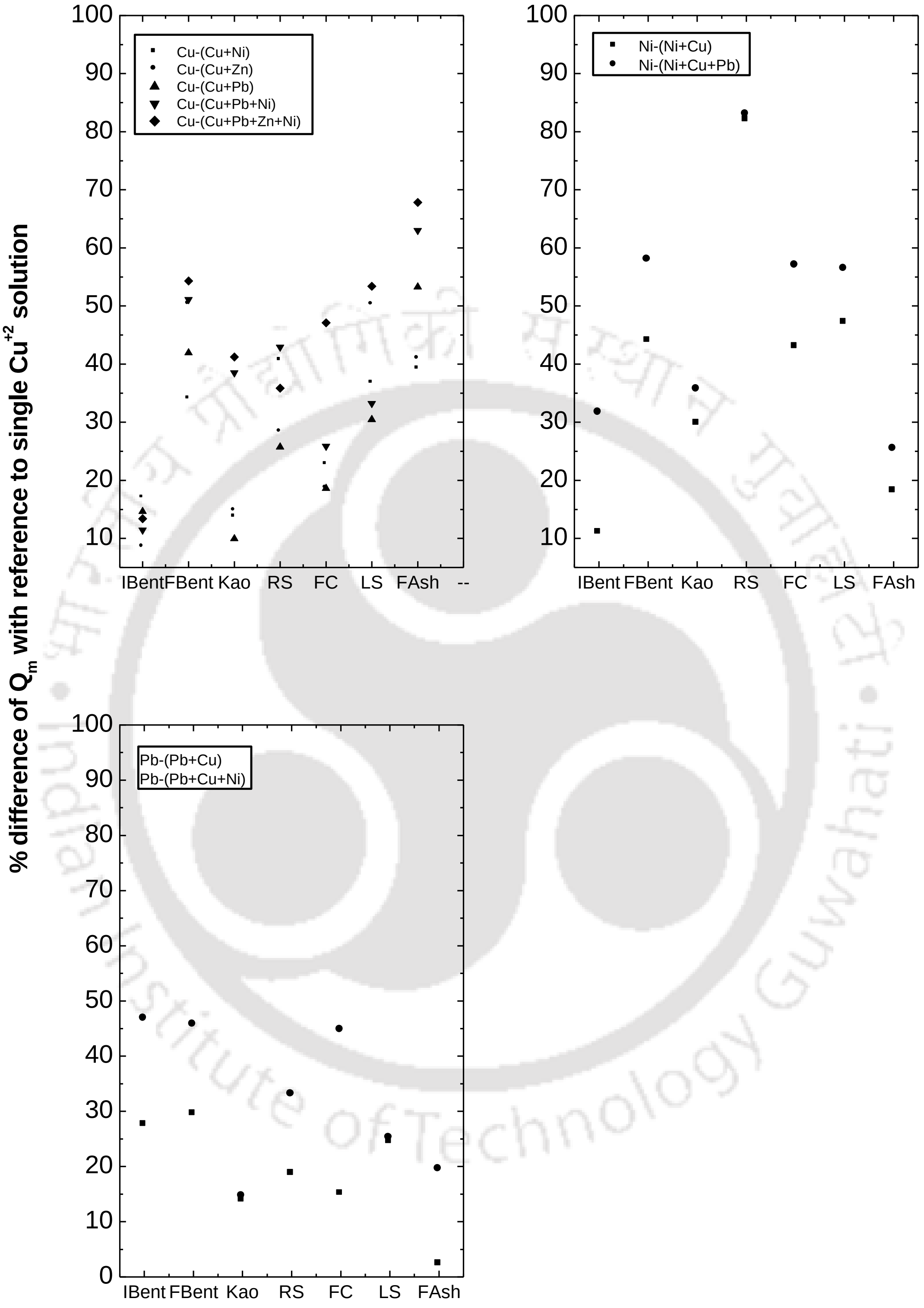


Fig 6.26 Graphical representation of Q_m % difference of Cu^{+2}, Pb^{+2} and Ni^{+2} in reference to single Q_m value

6.6 Correlation between retention parameters (K_F and Q_m) and soil specific properties

Studies reported in the literature (Wan Zuhairi et al., 2004) indicate that soil's physico-chemical properties significantly influenced the retention capacity. Total specific surface area (SSA), cation exchange capacity (CEC) and soil pH are factors that account for physico-chemical properties of geomaterials. There are not many studies that investigate the possibility of correlation between retention parameters and soil specific parameters.

In addition, such correlations are not understood particularly for multiple contaminant-soil interaction. The objective of this study is to make a detailed assessment of the correlation between retention parameters and soil specific properties. Langmuir and Freundlich isotherm parameters Q_m and K_F is considered as they represent the retention characteristics better than other parameters. The soil specific properties include SSA, CEC and soil pH listed in Table 4.3. Fig 6.27 shows a typical representation of Q_m correlation with the SSA, CEC and soil pH. It can be seen that the correlation is approximately linear. For the sake of brevity, other figures are not presented. The linear correlation between retention parameter and soil parameter is expressed by eqn.6.2 further graphs are avoided.

$$\text{Retention parameter} = J * \text{Soil parameters} \qquad (6.2)$$

where J is the constant. Table 6.27 to 6.31 shows the values of J obtained for different soil-contaminant interactions considered in this study. In the table, soil parameter SSA, CEC or soil pH is subdivided into K_F, R^2 and Q_m, R^2 where the column below K_F and Q_m indicates the constant J and the term R^2 indicates the goodness of fit obtained for both the cases. In the table 6.27, the value 3.57 is the J value for the correlation between K_F and SSA and goodness of fit R^2 is provided adjacent to column K_F. Similarly, the values of other correlations need to be deciphered.

There are contradictory results about the dependence of retention of heavy metals to CEC and SSA in the literature. John (1972) failed to have any such correlation. Reddy and Perkins (1974), found an inverse relation between CEC and Zn retention. Helios-Rybicka (1985), found that neither CEC nor SSA of clay minerals has any significant effect on the amount of sorption. However, majority of literature study states that retention capacity parameter (K_F and Q_m) is positively correlated to the CEC. The role of specific surface area (SSA) on the soil retention properties is well known but not many studies have been reported on its correlation.

From table 6.27 it is evident that total SSA correlated well with retention parameters for all the single common ions but poor correlation was developed for Ca^{+2} for CEC with respect to Q_m. Table 6.28 shows that total SSA was relatively better correlated to both Q_m and

K_F parameters for single heavy metal solution. Correlation developed as shown in table 6.29 for common ions in multiple solutions for both CEC and SSA gave satisfactory linear fit except for Ca^{+2}. Table 6.30 depicted that all heavy metal in multiple solution established better correlation as evident from its high R^2 value for both SSA and CEC. From table 6.31, the correlation developed between pH with parameters Q_m and K_F for both common ions and heavy metals from single ion solution was very poor. Considering this no correlation was attempted for soil pH and multiple contaminants.

The present study portrays that for heavy metal (single and multiple) CEC and SSA showed a good correlation. However, the same was not observed for common ions for Ca^{+2} for both CEC and SSA. The results of soil pH gave a poor correlation which contradicts the findings of earlier researchers who have reported about the enhanced sorption of metals with increasing soil pH (Harter, 1983; Msaky and Calvet, 1990; Basta and Tabatai, 1992; Raghupathi and Vasuki, 1993; Gomes et al., 2001; and Adhami et al., 2008).

6.7 Study on the variability of constant (J)

An attempt was made to study the variability of the constant J to understand if there exist any scope for correlation between retention parameters such as K_F and Q_m and soil properties (SSA, CEC and soil pH). The values of J constant were divided into a) complete data set for common ions and heavy metal comprising single and multiple interaction. b) all data sets for common ions comprising single and multiple interaction and c) all data sets for heavy metals comprising single and multiple interaction. Then it was further divided into the variation amongst individual common ions (Na, K and Ca) and heavy metal ions (Cu, Pb, Ni, Zn).

Figs. 6.28 to Fig 6.30 show the variation of J for K_F and Fig 6.31 to Fig 6.33 shows the variation of J for Q_m with respect to the classification mentioned above. Figs 628(a) and 6.31(a) shows a wide range of J which clearly indicates that there cannot be a general correlation for K_F and Q_m. When the data is divided into common ions (CI) and heavy metals (HM) as shown in Figs. 6.28b,c and Fig.6.31b,c the variability considerably reduces. However, even this variability of J cannot be treated appropriate for a robust correlation with individual ions, the J value may be considered relatively appropriate for heavy metals than common ions. This study is limited to identifying the possibility of correlation for retention parameter based on soil properties. As such, from this study no robust correlation can be proposed. This would require further detailed investigation.

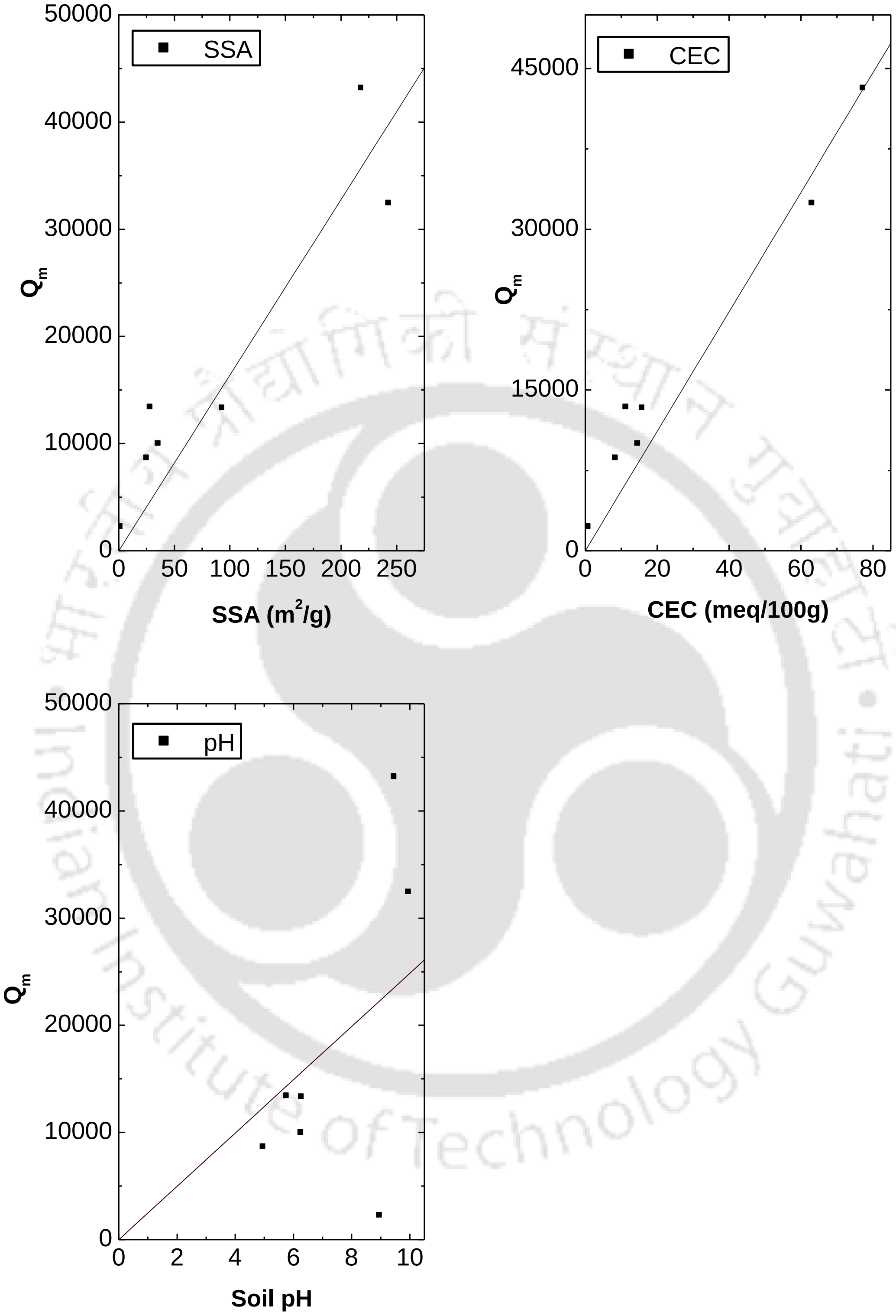


Fig 6.27 Model representation of Q_m correlation with SSA, CEC and soil pH for Cu^{+2} single solution

Table 6.27 Values of constant J for single common ions (CI) solution

Common Ions	**SSA**				**CEC**			
	K_F	**R^2**	**Q_m**	**R^2**	**K_F**	**R^2**	**Q_m**	**R^2**
K	3.57	0.83	85.81	0.89	11.78	0.80	289.70	0.95
Ca	2.15	0.74	79.55	0.20	5.372	0.70	271.00	0.33
NH_4	2.31	0.78	101.90	0.91	7.351	0.62	341.30	0.93

Table 6.28 Values of constant J for single heavy metal (HM) solution

Heavy Metals	**SSA**				**CEC**			
	K_F	**R^2**	**Q_m**	**R^2**	**K_F**	**R^2**	**Q_m**	**R^2**
Cu	15.64	0.91	163.90	0.82	52.13	0.91	557.3	0.92
Pb	22.41	0.77	244.50	0.88	77.51	0.91	827.8	0.95
Zn	13.68	0.88	137.30	0.85	34.82	0.91	459.8	0.87
Ni	10.5	0.88	61.65	0.6	45.07	0.84	215.3	0.82

Table 6.29 Values of constant J for multiple common ions (CI) solution

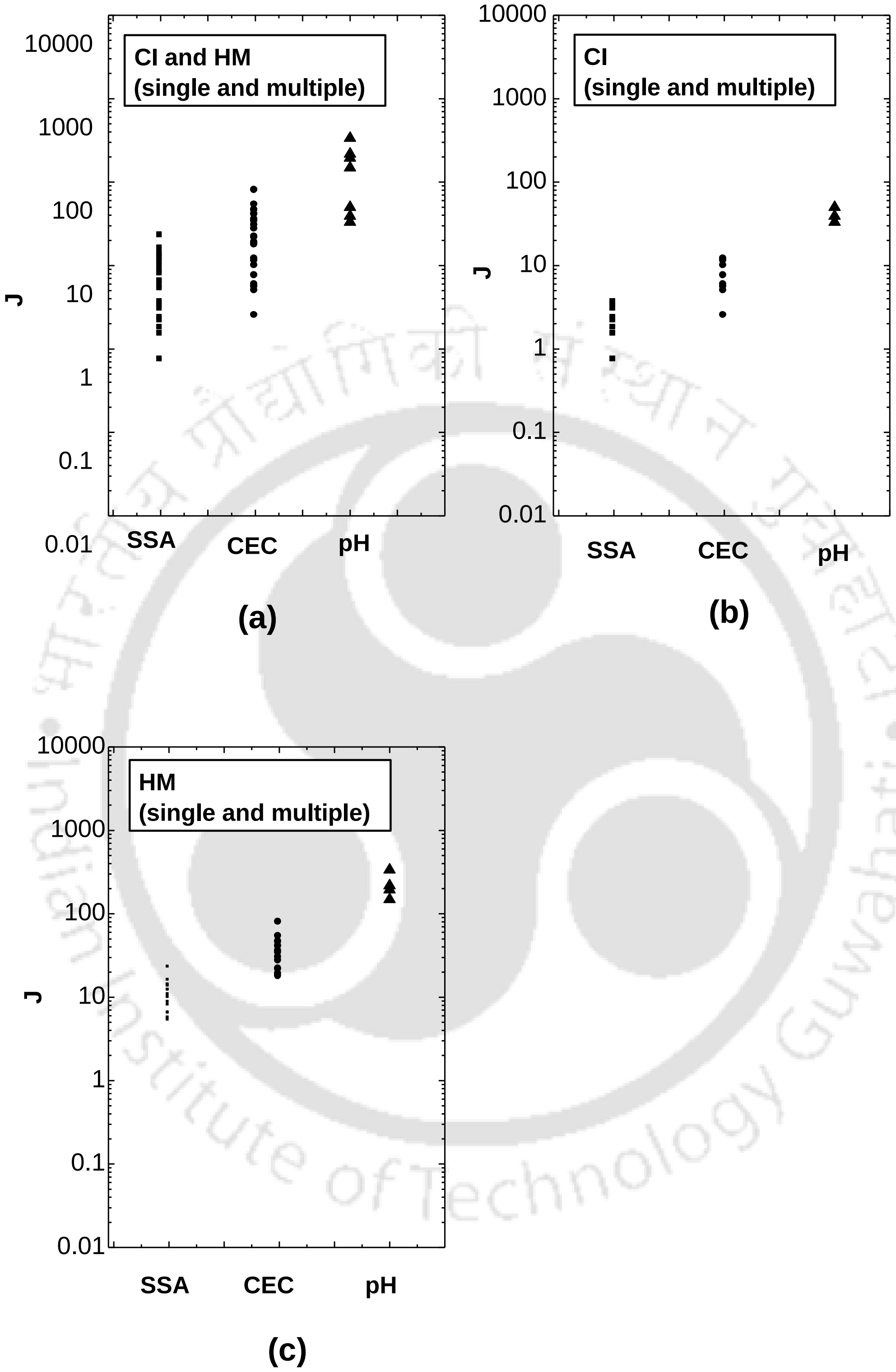
Common Ions	**SSA**				**CEC**			
	K_F	**R^2**	**Q_m**	**R^2**	**K_F**	**R^2**	**Q_m**	**R^2**
K-Na+K	2.97	0.85	47.72	0.88	9.72	0.78	160.6	0.92
K-NH4+K	3.29	0.89	69.85	0.78	11.02	0.91	239.2	0.91
K-Na+K+Ca	1.76	0.84	38.22	0.80	5.75	0.77	131.7	0.96
NH4-NH4+K	0.73	0.88	73.78	0.85	2.46	0.89	253.9	0.95
Ca-Na+K+Ca	1.49	0.71	27.04	0.82	4.85	0.61	93.03	0.98

Table 6.30 Values of constant J for multiple heavy metals (HM) solution

Heavy metal combination	SSA				CEC			
	K_F	R^2	Q_m	R^2	K_F	R^2	Q_m	R^2
Cu-Cu +Ni	11.89	0.90	121.6	0.92	39.70	0.91	404.8	0.92
Cu-Cu+Zn	8.49	0.79	114.1	0.91	29.37	0.94	369.4	0.76
Cu-Cu+Pb	9.68	0.88	117.9	0.89	33	0.96	388.1	0.82
Cu-Cu+Ni+Pb	7.86	0.89	93.04	0.82	26.53	0.94	310.6	0.83
Cu-Cu+Ni+Pb+Zn	6.29	0.88	88.59	0.91	21.44	0.96	293.5	0.88
Ni-Ni+Cu	6.35	0.90	42.85	0.79	20.96	0.87	144.3	0.83
Ni-Ni+Cu+Pb	5.52	0.92	32.77	0.79	18.37	0.92	110.0	0.82
Pb-Pb+Cu	13.29	0.93	176.5	0.87	44.31	0.93	596.3	0.93
Pb-Pb+Cu+Ni	11.87	0.92	134.0	0.85	39.84	0.95	453.0	0.92
Zn-Zn+Cu	5.19	0.81	128.1	0.91	17.25	0.80	429.7	0.94

Table 6.31 Values of constant J for correlation between soil, pH and parameter K_F & Q_M for single contaminant solution

Heavy metal combination	pH			
	K_F	R^2	Q_m	R^2
K	49.9	0.28	1239	0.29
NH_4	33.11	0.23	955.3	0.24
Ca	39.03	0.53	1595	0.49
Cu	217.4	0.32	2485	0.29
Ni	193.8	0.31	951.2	0.29
Pb	335.9	0.36	3550	0.34
Zn	148.7	0.32	2157	0.42



(a) (b) (c)

Fig. 6.28 Variation of constant J for K_F correlation corresponding to (a) complete data set (CI and HM) (b) CI (c) HM for single and multiple contaminant solution with respect to SSA, CEC and pH

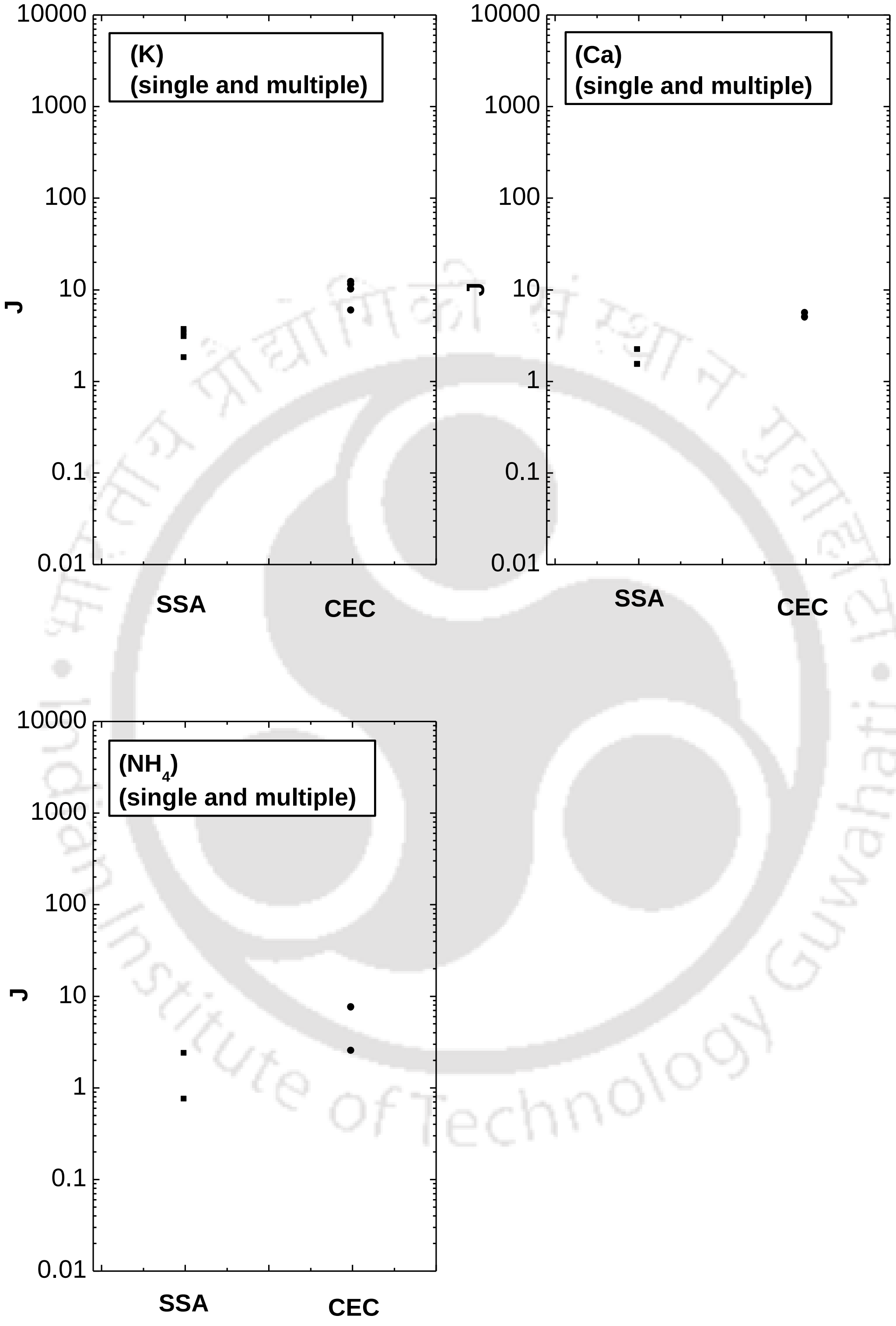


Fig. 6.29 Variation of constant J for K_F correlation corresponding all common ion (CI) combination

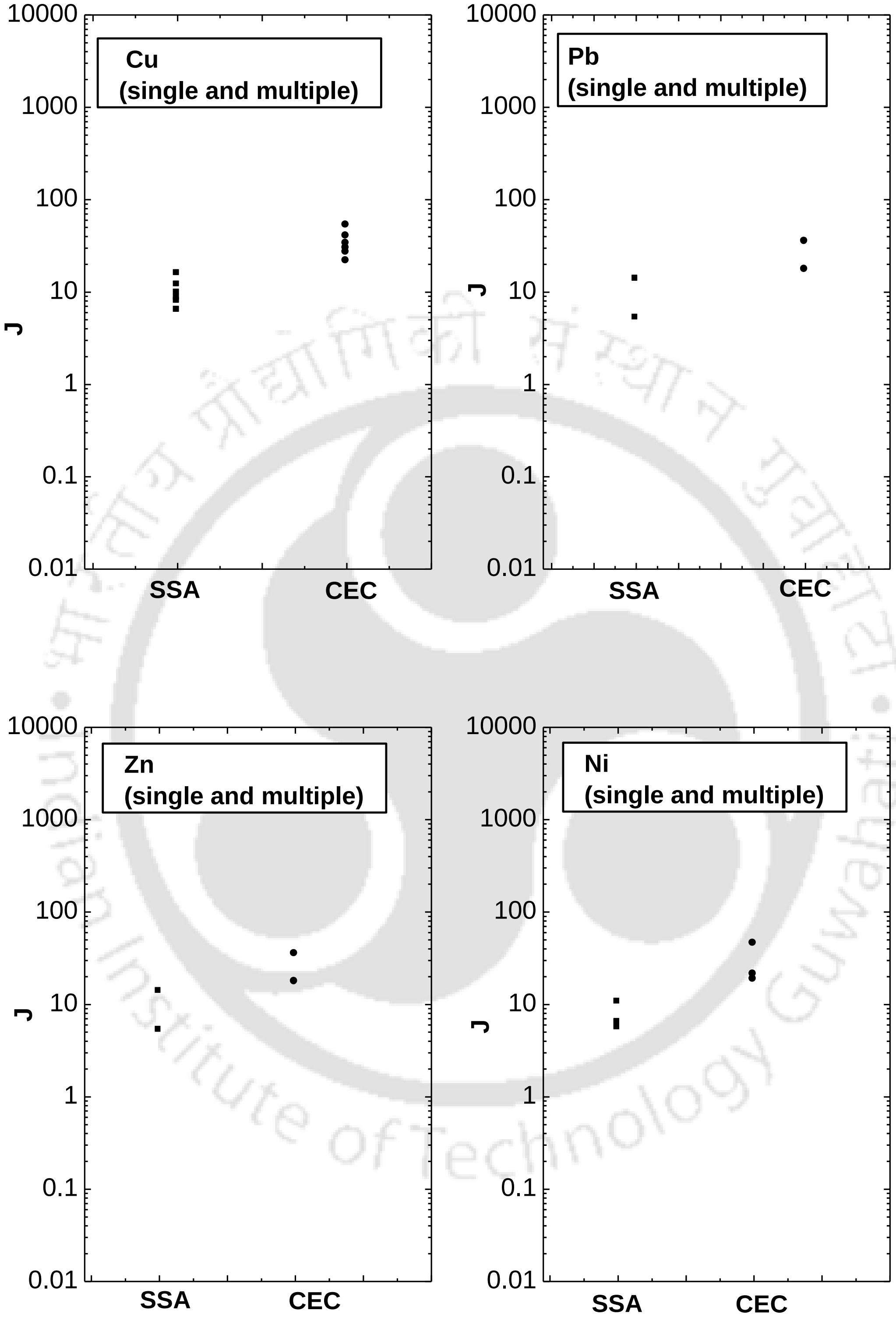


Fig. 6.30 Variation of constant J for K_F correlation corresponding to all heavy metal combination

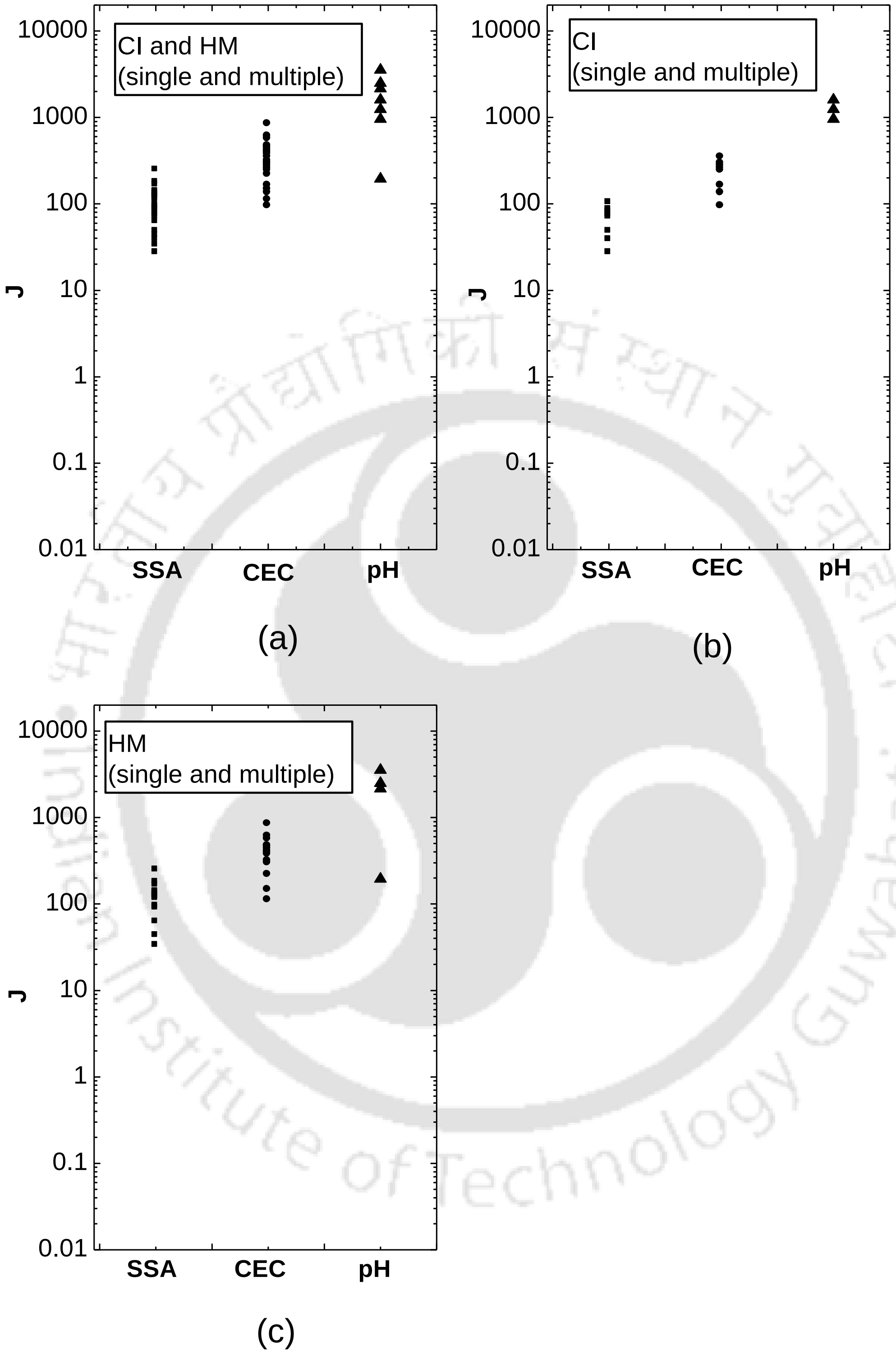


Fig.6.31 Variation of constant J for Q_m correlation corresponding to (a) complete data set (CI and HM) (b) CI (c) HM for single and multiple contaminant solution with respect to SSA, CEC and pH

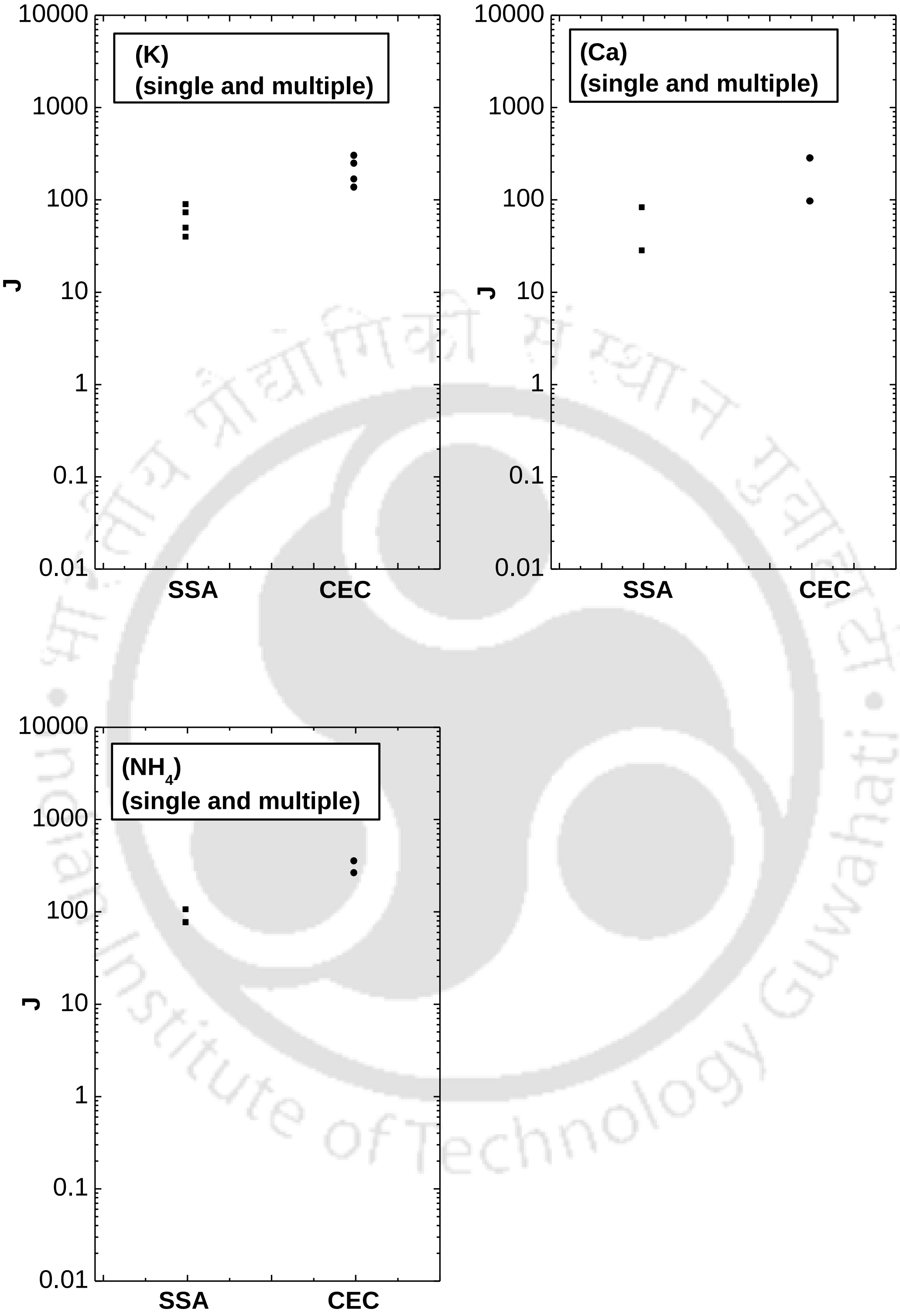


Fig. 6.32 Variation of constant J for Q_m correlation for all common ion combination

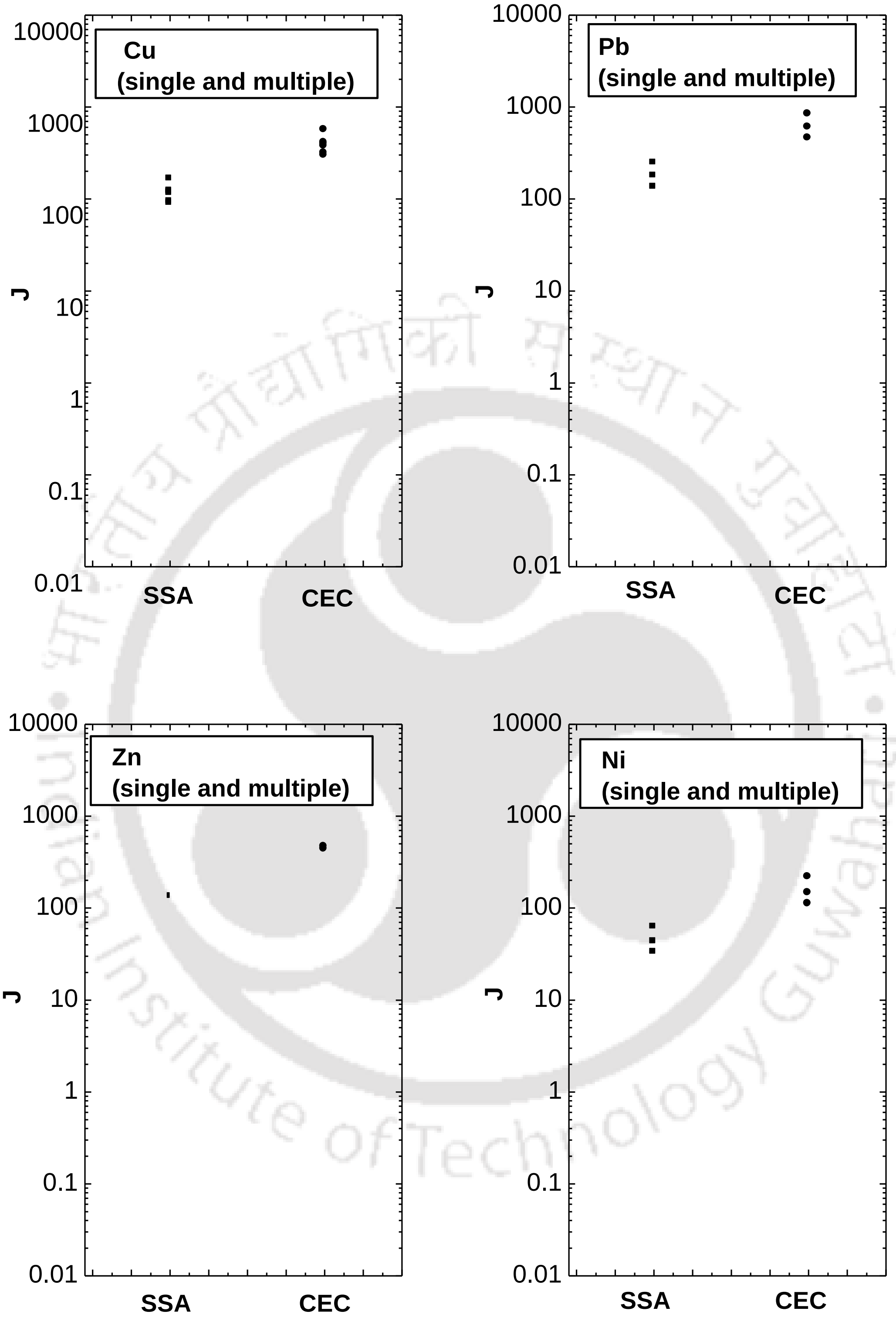


Fig. 6.33 Variation of constant J for Q_m correlation for all heavy metal combination

6.8 Summary

The important observation based on the multiple contaminant-soil interaction results are summarized below

1. It can be highlighted from the present study that range of concentration has significant effect on multiple ions retention in soils. Therefore, it is ideal to characterize soil-contaminant interaction with prior knowledge of the range of concentration that would exist in real life situation. The choice of retention isotherms would depend upon the range of concentration adopted. Simple linear isotherms are appropriate only for small range of concentration. The study demonstrates that wrong choice of linear or non-linear isotherms can result in gross inconsistencies while characterizing soil-contaminant interactions.
2. The influence of multiple contaminant interaction in binary and tertiary system for common ions has been investigated for seven soils. It was found that for Na^+ in presence of K^+ there is no definite trend for retention for most soils except FC and Kao net release occurred of Na^+ for the entire range of concentration. As such no isotherm fitting could be carried out in those cases. The results of retention of K^+ in the presence of Na^+ decreased for all soil.
3. Studies on K^+ and NH_4^+ binary solution indicates that each of the ion has a definite influence on soil retention, where multiple retention decreased as compared to single ion retention. It can be observed that at lower concentration the NH_4^+ and K^+ ion competed equally in most of the soils but after a certain range of concentration, unique for each soil, the soils in some cases were efficient in sorbing NH_4^+ (FBent, Kao and LS) and in the rest of the soil K^+.
4. Affinity of soil for K^+ is greater than that for Ca^{+2} except for FC and LS where Ca^{+2} sorbed more than K^+.
5. The study reveals that retention progressively decreases from single to binary to tertiary and quaternary ion solution in almost all the cases for heavy metal.
6. The study states that for soils with varying index properties metal retention cannot solely be predicted by any given affinity series. As for example if metal retention was entirely based on electronegativity the sequence would have been $Cu^{+2} > Ni^{+2} > Pb^{+2} > Zn^{+2}$. Metal retention in this study was not solely based on hydrated radius where the sequence would had been $Pb^{+2} > Ni^{+2} > Cu^{+2} > Zn^{+2}$. The retention was not entirely based on covalent bond either, because covalent bonds would predict the following

affinity sequence Ni^{+2} > Zn^{+2}. These results indicate that the main physical and chemical factors governing the retention depend not only on metal properties but also on soil properties, and environmental factors. In addition, the ion affinity from single and multiple contaminant solution is not consistent for all soils. A systematic investigation on why certain soil surface characteristics show a particular affinity for ions could not be attempted in this research work.

7. The retention of Cu^{+2} in multiple contaminant solution decreased from single ion retention to binary, tertiary and quaternary solution. This can be attributed to the interference of other metal ions during the retention process i.e., competitive reactions
8. The study investigates both the Freundlich and Langmuir isotherms models for analysis of the retention data for different soils from single and multiple contaminant study. From the analysis of the isotherms results, it can be noted that in certain cases the outcome predicted by both the isotherms are not same. This difference of prediction between the two was more prominent when retention approached saturation (when the retention does not increase with the increase of equilibrium concentration). It was revealed that in these cases, Freundlich isotherm does not take into account the region close to near saturation leading to overestimation of the K_F parameter. At higher range of concentration Freundlich isotherm fails increasing more risk in the prediction of fate of contaminants. In such cases, Langmuir isotherm will be better successful isotherm model than the Freundlich.
9. For some cases of soil-multiple contaminant interaction, it was noted that mathematical quantification did not portray the experimental observations. This means that care should be taken while using these isotherm parameters for contaminant fate prediction. The findings also raises questions on the validity of using those well established isotherms specially Freundlich when the range of concentration is large and saturation is achieved.
10. For some cases of soil-multiple contaminant interaction, it was noted that mathematical quantification did not portray the experimental observations. This means that care should be taken while using these isotherm parameters for contaminant fate prediction. The finding also raises questions on the validity of using those well established isotherms specially Freundlich when retention saturation is achieved.
11. The relationship of Freundlich and Langmuir non-linear isotherm parameters K_F and Q_m with specific surface area (SSA),cation Exchange Capacity (CEC) and soil pH

was investigated based on the results of both single and multiple contaminant retention. It was noted that the trends was linear. However, a robust correlation could not be developed in the present study. The variability of such correlation indicates that a simple correlation is not possible for estimating K_F and Q_m

12. The study also brings out the retention ability of FAsh which is generally considered to be an inert material. Addition of these flyash with bentonite in place of sand will not only increase the strength and reduce the shrinkage behavior of bentonite but at the same time help in sorbing heavy metals than the inert sand. This will be advantageous from the environmental perspective where it can be used in waste containment liners.
13. This study also investigates single and multiple retention characteristics of local soils of northeast India such as LS and RS which is not done in the past. These soils exhibit satisfactory retention characteristics of common ions and heavy metals.

Chapter 7

Influence of retention isotherms on contaminant fate prediction

7.1 General

There are different isotherms for quantifying the results of batch test and determining the parameter that represents the partitioning of contaminants between solid (soil particles) and liquid phase (pore solution). This in turn represents soil-contaminant interaction which influence the fate of contaminant in sub surface. In order to model transport of contaminants through the subsurface a linear retention isotherm is usually used because of its simplicity (Sharma and Reddy 2004). With increasing contaminant concentration range, soil-contaminant interaction becomes nonlinear. Soil retention experiments have been widely modelled with the empirical nonlinear Freundlich and Langmuir isotherm as explained in previous chapters. The output from these isotherms is helpful in understanding the fate of specific contaminants. There are not many studies that systematically investigate the influence of different isotherm parameters of contaminant fate prediction. This is specifically true for multiple contaminant- soil interaction. So, the present study will investigate the influence of multiple contaminant-soil interaction on contaminant fate prediction. The influence of different ranges of contaminant concentration on fate prediction is also studied.

7.2 Modelling fate of contaminants

Soil-contaminant interaction directly affects fate of contaminants in geoenvironment and also their bioavailability and transformation. Most of the contaminant transport models account for retention by assuming a linear equilibrium partitioning of contaminants between the solid and liquid-phase concentrations. Linear approximation to retention equilibrium data is useful as it substantially reduces the mathematical complexity of the modelling (Weber et al., 1991). Evidence of nonlinear retention characteristics of contaminants to soil and aquifer material has been documented both on a laboratory scale (Lijun et al., 1997; Hu and Brusseau 1998; Weber and Miller 1998; Young and Ball 1999; Appert-Collin et al., 1999; Chang et al., 2001; Huang et al., 2003) and in the field (Hutzler et al., 1986; Roberts et al., 1986; Allen-King et al., 1996; Brusseau and Srivastava 1997; Shepherd et al., 2002; Jean et al., 2002). Typically, decisions on retention behavior are made through interpretation of data obtained from batch retention isotherm. Linear retention may be valid over a range of concentration employed in a batch study, but may not be applicable over wide range of concentration (Weber et al., 1991). Modelling the transport of nonlinearly sorbed solutes using a linear model may sacrifice significant accuracy (Weber et al., 1999; Brusseau 1995) and potentially hinder remediation efforts or underestimate the hazard of waste repositories (Marseguerraand Zio 2001) if the retention behaviour is non linear. This along with the role of multiple contaminant soil interaction on contaminant fate prediction is investigated as follows.

7.2.1 Contaminant fate prediction of common ions

In the present study, contaminant transport of common cations such as sodium and potassium in soil RS were studied. These cations are commonly present in the leachate generated from the domestic municipal solid waste dumps. The batch test results were performed for a liquid to solid ratio of 10 and pH close to neutral. The tests were conducted for single ions and multiple ions in order to understand the influence of multiple contaminants on determination of retardation factor and hence contaminant fate prediction. The details of the experimental results are discussed in chapter 5 and 6 .For the present analysis, only K^+ results were considered for the contaminant fate prediction by using retardation factors obtained for Linear, Langmuir and Freundlich isotherms. The values of retardation factors (R) for K^+ corresponding to single and multiple contaminant solution are listed in tables 7.1 and 7.2, respectively. For non-linear isotherms such as Langmuir and Freundlich, R values have been obtained for C_e equal to 100, 500 and 1000 mg/L. Eqn 3.6 to 3.8 from section 3.8 of chapter 3 were used to determine R Values corresponding to linear, Langmuir and Freundlich isotherm respectively.

These results are plotted together, as shown in Fig. 7.1, to understand the influence of single and multiple solution on R. It can be noted that linear isotherm based on $C_e < 60$ mg/L data gave maximum retardation factor. For linear isotherm based on $C_e > 60$ mg/L and entire C_e data, the values of R_{Li} are nearly same and much less than $C_e < 60$ mg/L data. Except for R_{La} corresponding to $C_e = 100$ mg/L, all R values corresponding to non-linear isotherm are less than R_{Li}. In general, it can be noted that R values of K^+ based on multiple salt is less than that obtained using single salt. However, for non-linear isotherms the difference in R values between single and multiple salt solution decreases with increase in C_e.

Table 7.1 Retardation values for K^+ for different isotherms obtained from single salt solution

C_e (mg/L)	Linear (R_{Li})			Langmuir (R_{La})	Freundlich (R_F)
	< 60 mg/L	> 60 mg/L	Entire data		
100	34.93	10.72	10.81	18.35	13.81
500	34.93	10.72	10.81	6.36	7.09
1000	34.93	10.72	10.81	3.21	5.42

Table 7.2 Retardation values for K^+ for different isotherms obtained from multiple salt solution (Na+K)

C_e (mg/L)	Linear (R_{Li})			Langmuir (R_{La})	Freundlich (R_F)
	< 60 mg/L	> 60 mg/L	Entire data		
100	26.83	6.27	6.33	11.17	7.79
500	26.83	6.27	6.33	2.81	3.83
1000	26.83	6.27	6.33	1.61	2.94

The above listed values of retardation factors were employed to obtain breakthrough curves for K^+ corresponding to single and multiple contaminant solution. For this purpose, saturated soil column of 2.5 cm diameter and 2.5 cm depth has been taken. The soil sample was compacted to a dry density of soil sample was 1.33 kg/m^3 and volumetric water content is 0.4. Single step input of the contaminant with initial normalized concentration (C_t/C_0) equal to one was considered, where C_t is the concentration at any time t and C_0 is the initial concentration. The Darcy velocity is taken as $1.83*10^{-5}$ m/s and the value of dispersion coefficient for K^+ is $1.1*10^{-6}$m^2/s (Chang et al. 2001).The normalized concentration versus time breakthrough curves corresponding to different retardation factors and different values of equilibrium concentration as listed in Tables 7.2 and 7.3 are presented in Figs. 7.2 to 7.4 for single and multiple contaminant solution. It can be noted from the figures that the BTC's obtained based on R_{Li}, R_{La}, R_F are different. In general, C_t/C_0 is low for linear isotherm based on C_e < 60 mg/L. For non-linear isotherm, Langmuir gave less contaminant prediction as compared to Freundich for C_e = 100 mg/L. For C_e = 500 and 1000 mg/L, the contaminant retardation follows the sequence $R_{Li} > R_F > R_{La}$. For all the cases, R_{Li} based on C_e < 60 mg/L is always greater than that based on C_e > 60 mg/L and entire C_e data. This indicates that proper discretion should be there while using R_{Li} for contaminant prediction.

To understand the role of range of C_e on BTC's obtained based on R_{Li}, R_{La} and R_F, the fate of contaminant at the end of 10 hrs is compared as shown in Fig. 7.5 for single and multiple contaminant solution. It can be noted from the figure that the fate of contaminant corresponding to a particular position (2.5 cm of soil depth) at the end of 10 hrs is quite different for three different isotherms. Also, the range of data considered for obtaining R_{Li} influences contaminant prediction. For a low value and range of C_e, linear isotherm exhibits high retardation. For R_{Li} based on higher range and entire data, contaminant prediction is higher. Except for C_e = 100 mg/L, the contaminant prediction based on these values are higher than those obtained using R_{La} and R_F. Among non-linear isotherms, R_F predicts more than R_{La} for lower value of C_e and vice versa for higher value of C_e. The difference in contaminant prediction based on R_{La} and R_F gradually decreases as C_e increases.

The influence of single and multiple contaminant solution on isotherms and hence BTCs is investigated as depicted in Figs. 7.6 to 7.8 for different values of C_e. Since, the BTC's for linear isotherms are not influenced by C_e, the results are presented only for C_e equal to 100 mg/L. It can be noted from the figures that, contaminant fate prediction is higher for retardation factor obtained from the results of multiple solution for all the time investigated in the present study. The difference between contaminant prediction based on single and multiple solution decreases with increase in C_e. This is mainly due to the fact that the difference in R values gradually decreases as C_e increases.

To have a better understanding of single and multiple contaminant solution on contaminant prediction, C_t/C_0 values corresponding to 10 hrs have been plotted as depicted in Fig. 7.9. It can be noted from the figure that the contaminant prediction is low for linear isotherm obtained based on C_e data less than 60 mg/L. The results of C_t/C_0 for linear isotherms based on C_e > 60 mg/L and entire data matches well. Also, the plots indicate that C_t/C_0 of K^+ is higher for multiple contaminant solution. The results are true for non-linear isotherms such as Langmuir and Freundlich. Another important observation is that for non-linear isotherms, the difference in C_t/C_0 for single and multiple contaminant solution decreases as C_e increases. The discussion indicates that the contaminant fate prediction based on different isotherms are quite different for both single and multiple contaminants.

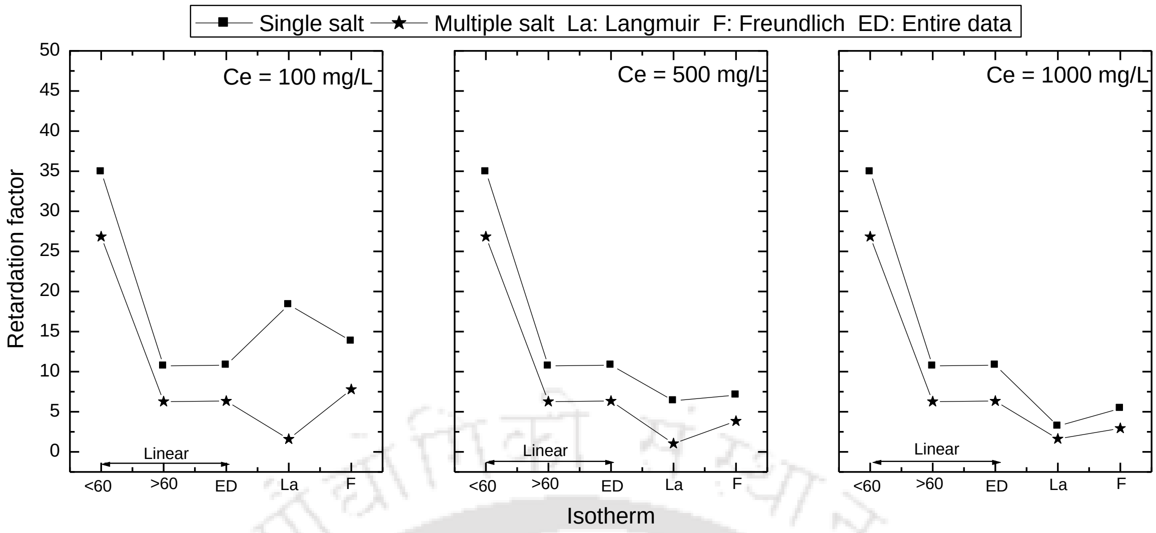


Fig. 7.1 Variation of retardation factor for K^+ corresponding to single and multiple salt solution and different C_e

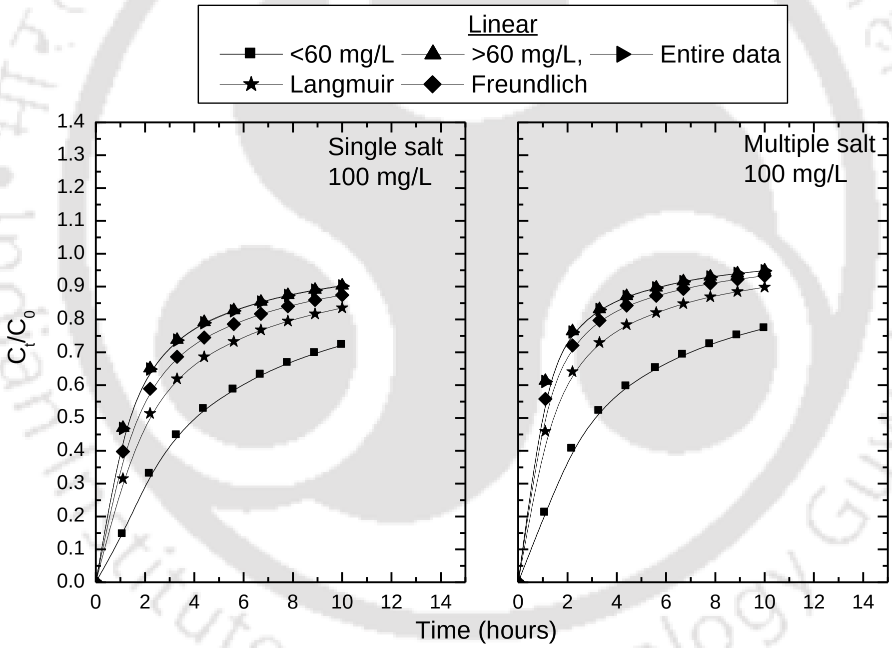


Fig. 7.2 Comparison of BTCs obtained for K^+ corresponding to retardation factors of different isotherms and C_e = 100 mg/L

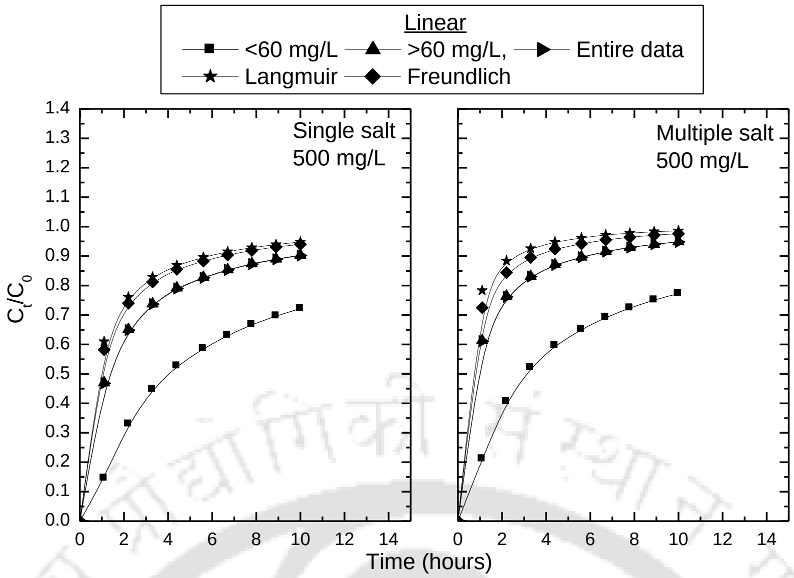


Fig. 7.3 Comparison of BTCs obtained for K^+ corresponding to retardation factors of different isotherms and C_e = 500 mg/L

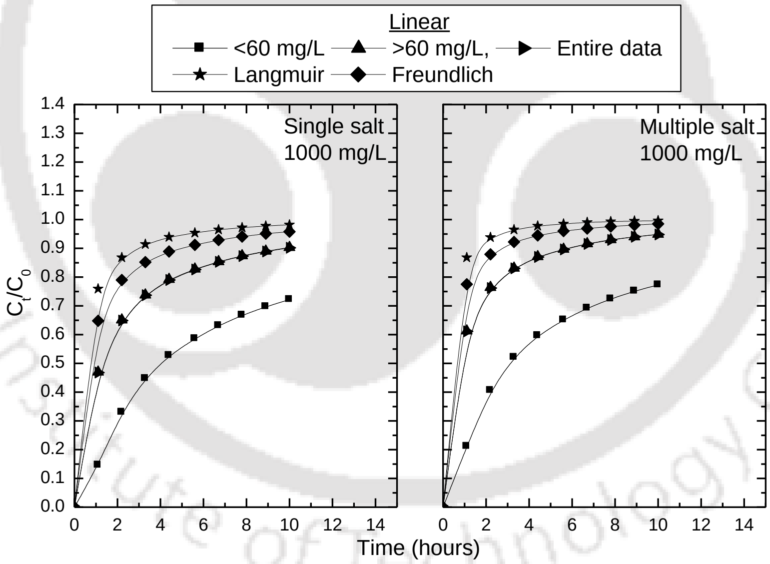


Fig. 7.4 Comparison of BTCs obtained for K^+ corresponding to retardation factors of different isotherms and C_e = 1000 mg/L

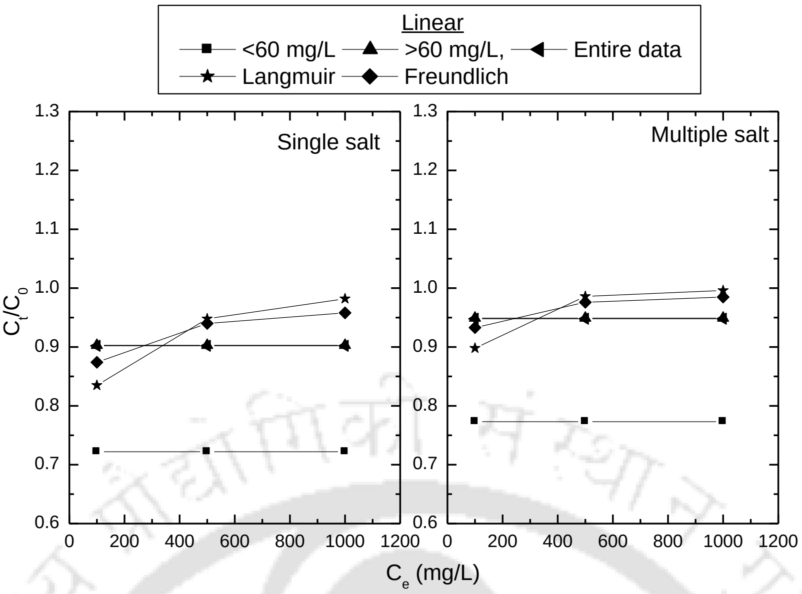


Fig. 7.5 Influence of C_e on predicting the fate of K^+ at the end of 10 hours corresponding to single and multiple salt

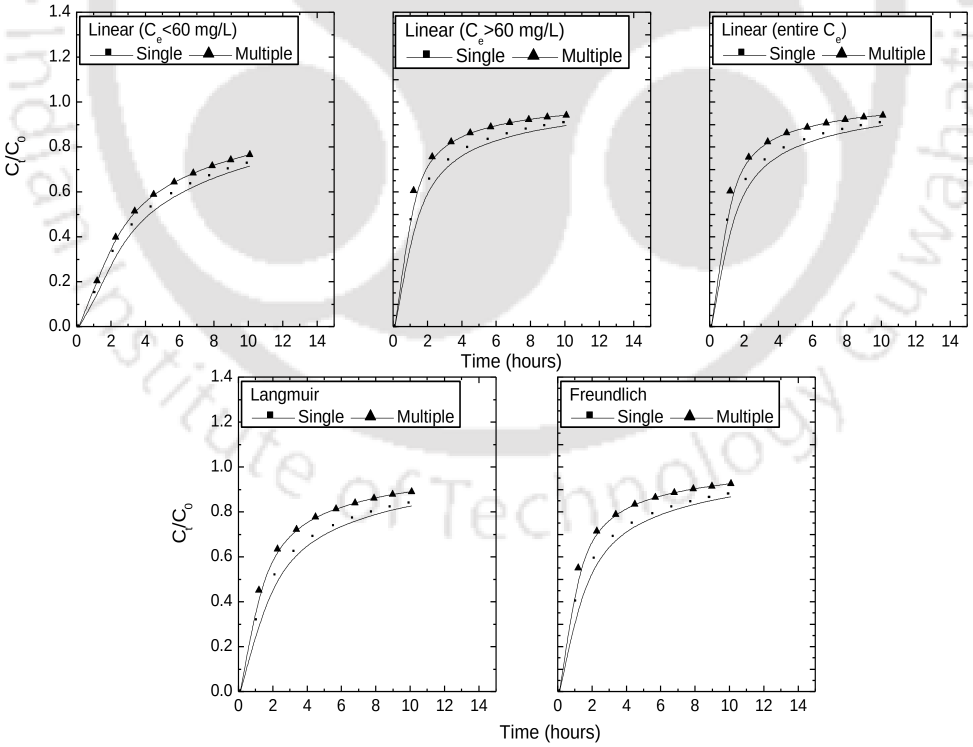


Fig. 7.6 Comparison of BTCs obtained for K^+ from single and multiple salt solution for different isotherms and C_e = 100 mg/L

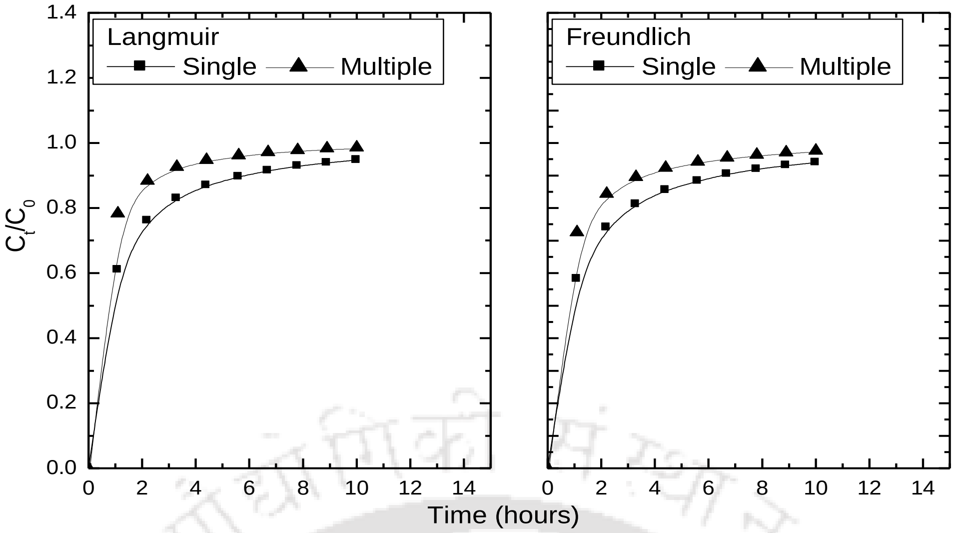


Fig. 7.7 Comparison of BTCs obtained for K^+ from single and multiple salt solution for different isotherms and C_e = 500 mg/L

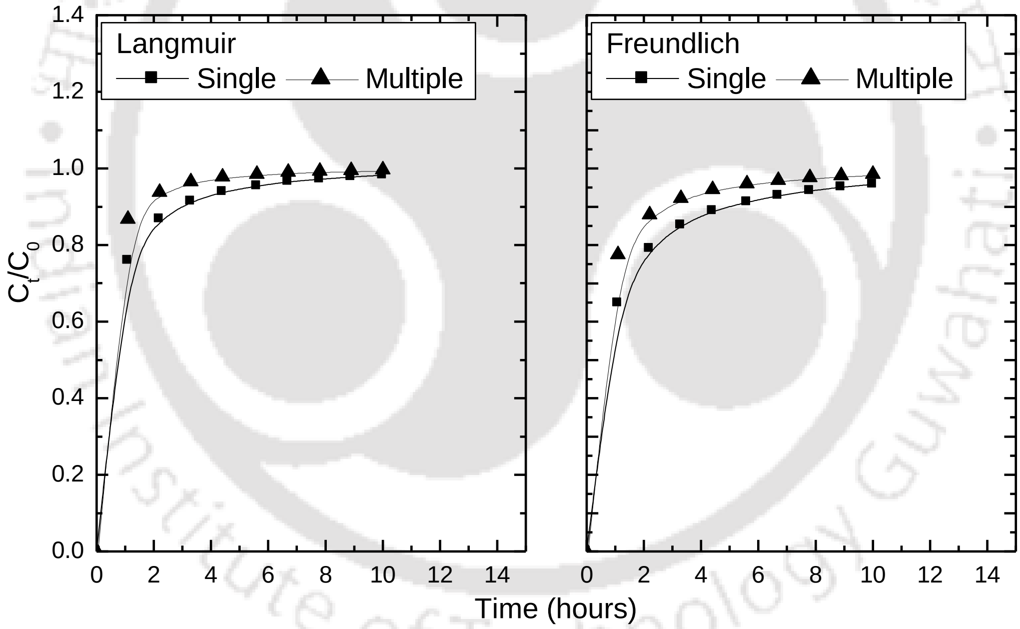


Fig. 7.8 Comparison of BTCs obtained for K^+ from single and multiple salt solution for different isotherms and C_e = 1000 mg/L

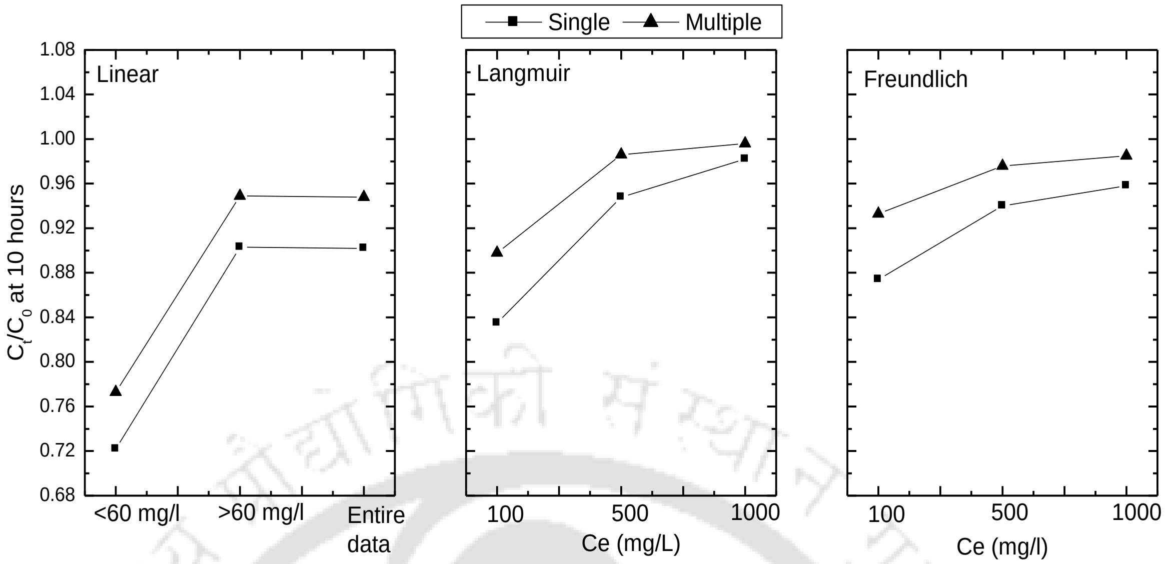


Fig. 7.9 Comparison of contaminant fate prediction at 10 hours for K^+ from single and multiple salt solution for different isotherms

7.3 Contaminant fate prediction of heavy metals

Contaminant fate prediction of copper is performed based on the soil-contaminant results of single, binary, tertiary and quaternary solution for three geomaterials Kao, RS and FAsh. The bulk density, porosity, dispersion coefficient and seepage velocity used for contaminant fate prediction, for the soil samples are listed in table 7.3 (Shafique et al. 2003; Shackelford and Glade 1997). In reality dispersion coefficient will vary for multiple solution as compared to single. Since the main aim of the study is to understand the sensitivity of the retention parameters as constant fate prediction, the parameter listed in table 7.3 is kept same for both single and multiple contaminant solution.

Single step input of the contaminant with initial normalized concentration (C_t/C_0) equal to one was considered, where C_t is the concentration at any time t and C_0 is the initial concentration. This section deals with the discussion of results corresponding to an advective-dispersive transport of copper through a saturated soil column of 2.5 cm in length and 2.5 cm in diameter. The contaminant solution is placed at the top of the column. The theoretical breakthrough curves (BTC) has been obtained for the isotherm results of Cu^{+2} reported in chapter 6. The same initial and boundary conditions, as discussed in the previous section, have been adopted. The main purpose of this study is to investigate the sensitivity of different non-linear isotherms obtained from the batch experiments (attributing to different retardation factors (R)) and single, multiple contaminant-soil interaction on contaminant fate prediction for heavy metal Cu^{+2}. For unambiguous analysis and comparison, all other modelling parameters of ADE such as dispersion coefficient, pore water velocity is kept constant. The values of retardation factor determined based on non-linear isotherm results for soil Kao, RS and FAsh corresponding to different equilibrium concentration (C_e) and different ion combination are listed in Table 7.4 to 7.9

Table 7.3 Transport Input parameters used in the study

Soils	Dispersion Coefficient	Seepage velocity (m/s)	Porosity	Density
Kao	$8.58*10^{-10}$	$9.6*10^{-8}$	0.461	1.4
RS	$5.61*10^{-9}$	$1.83*10^{-6}$	0.4	1.33
FAsh	$1.02*10^{-8}$	$3.55*10^{-5}$	0.38	1.38

Table7.4 Retardation values for Cu^{+2} for different isotherms obtained from single salt solution

Cu^{+2}						
C_e (mg/L	Kao		RS		FAsh	
	Freundlich	Langmuir	Freundlich	Langmuir	Freundlich	Langmuir
100	111.92	95.65	92.37	104.26	18.72	24.26
500	48.04	8.89	45.64	17.52	6.57	2.69
1000	33.51	3.21	33.79	6.39	4.38	1.46

Table 7.5 Retardation values for Cu^{+2} for different isotherms obtained from binary salt solution (Cu+Ni)

Cu^{+2} -Cu+Ni						
C_e (mg/L)	Kao		RS		FAsh	
	Freundlich	Langmuir	Freundlich	Langmuir	Freundlich	Langmuir
100	64.07	76.08	76.91	89.89	10.54	12.18
500	25.01	7.75	37.20	15.22	3.75	1.66
1000	16.84	2.92	27.32	5.64	2.61	1.17

Table 7.6 Retardation values for Cu^{+2} for different isotherms obtained from binary salt solution (Cu+Zn)

Cu^{+2} - Cu+Zn						
C_e (mg/L)	Kao		RS		FAsh	
	Freundlich	Langmuir	Freundlich	Langmuir	Freundlich	Langmuir
100	79.27	78.46	84.93	88.53	10.33	8.26
500	33.82	7.555	46.16	15.12	3.63	1.36
1000	23.57	2.842	35.58	5.62	2.52	1.09

Table 7.7 Retardation values for Cu^{+2} for different isotherms obtained from binary salt solution (Cu+Pb)

Cu^{+2} -Cu+Pb						
C_e (mg/L)	Kao		RS		FAsh	
	Freundlich	Langmuir	Freundlich	Langmuir	Freundlich	Langmuir
100	85.32	75.86	83.38	92.55	8.488	12.32
500	36.30	6.89	46.21	16.22	3.250	1.875
1000	25.26	2.63	35.90	6.02	2.340	1.241

Table 7.8 Retardation values for Cu^{+2} for different isotherms obtained from binary salt solution (Cu+Ni+Pb)

Cu^{+2} - Cu+Ni+Pb						
C_e (mg/L)	Kao		RS		FAsh	
	Freundlich	Langmuir	Freundlich	Langmuir	Freundlich	Langmuir
100	62.63	74.94	49.00	62.16	6.74	8.64
500	26.76	8.717	24.60	11.74	2.64	1.49
1000	18.69	3.264	18.38	4.60	1.96	1.13

Table 7.9 Retardation values for Cu^{+2} for different isotherms obtained from binary salt solution (Cu+Ni+Pb+Zn)

Cu-Cu+Ni+Pb+Zn						
C_e (mg/L)	Kao		RS		FAsh	
	Freundlich	Langmuir	Freundlich	Langmuir	Freundlich	Langmuir
100	39.63	53.79	42.43	54.29	5.74	7.75
500	16.94	6.51	21.97	12.38	2.33	1.43
1000	11.88	2.61	16.64	5.073	1.76	1.11

7.3.1 Sensitivity of isotherm results on Cu^{+2} fate prediction for Kaolinite (Kao)

Contaminant fate prediction of heavy metal Cu^{+2} based on the retention results of single and its combination with other heavy metals Ni^{+2}, Zn^{+2}, Pb^{+2} are studied for Kao. The values of retardation factors (R) obtained for different C_e as listed tables 7.4 to 7.9. The variability of retardation coefficient for Cu^{+2} obtained from single and multiple solution. The sequence of R values based on both isotherms are given below in the Eq. 7.12 to 7.17

R sequence obtained from Freundlich isotherm results

$$R_{Cu} > R_{(Cu+Pb)} > R_{(Cu+Zn)} > R_{(Cu+Ni)} > R_{Tertiary} > R_{Quaternary} \qquad (100\ mg/L) \qquad (7.12)$$

$$R_{Cu} > R_{(Cu+Pb)} > R_{(Cu+Zn)} > R_{Tertiary} > R_{(Cu+Ni)} > R_{Quaternary} \qquad (500\ mg/L) \qquad (7.13)$$

$$R_{Cu} \approx R_{(Cu+Pb)} \approx R_{(Cu+Zn)}\,) \approx R_{Tertiary} \approx R_{(Cu+Ni)} \approx R_{Quaternary} \qquad (1000\ mg/L) \qquad (7.14)$$

R sequence obtained from Langmuir isotherm results

$$R_{Cu} > R_{(Cu+Zn)} > R_{(Cu+Ni)} > R_{(Cu+Pb)} > R_{Tertiary} > R_{Quaternary} \qquad (100\ mg/L) \qquad (7.15)$$

$$R_{Cu} > R_{Tertiary} > R_{(Cu+Ni)} > R_{(Cu+Zn)} > R_{(Cu+Pb)} > R_{Quaternary} \qquad (500\ mg/L) \qquad (7.16)$$

$$R_{Tertiary} \approx R_{Cu} > R_{(Cu+Ni)} > R_{(Cu+Zn)} > R_{(Cu+Pb)} > R_{Quaternary} \qquad (1000\ mg/L) \qquad (7.17)$$

To have a better understanding of the influence of range of single and multiple contaminant solution on contaminant prediction, the R values corresponding to different range have been plotted as depicted in Fig. 7.10. It can be noted from the figure that the contaminant prediction is higher for single in most of the cases. The results are true for both Langmuir and Freundlich isotherm. Another important observation is that for non-linear isotherms, the difference in R for single and multiple contaminant solution, decreases as C_e increases. At low C_e for multiple contaminant solution, Langmuir isotherm gives more retardation than Freundlich in all the cases except Cu^{+2} in the presence of Pb^{+2} and vice versa for higher C_e. It must be specifically noted that the contaminant fate prediction based on single and multiple contaminants are different for both isotherm, especially binary one.

Figure 7.11 and 7.12 presents the breakthrough curves (BTCs) for the transport of Cu^{+2} single and Cu^{+2} in competitions for Freundlich and Langmuir isotherm respectively. From the figures, it can be noted that Cu^{+2} in single was strongly retarded in all the range of concentration for Freundlich isotherm model. For Langmuir isotherm, at C_e equal to 1000 mg/L even though the soil in single retained more but it is retarded less than the ones in tertiary system indicating its anomalous nature. The retardation follows the sequence $R_{100} > R_{500} > R_{1000}$. As shown in the figure 7.11 competition significantly reduced the retardation of Cu^{+2} in presence of tertiary and quaternary system but marginally affected Cu^{+2} transport in binary system (Pb^{+2} and Zn^{+2}). However, the presence of Ni^{+2} retarded Cu^{+2} less than expected leading to more migration. As depicted in Fig 7.12 for Langmuir isotherm tertiary system seems to retard the most. From the figures it can also be seen that the difference between the BTC curve evolution was less at higher C_e of 500 and 1000 mg/L. For Cu^{+2} concentration in competitive transport (Fig7.11), C_t/C_o of Cu^{+2} in tertiary system is less thus delaying its migration than Cu^{+2} single. Additionally, the BTC curve for the nonlinear Langmuir case also has similar observations. Thus the study indicated that even though the Langmuir and Freundlich retention model was fitted well to the batch retention experiments, these models cannot be regarded as flawless due to the inconsistent breakthrough predictions in some cases. Referring to Table 6.23a in chapter 6 it can be noted that for Kao Cu^{+2} in the presence of Ni^{+2} has the lowest K_F % difference (9.622) with respect to single solution, followed by Pb^{+2} (19.758%), Zn^{+2} (26.012%), tertiary system (40.94%) and quaternary (60.94%).Thus Ni^{+2} presence didn't influence the Cu^{+2} retention much. Based on it it can be presumed that among all these combination Cu^{+2} in Ni^{+2} presence will have less C_t/C_o value than all these combination and migrate later. But this presumption proved to be wrong as observed by its low R value and in Fig. 7.11 where Cu^{+2} in the presence of Ni^{+2} migrated rapidly than other binary system in lower range of C_e (100 mg/L) while at higher concentration it migrated far ahead of all the range of concentration. As can be seen from the table % N difference of Cu^{+2} in presence was the highest (12.41 %)compared to the rest of the multiple combination Pb^{+2} (1.71%), Zn^{+2} (1.28%), tertiary system (1.92%) and quaternary (3.85%). This gives an insight to the anomalous behavior of our predicted and simulated curve. It can be noted that shape of the isotherm curve curve has a significant influence on the retardation coefficient. The Freundlich parameter N also had a very sensitive role in the determination of retardation factor and hence predicting contaminant fate.

Thus the study brings forth that having a high K_F value doesn't guarantee the arrival of BTC curve at later time but it is entirely dependent on both the parameters (K_F and N). This also poses the question that whether retention isotherm curves which have different shapes can be compared at all. For Langmuir isotherm generally the Q_m factor which is the maximum retention capacity is given importance. Referring to Table 6.23b in chapter 6 it can be noted that the % difference in terms of increasing order is Pb^{+2} (18.58%), Zn^{+2} (18.62%), Ni^{+2} (22.74), tertiary system (25.87%) and quaternary system (47.11%). The K_L % percentage difference was positive in all cases except for Cu^{+2} in presence of Pb^{+2}(-5.79%). The sensitivities of the K_L parameter specially is reflected from fig 7.12 where the simulated trends Cu^{+2} in competition with Pb^{+2} migrated faster than other binary system for C_e 100mg/L and also both binary and tertiary at 500 and 1000mg/L conflicting our expected trend.

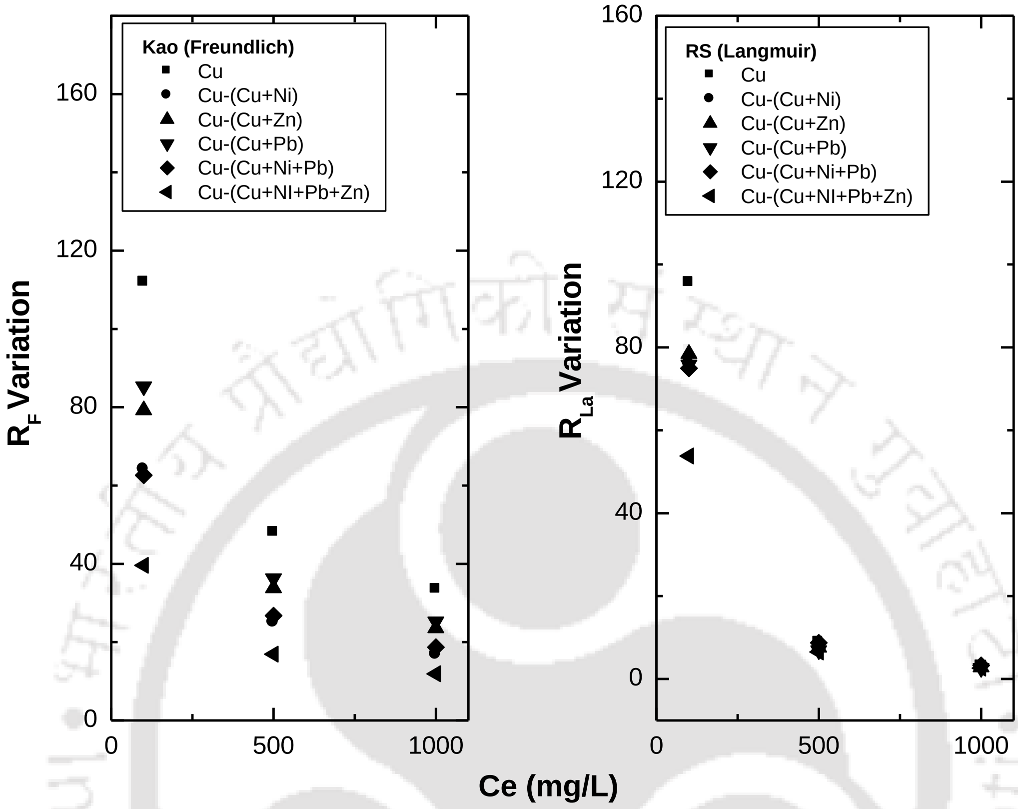


Fig. 7.10 Comparison of R corresponding to single and multiple contaminant solution

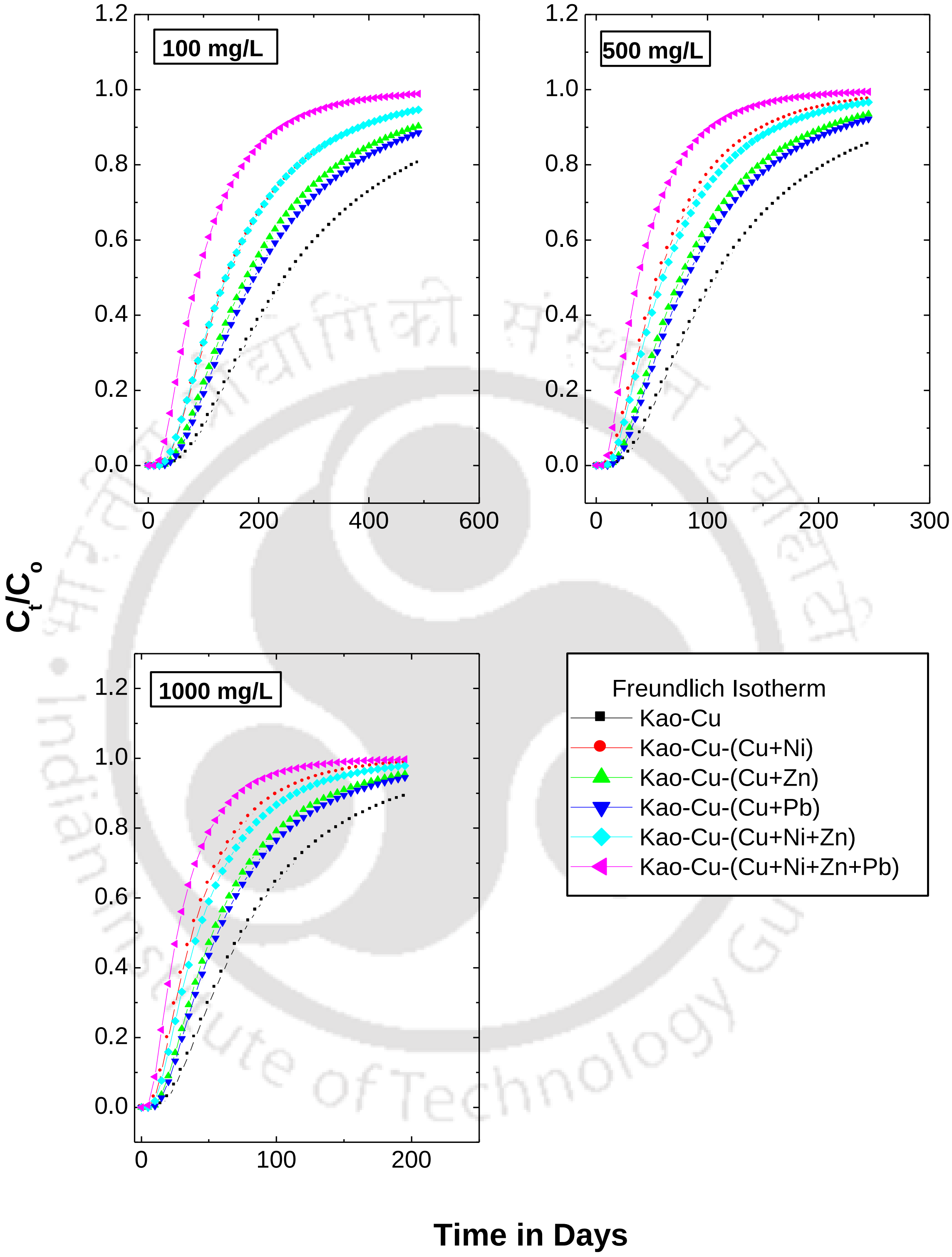


Fig 7.11 Comparison of BTCs obtained for Kao- Cu^{+2} interaction represented by Freundlich isotherms for single and multiple contaminant solution and C_e = 1000, 500 and 1000 mg/L

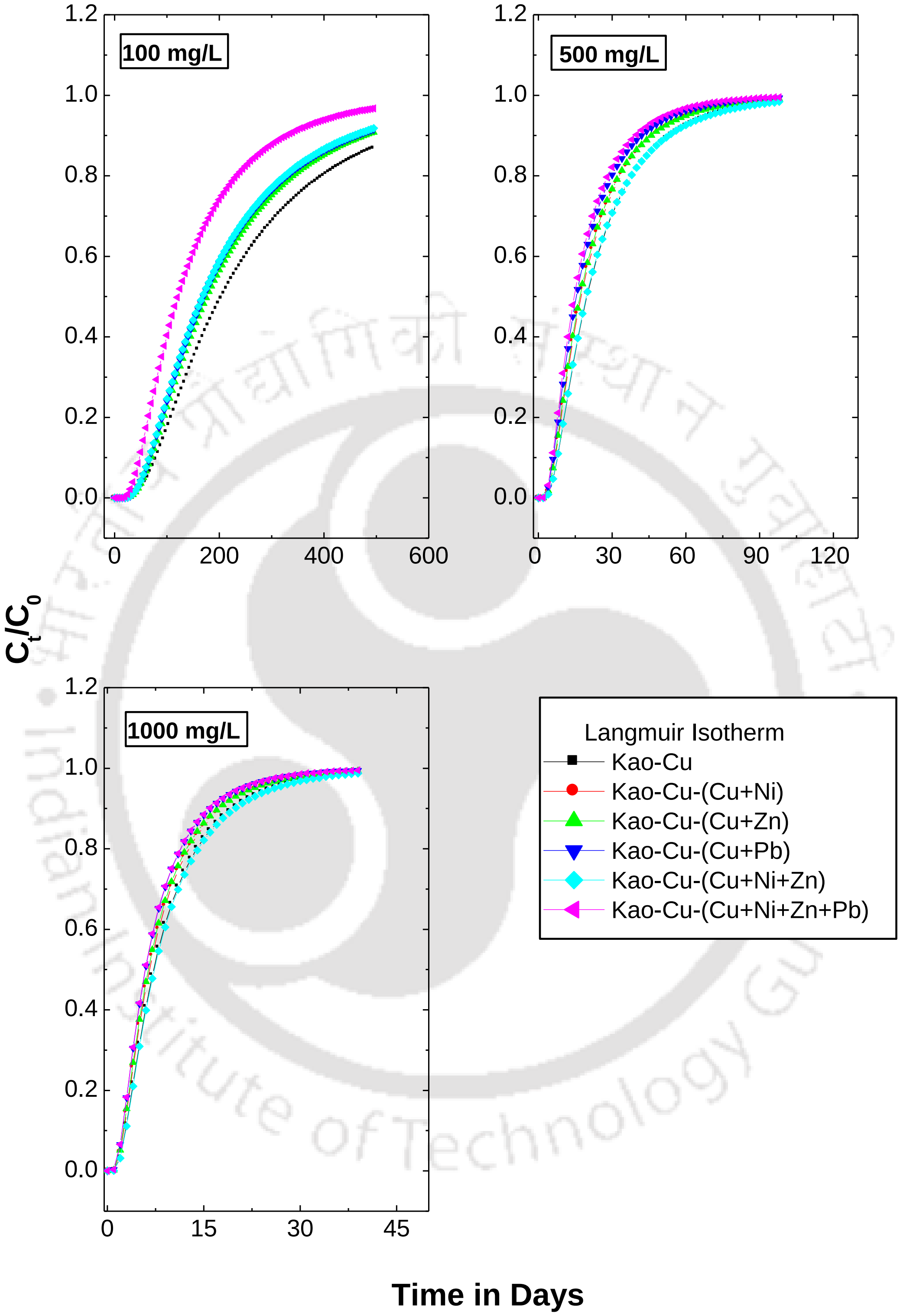


Fig 7.12 Comparison of BTCs obtained for Kao- Cu^{+2} interaction represented by Langmuir isotherms for single and multiple contaminant solution for and C_e = 1000, 500 and 1000 mg/L

7.3.2 Sensitivity of isothem results on Cu^{+2} fate prediction for Redsoil (RS)

Contaminant fate prediction of heavy metal Cu^{+2} based on the retention results of single and multiple solution Ni^{+2}, Zn^{+2}, Pb^{+2} are studied for RS. The values of retardation factors (R) obtained for different C_e corresponding to are listed in tables 7.5 to 7.10. The sequence of R values based on both isotherms are given below in Eq.7.18 to 7.23.

R sequence for Freundlich isotherm results

$R_{Cu} > R_{(Cu+Zn)} > R_{(Cu+Pb)} > R_{(Cu+Ni)} > R_{Tertiary} > R_{Quaternary}$ (100 mg/L) (7.18)

$R_{(Cu+Pb)} \approx R_{(Cu+Zn)} > R_{Cu} \approx R_{(Cu+Ni)} \approx R_{Tertiary} \approx R_{Quaternary}$ (500mg/L) (7.19)

$R_{(Cu+Pb)} \approx R_{(Cu+Zn)} \approx R_{Cu} \approx R_{(Cu+Ni)} \approx R_{Tertiary} \approx R_{Quaternary}$ (1000 mg/L) (7.20)

R sequence for Langmuir isotherm results

$R_{Cu} > R_{(Cu+Pb)} > R_{(Cu+Ni)} > R_{(Cu+Zn)} > R_{Tertiary} > R_{Quaternary}$ (100 mg/L) (7.21)

$R_{Cu} \approx R_{(Cu+Pb)} \approx R_{(Cu+Ni)} \approx R_{(Cu+Zn)} \approx R_{Quaternary} \approx R_{Tertiary}$ (500 mg/L) (7.22)

$R_{Cu} \approx R_{(Cu+Pb)} \approx R_{(Cu+Ni)} \approx R_{(Cu+Zn)} \approx R_{Quaternary} \approx R_{Tertiary}$ (1000 mg/L) (7.23)

Fig. 7.13 presents the R values for Freundlich and Langmuir isotherms for different C_e values. It can be noted from the figure that R value is higher for single in most of the cases. The results are true for both Langmuir and Freundlich isotherm. At low C_e (100mg/L) Langmuir isotherm gives more retardation than Freundlich in all the cases (binary, tertiary and quaternary) and vice versa for higher C_e. It must be specifically noted that the contaminant fate prediction based on different isotherms are quite different for both single and multiple contaminants.

From the BTC presented in Fig 7.14 it was observed that for Freundlich isotherm for equilibrium concentration 500 and 1000mg/L Cu in presence of Zn^{+2} and Pb^{+2} has lower C_t/C_o value for a particular time which reflected the R sequence. This findings warrants the significance of range of concentration and how trends gets reversed with the range of concentration. From the Fig 7.14, it is clear that Cu^{+2} in quaternary and tertiary system migrated faster because of its low retardation factor as evident in table 7.9 and 7.10. This indicates that competition significantly reduced the retardation of Cu^{+2}. Amongst the binary system Cu^{+2} in presence of Pb^{+2} retarded the most followed by Zn^{+2} and Ni^{+2}.

From Fig 7.15 it can be well demonstrated that BTC for Cu^{+2} in single evolved later than the rest of the combination. For binary system Cu^{+2} in the presence of Pb^{+2} evolved later followed by Ni^{+2} and Zn^{+2}. For 100 mg/L, tertiary system retarded more than that of quaternary but at higher concentration the trends got reversed owing to the high retardation value as seen in Table 7.9 and 7.10. To understand this anomalies better table 6.23a, 6.23b in chapter 6 is referred. It can be noted that for RS, Cu^{+2} in the presence of Ni^{+2} has the lowest % reduction of K_F (8%) with respect to single Cu^{+2} followed by Zn^{+2} (36.78%), Pb^{+2} (43.41%),tertiary system (48.52%) and quaternary (66.43%). This indicates the relative order of influence of these heavy metal combinations on Cu^{+2}. From the above sequence it is clear that Cu^{+2} in competition with Ni^{+2} did not have significant decrease in its retention capacity compared to this indicate that among all these ions Cu-(Cu+Ni) will migrate later than all these combination. But interestingly the simulated curves did not reflect the expected trends based on batch test results and Cu^{+2} in the presence of Ni^{+2} migrated sooner than the other binary system in all the range of concentration. This contradicts the understanding that greater the K_F value, the retardation is more. Analysis of % reduction of N parameter of Freundlich isotherm (table 6.23a) portrayed that apart from Ni^{+2} having a % reduction of 2.34 and the rest of the multiple combination has negative % reduction with respect to single Cu^{+2} {Pb^{+2} (-12.973%), Zn^{+2} (-9.18%), tertiary system (-0.72%) and quaternary (-17.83%)}. This -ve % reduction indicates that N was high when in competition compared to that of single. This gives an insight to the anomalous behavior of the predicted and simulated curve.

The % reduction of Langmuir Q_m values in terms of increasing order is Pb^{+2} (9.925%), Ni^{+2} (13.709%), Zn^{+2} (14.77%), tertiary system (38.522%) and quaternary system (41.21%). The K_L % reduction was positive in all cases except for Cu^{+2} in presence of Zn^{+2} (-1.67%). As can be noted from Fig 7.14 for equilibrium concentration C_e 500 mg/L and 1000mg/L, for quaternary system the amount of Ct/Co is less than that of tertiary which might be related to the difference of K_L value. Thus it can be seen that in spite of the batch test results there can be anomalies in the R value value and fate prediction. Thus the study highlights that having a high K_F and Q_m value doesn't guarantee the migration late; but it is sensitive to both the parameters (K_F and N). It can be noted that shape of the isotherm curve has a significant influence on the retardation coefficient and raises the issue whether retention curves, which has different shapes can be compared at all. This observation is same as that for Kao. The reason is both isotherm parameters are important for R determination. Hence, such anomalies can be expected.

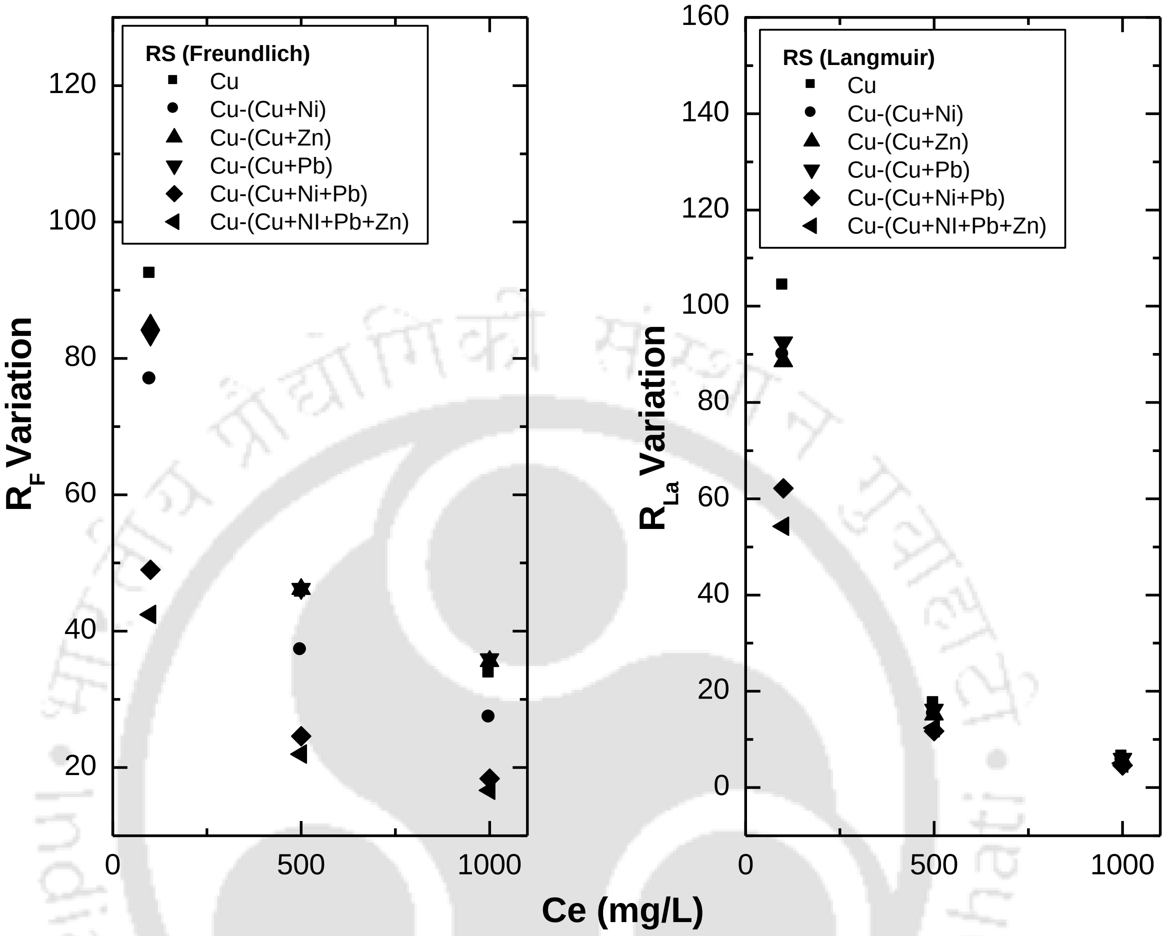


Fig. 7.13 Comparison of R values for different range of equilibrium concentration from single and multiple contaminant solution for different isotherms for RS

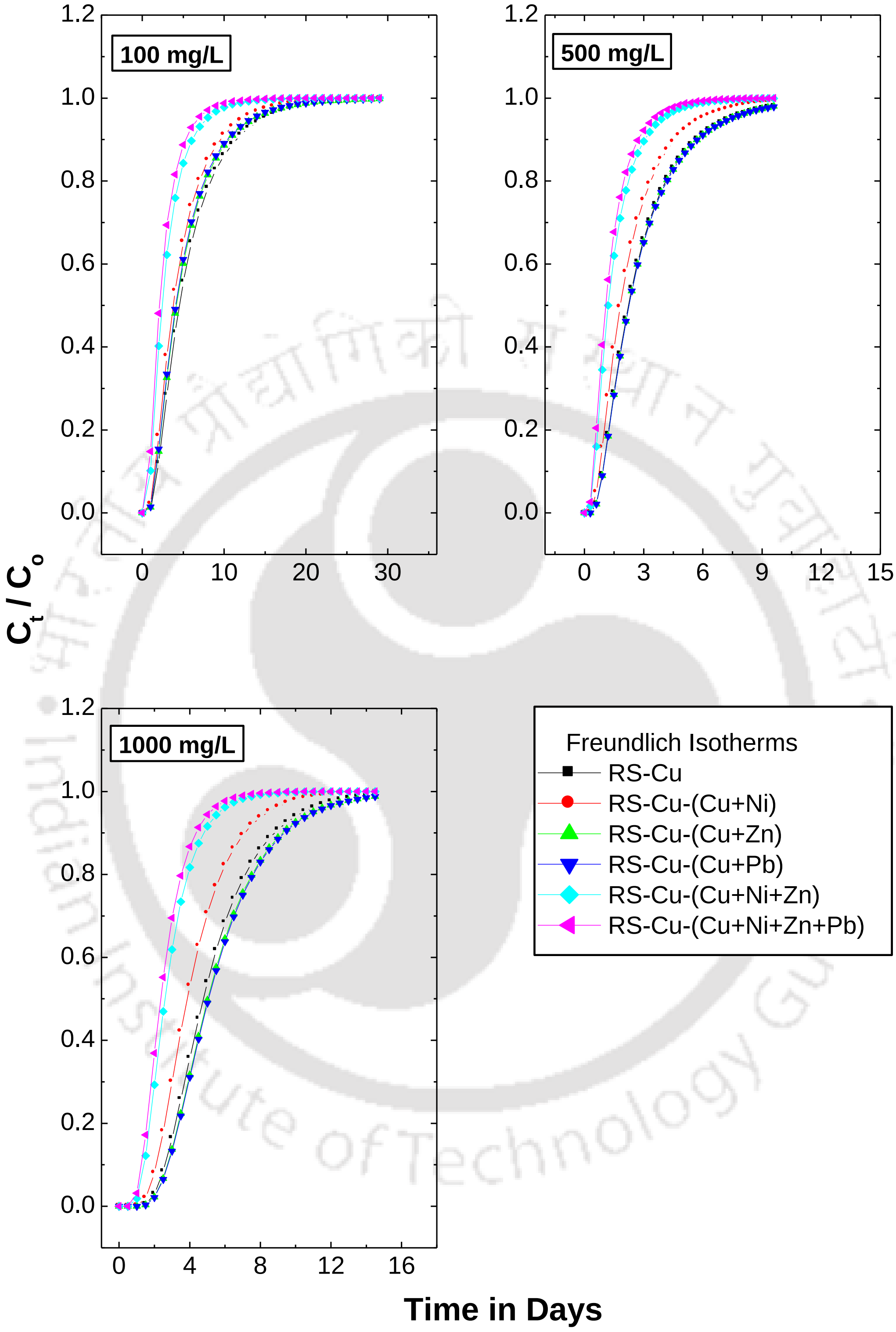


Fig.7.14 Comparison of BTCs obtained for RS- Cu^{+2} interaction represented by Freundlich isotherms for single and multiple contaminant solution and C_e = 1000, 500 and 1000 mg/L

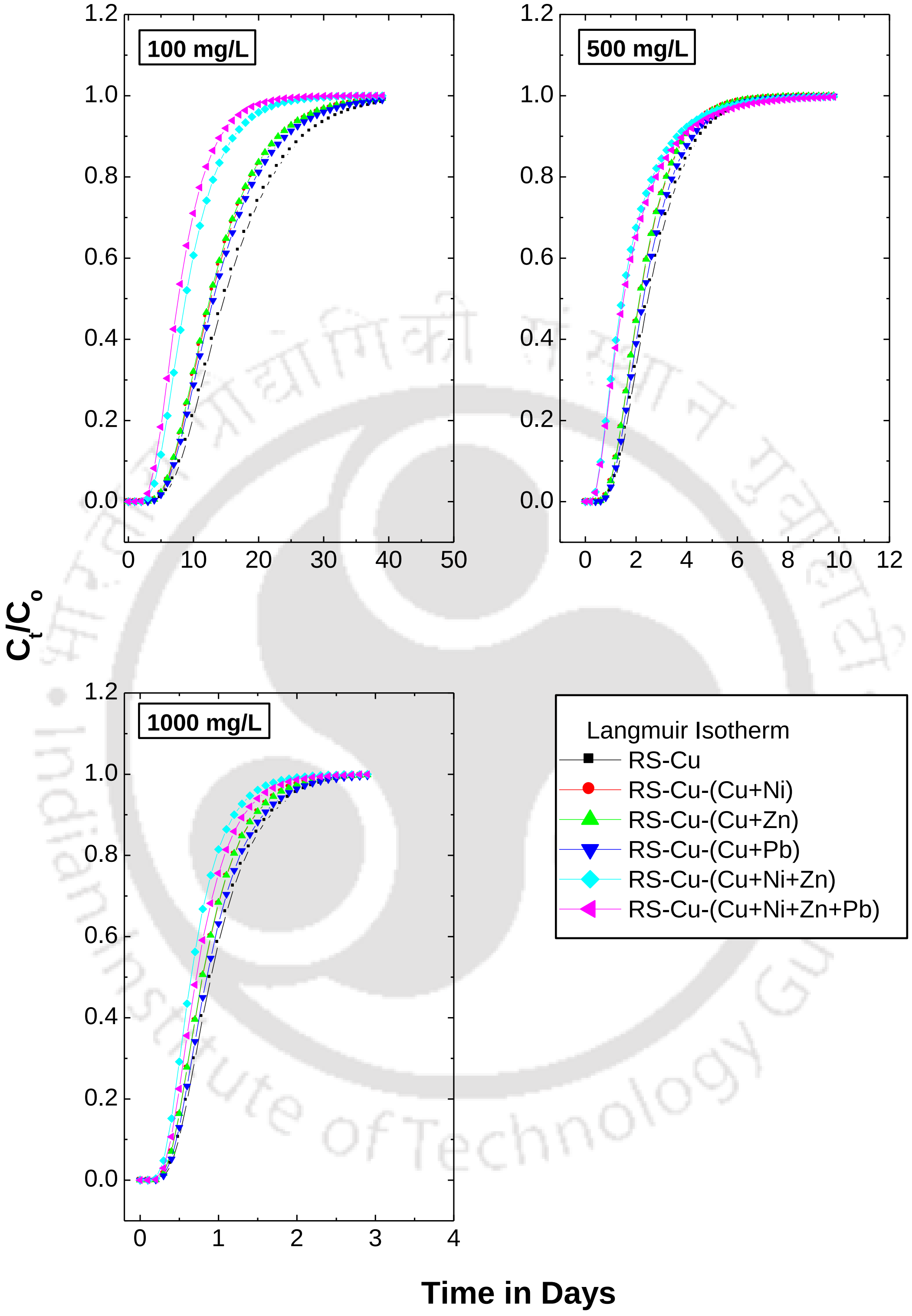


Fig.7.15 Comparison of BTCs obtained for RS-Cu^{+2} interaction represented by Langmuir isotherms for single and multiple contaminant solution and C_e = 1000, 500 and 1000 mg/L

7.3.3 Sensitivity of isothem results on Cu^{+2} fate prediction for Flyash (FAsh)

Contaminant fate prediction based on the retention results of single and multiple contaminant solution Ni^{+2}, Zn^{+2}, Pb^{+2} are studied for FAsh. The values of retardation factors (R) for different C_e as listed in tables 7.5 to 7.10 respectively. The variability of retardation coefficient for Cu^{+2} obtained from single and multiple solution are given below in 7.24 to 7.29.

R sequence obtained from Fruendlich isotherm results

$$R_{Cu} > R_{(Cu+Ni)} > R_{(Cu+Zn)} > R_{(Cu+Pb)} > R_{Tertiary} > R_{Quaternary} \quad (100\ mg/L) \qquad (7.24)$$

$$R_{Cu} > R_{(Cu+Ni)} > R_{(Cu+Zn)} > R_{(Cu+Pb)} > R_{Tertiary} > R_{Quaternary} \quad (500\ mg/L) \qquad (7.25)$$

$$R_{Cu} > R_{(Cu+Ni)} > R_{(Cu+Zn)} > R_{(Cu+Pb)} > R_{Tertiary} > R_{Quaternary} \quad (1000\ mg/L) \qquad (7.26)$$

R sequence obtained from Langmuir isotherm results

$$R_{Cu} > R_{(Cu+Pb)} > R_{(Cu+Ni)} > R_{Tertiary} \approx R_{(Cu+Zn)} > R_{Quaternary} \quad (100\ mg/L) \qquad (7.27)$$

$$R_{Cu} > R_{(Cu+Pb)} > R_{(Cu+Ni)} > R_{Tertiary} \approx R_{Quaternary} \approx R_{(Cu+Zn)} \quad (500\ mg/L) \qquad (7.28)$$

$$R_{Cu} > R_{(Cu+Pb)} > R_{(Cu+Ni)} \approx R_{Tertiary} \approx R_{Quaternary} \approx R_{(Cu+Zn)} \quad (1000\ mg/L) \qquad (7.29)$$

The R values corresponding to different range for FAsh have been plotted as depicted in Fig. 7.16. It can be noted from the figure that the contaminant prediction is higher for single in most of the cases. The results are true for both Langmuir and Freundlich isotherm. Another important observation is that for non linear isotherms, the difference in R for single and multiple contaminant solution decreases as C_e increases. At low C_e (100mg/L) for both single and multiple contaminant solution Langmuir isotherm gives more retardation than Freundlich in all the cases (binary, tertiary and quaternary) and vice versa for higher C_e.

It can be seen from Fig 7.17 that for Freundlich isotherm model, Cu^{+2} single retarded the most followed by binary, tertiary and quarternary. For binary Cu^{+2} in the presence of nickel retarded the most followed by Zn^{+2} and Pb^{+2}.These trends get reversed when using Langmuir model and the trends of the BTC followed the trends of the R sequence of Langmuir isotherms. Referring to tables 6.23a and 6.23b it can be noted that the % reduction with respect to single Cu^{+2} for Freundlich K_F was the highest for quaternary (50.331%) followed by tertiary (47.179%) and binary{Pb^{+2}(46.619%), Ni^{+2} (15.357%), Zn^{+2} (4.942%)}, which clear indicates how competition reduced the retention and increased the transport of Cu^{+2} in FAsh. The % difference for N indicated its decrease for multiple solution. This trend could be represented well in the BTC except for Cu^{+2} in presence of Zn^{+2} which migrated ahead of Ni^{+2}. This is because of the % reduction of N of Zn^{+2} being more than Ni^{+2}. For

Langmuir modelling the Q_m % reduction of quaternary was the highest (67.84%) followed by tertiary (63.034%) and binary (Pb^{+2} (53.29%), Zn^{+2} (40.954%) and Ni^{+2} (39.195%) whereas the K_L % reduction was negative in all cases except for Cu^{+2} in presence of Pb^{+2}. For Zn^{+2} the % reduction was (-207.619 %) which means that K_L was quite high when Cu^{+2} was in multiple solution which might also explain the unexpected trend that it migrated faster than all other combination at higher equilibrium concentration.

The study highlights that merely having a high Qm and K_F value does not mean that the soil has high retention capacity when fate prediction of these ions are conducted. It was observed that fate prediction is highly sensitive to N and K_L parameters of the Freundlich and Langmuir isotherms in addition to K_F and Q_m. While studying different ions in combination there are cases where isotherm parameters R, simulated BTC do not portray the trend that justifies experimental observation. This is mainly due to the mathematical quantification of isotherm parameter. Further studies are required to outline the use of isotherms while comparing different cases of retention. It is felt that the shape of isotherms need to be considered while doing such comparisons.

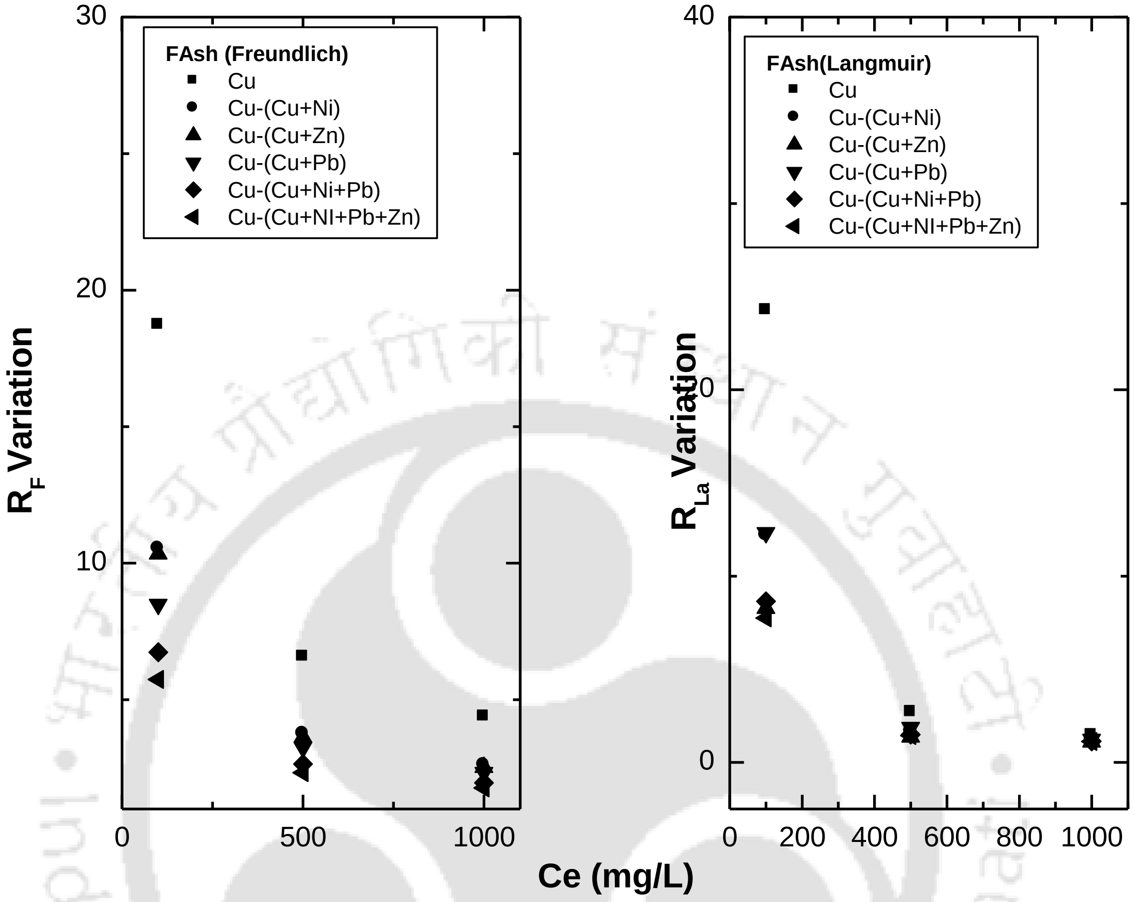


Fig. 7.16 Comparison of R values of FAsh corresponding to single and multiple contaminant solution for corresponding to single and multiple contaminant solution

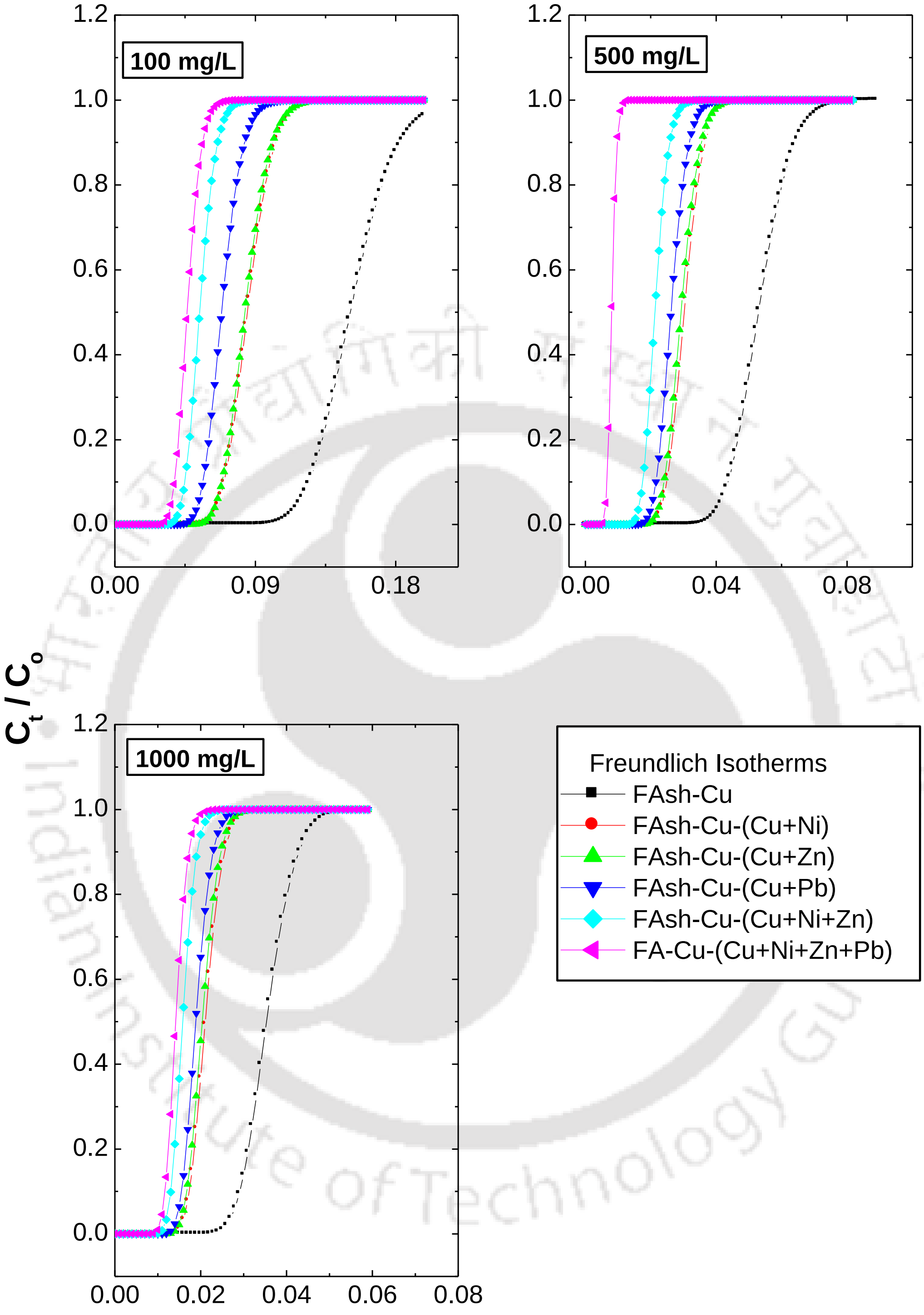


Fig.7.17 Comparison of BTCs obtained for FAsh- Cu^{+2} interaction represented by Langmuir isotherms for single and multiple contaminant solution and C_e = 1000, 500 and 1000 mg/L

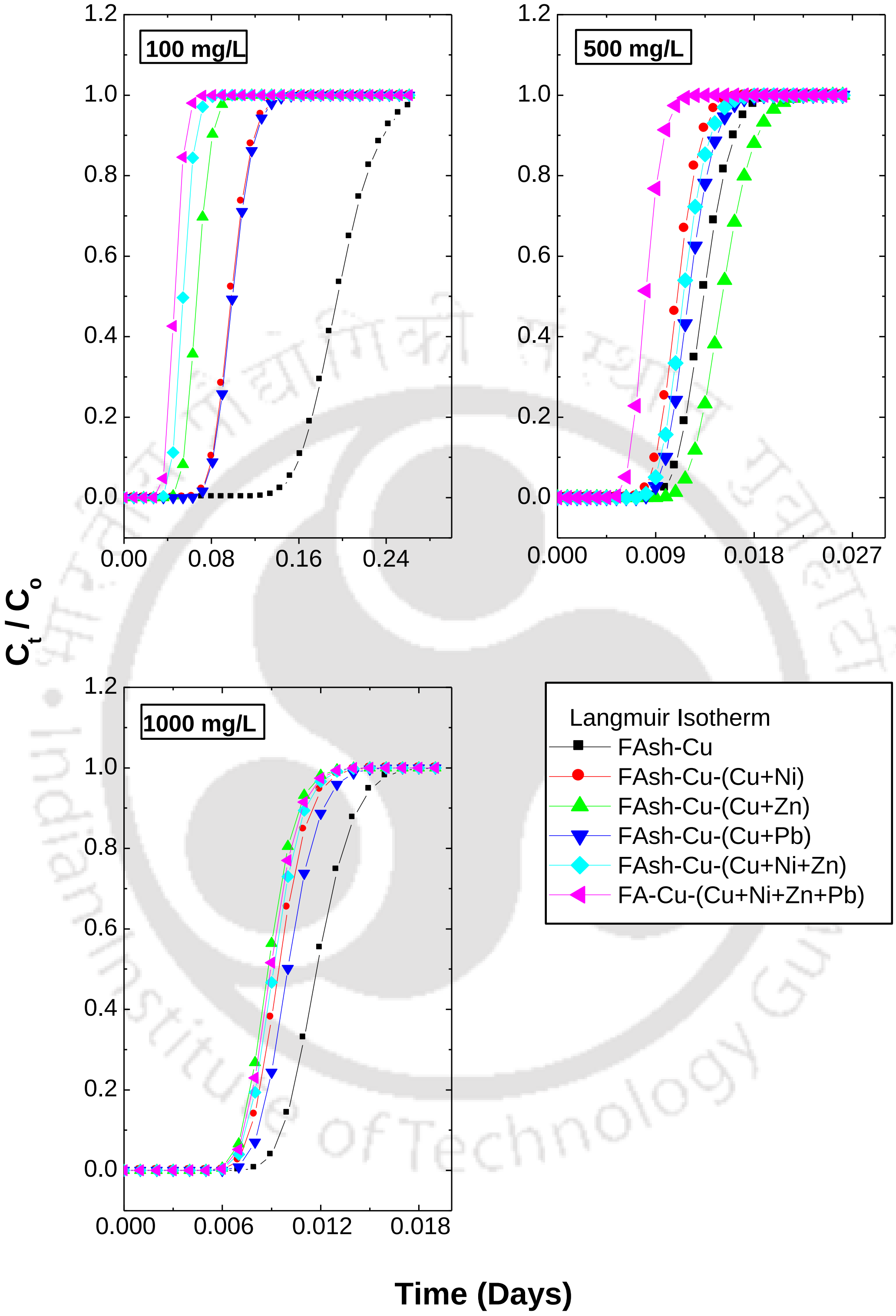


Fig 7.18 Comparison of BTCs obtained for FAsh-Cu^{+2} interaction represented by Langmuir isotherms for single and multiple contaminant solution and C$_e$ = 1000, 500 and 1000 mg/L

7.4 Summary

This chapter deals with an investigation on the influence of soil-multiple contaminant interaction results on contaminant fate prediction. The summary of observations from this chapter is as follows:

- The study indicates that linear retention isotherms are significantly influenced by the range of equilibrium concentration (C_e) for single and multiple contaminant interaction. Therefore, proper discretion should be used when using retardation factors obtained from linear retention isotherms for contaminant fate prediction.
- Contaminant fate prediction based on two non-linear isotherms was different for both single and multiple contaminants interaction**.** This finding was consistent for all the three soils. In general, it was noted that retardation factor obtained from Freundlich (R_F) isotherm predicts more than Langmuir (R_{La}). This observation is more explicit at the higher range of equilibrium concentration. However at lower C_e (100mg/L) Langmuir isotherm gave slightly higher value R_{La} or comparable to $R_{F.}$
- Fate prediction based on retardation value obtained from retention isotherms exibited some anamolous trends. In some cases, it was observed that the isotherm parameter R simulated BTC gives unexpected results that do not portray to the experimental findings. This is mainly because retardation coefficient R is highly sensitive to the combination of isotherm parameters used for its determination. Due to this, the contaminant fate prediction for certain cases was misleading.

Chapter 8

Conclusions and Future Scope of Research

8.1. Conclusions

This study deals with the multiple contaminant-soil interaction of common ions and heavy metal ions with seven different soils. Following are the important conclusions observed from the research work.

1. The study at first investigates individual (single) contaminant-soil interaction, which is the basis for understanding multiple contaminant interactions. Common ion like Na^+ that are abundantly present in soils exhibited desorption in majority of the soils considered in this study. Therefore, Na^+ ions should not be used as a sorbent for assessing and comparing soil-contaminant interaction. The other common ions such as K^+ and $NH4^+$ had undergone normal sorption reaction. For majority of the soils, the sorption of single heavy metals followed the sequence $Pb^{+2} > Cu^{+2} > Zn^{+2} > Ni^{+2}$.
2. The study also brings to light the sorption ability of retaining heavy metals by FAsh which is generally considered to be an inert material. Addition of these flyash with bentonite in place of sand will not only increase the strength and reduce the shrinkage behavior of bentonite but also at the same time help in sorbing heavy metals than the inert sand. This will be advantageous from the environmental point of view too.
3. It can be highlighted from the present study that range of concentration has significant effect on single and multiple contaminant sorption in soils. Therefore, it is ideal to characterize soil-contaminant interaction with prior knowledge of the range of concentration that would exist in real life situation. The choice of sorption isotherms would depend upon the range of concentration adopted. Simple linear isotherms are appropriate only for small range of concentration. The study demonstrates that wrong choice of linear or non-linear isotherms can result in gross estimation while characterizing soil-contaminant interactions.
4. The study reveals that sorption decrease in the sequence single > binary > tertiary > quaternary ion combination for heavy metals due to competitive sorption. For some soils, the decrease in sorption from multiple contaminant solution was marginal for Ni^{2+}.
5. The study states that for soils, metal sorption cannot be solely predicted by any given affinity selectivity models. For example; if metal sorption was entirely based on electronegativity the sequence would have been $Cu^{+2} > Ni^{+2} > Pb^{+2} > Zn^{+2}$. Metal sorption

in this study was not based either on hydrated radius where the sequence would be Pb^{+2} > Ni^{+2} > Cu^{+2} > Zn^{+2}. The study reiterates the fact that soil properties and environmental factors also influence single and multiple contaminant sorption. In addition, the ion affinity from single and multiple contaminant solution is not consistent for all soils.

6. The study investigates the appropriateness of Freundlich and Langmuir non-linear isotherm models for comparing the soil sorption results from single and multiple contaminant solution. From the analysis of the isotherm results, it can be noted that in certain cases the outcome predicted by both the isotherms are not same. This difference in prediction between the two was more prominent when the compared experimental data exhibited different curvature.
7. The limitation of isotherm models for comparing multiple contaminant sorption has been demonstrated based on the systematic comparisons performed in this study. Even though the experimental observation followed the expected trend in multiple contaminant sorption, the same was not captured in the similar lines by mathematical isotherm quantification. This indicates that the popular non-linear Freundlich and Langmuir isotherm models may fail to represent certain cases of soil-contaminant interaction reaction. This is mainly due to the empirical nature of the equation and the lack of physical significance of isotherm equation parameters.
8. The relationship of Freundlich and Langmuir non-linear isotherm parameters with specific surface area (SSA) and cation Exchange Capacity (CEC) has been investigated based on the results of both single and multiple contaminant sorptions. It is noted that a meaningful correlation was obtained only for heavy metal sorption.
9. It is observed that the contaminant fate prediction based on different isotherms is quite different for both single and multiple contaminants. The fate prediction was influenced by the choice of equilibrium concentration also. This variation in fate prediction is due to the differences in retardation coefficient (outcome of soil-contaminant interaction), which is the focus of this study.
10. The range of concentration selected for sorption study would considerably influence retardation coefficient determination and fate prediction.
11. The retardation coefficient is highly sensitive to the combination of isotherm parameters used for its determination. In some cases, this resulted in unexpected trends of retardation coefficient that are contrary to the experimental findings. Due to this, the contaminant fate prediction for certain cases was misleading, which is fully attributed to the empirical nature of isotherm parameters.

8.2. Future Scope of Research

Following are the future scope of research where further investigations need to be carried out.

- **Limitations of isotherms:** The limitation of isotherms while comparing multiple contaminant sorption on soils was highlighted in the present study. Modification of mathematical quantification of soil sorption is required for unambiguous comparisons of different cases.
- **Validations with the column test:** The retardation values obtained from batch test needs to be compared with column study for multiple contaminants.
- **Advective-dispersive transport of multiple contaminants:** Determination of transport parameters such as dispersion coefficient for multiple contaminant migration.
- **Multiple contaminant diffusion:** The batch test does not represent the ion-interaction occurring in unsaturated soils. A systematic study on multiple contaminant diffusion is required where the advection is negligible.

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