Liquid Membrane based Technology for the Separation of Toxic Heavy Metals from Industrial Effluents

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Liquid Membrane based Technology for the Separation of Toxic Heavy Metals from Industrial Effluents

Thesis

Submitted in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

by

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Dedication

To My Family

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CERTIFICATE

It is certified that the work contained in the thesis entitled "**Liquid Membrane based Technology for the Separation of Toxic Heavy Metals from Industrial Effluents"** by **Kamal Kumar Bhatluri** has been carried out under our supervision and that this work has not been submitted elsewhere for a degree.

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(Kamal Kumar Bhatluri)

Abstract

Liquid membrane (LM) technology has drawn attention of the research community since the early '90s and it has increased manifold in recent years. This thesis aims at exploring the efficacy of LM technology for the separation and pre-concentration of Cd(II) and Pb(II) from their aqueous solutions. A suitable LM that can extract the said solutes is identified through equilibrium study. Experimentation with various solvents and carrier agents reveal that the coconut oil-Aliquat 336 and coconut oil-D2EHPA are two favorable combinations for separation of the cadmium (II) and lead (II). The performances of various LM based processes are investigated. The processes include the techniques based on Bulk Liquid Membrane (BLM), Flat Sheet-Supported Liquid Membrane (FS-SLM) and FS-SLM assisted simultaneous precipitation of lead (II) and cadmium (II) in stripping chamber and also the electro-deposition of target metals on the cathode plate placed in the stripping chamber.

The components of LM *i.e.* the solvent and the carrier were selected in two phase equilibrium studies. The distribution coefficient (*D*) of heavy metals between the membrane phase and the aqueous feed phase provides the heavy metals extraction feasibility by the membrane phase. The stripping agents are selected based on their capacity for stripping the metals and recovery of metals in different ways *i.e.* precipitation and electro-deposition. The various physico-chemical parameters like pH of aqueous solutions, concentration of extractant in the organic solution, initial concentration of the feed solution, experimental temperature *etc*. were primarily evaluated in two phase equilibrium studies. The optimum parameters obtained in two phase equilibrium studies were later verified and improved in three phase transportation studies. The three phase transportation studies involve the diffusion step in between extraction and re-extraction or stripping of the heavy metals at the respective interfaces of the LM.

This doctoral project aims at studying simultaneous extraction and recovery of heavy metals using LM techniques. After the initial investigation on the merits of LM based techniques to separate the cadmium (II) and lead (II) in two phase equilibrium study and simplest BLM configuration, the heart of the study was involved FS-SLM configuration. The extraction and recovery of cadmium (II) through BLM configuration were found to be 72% and 64%, respectively. Further experimentations through BLM were conducted for transportation of lead (II) with the same set of operating parameters. Both the extraction (82%) and recovery (77%) are found comparatively higher for lead (II) as compared to that of cadmium (II). Two objectives were fixed *i.e.* recovery of Cd(II) and Pb(II) as solid waste and conversion of heavy metals into value-added product. The methodologies for extraction and diffusion processes through FS-SLM remain the same primarily. Transportation of cadmium (II) and lead (II) were accomplished in FS-SLM based simultaneous separation and electro-deposition prior to its recovery as precipitation and electroplated product. Accordingly the stripping agent and the conditions like pH of stripping phase were maintained. The chelating characteristics of $Na_2 - EDTA$ was exploited as it was selected as stripping agent and it re-extracts metal ions from the metal-carrier complex at the membrane/strip interface and forms another complex metal-EDTA in the stripping phase. The optimum process conditions for the transportation of Cd(II) were found as follows: 0.5% (v/v) Aliquat 336 as carrier agent, 0.015 M Na_2-EDTA as stripping agent, pH of 6.5 in the feed phase. The extraction and recovery were found as 78.77% and 67.14% for Cd(II) and 84.23% and 77.73% respectively for Pb(II). Later Na_2CO_3 was used as precipitating agent as well as stripping agent and aqueous solution of it was used as stripping phase that recovers the Pb(II) and Cd(II) as solid precipitate in the stripping solution. The optimal operating conditions for FS-SLM studies were found as: pH of feed phase = 5, concentration of carrier (D2EHPA) = 4% (v/v), concentration of strip phase = 0.2 M Na_2CO_3. The permeability and flux values of single

metal (in pure form) transport were found as 12.16×10^{-4} m/s and 6.08×10^{-8} kg/m^2.s for Cd(II) and 15.20×10^{-4} m/s and 7.60×10^{-8} kg/m^2.s respectively for Pb(II). The total permeability as well as total flux values for various ratios of metals indicated that the presence of second metal reduces the transportation as compared to the pure metal. Both the overall permeability and the flux were minimum for the case of 1:1 ratio of the Cd(II) and Pb(II) *i.e.* when transportation of one metal is maximum affected by the presence of the maximum amount of the other. With decreasing amount of the second metal, both the permeability and flux increased to achieve the value of distinct pure metal. Recovered Cd(II) and Pb(II) was converted to value-added product in the stripping phase by changing the pH condition of stripping phase with the addition of HNO_3 and putting a electroplating facilities in the stripping chamber. At the optimum condition, *i.e.* pH of 4, electric potential of 2.5 V and area of cathode plate of 16.20 cm^2, the deposition of cadmium (II) was found 72% as compared to 88% of lead (II). Separation efficiency was improved by increasing the driving force to mass transfer in both the cases *i.e*. precipitation and electroplating methods.

Keywords: Bulk liquid membrane (BLM), Supported liquid membrane (SLM), Liquid membrane (LM), Cadmium (II), Lead (II), Aliquat 336, D2EHPA, Vegetable oil, Metal-EDTA complexation, Metal precipitations, Electro-deposition.

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List of nomenclature

D	:	Diffusivity (cm^2/s)
k	:	Boltzmann constant (J/K)
η	:	Viscosity of the organic phase (cP)
T	:	Absolute temperature (K)
r	:	Molecular radius (cm)
V_p	:	Volume fraction of the polymeric framework
ε	:	Porosity of the support membrane
μ_T	:	Viscosity (Pa.s) of vegetable oils at temperature T
μ_0	:	Viscosity at 0 ^oC
m	:	Slope of the Equation 2.1
ΔT	:	Temperature difference (^oC)
$C_{f_{in}}$	:	Initial concentration in feed phase (ppm)
C_f	:	Final concentration in feed phase (ppm)
$C_{S_{in}}$	:	Initial concentration in stripping phase (ppm)
C_s	:	Final concentration in stripping phase (ppm)
V_F	:	Volume of feed phase (mL)
V_{Org}	:	Volume of organic phase (mL)
V_S	:	Volume of stripping phase (mL)
t	:	Experiment time (h)
T	:	Temperature (^oC)
Aq	:	Aqueous solution of feed and stripping phases
Org	:	Organic phase
pH_F	:	pH value of feed solution
pH_S	:	pH value of stripping solution

List of abbreviations

LM	:	Liquid Membrane
BLM	:	Bulk Liquid Membrane
SLM	:	Supported Liquid Membrane
FESLM	:	Flat Sheet Supported Liquid Membrane
ELM	:	Emulsion Liquid Membrane
ML	:	Membrane Liquid
Na_2-EDTA	:	Disodium-ethelenediaminetetraacetate
DMOA	:	*N*,*N*-Dimethyloctylamine
Aliquat 336	:	*N*-Methyl-*N*,*N*,*N*-trioctylammonium chloride
TOA	:	Trioctylamine
TBP	:	Tributyl phosphate
D2EHPA	:	Di-(2-ethylhexyl) phosphoric acid
AAS	:	Atomic Absorption Spectrometer
SEM	:	Scanning Electron Microscope
EDX	:	Electron Dispersive X-ray
FESEM	:	Field Emission Scanning Electron Microscope
PVDF	:	Polyvinylidenefluoride

CHAPTER-I

Introduction and Literature Review

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Introduction and Literature Review

This chapter presents a brief discussion on the background information and the purpose of the research. The literature review on the sources of heavy metals, viz. cadmium (II) and lead (II), from the industrial wastewater and their influences on environment are discussed in details. Various physico-chemical methods for the separation of heavy metals from wastewater are discussed along with their advantages and limitations. The salient aspects and highlights of the LM technology and its applications, features and classifications along with the merits and demerits are discussed in details. The literature review explains the present context of LM based separation process and its uniqueness along with scope of application for separation of Cd(II) and Pb(II). The role of vegetable oil (coconut oil) as green solvent in liquid membrane is discussed in this chapter. Finally, the importance and objectives of the thesis are highlighted.

1. Introduction

The growing environmental concern all over the world obligates the chemical industries to minimize the discharge of effluents (wastewater) that contain various pollutants, especially heavy metals (Cd, Hg, Pb, Ni, As and Cr, *etc*.). Heavy metals are hazardous to environment and living organism [1, 2]. Moreover, they are not biodegradable. The toxicity of heavy metals cause several health problems to living organisms such as reduction of hemoglobin and oxygen transport to all tissues, neural, renal endocrine and hepatic effects [3-5]. The World Health Organization (WHO) has specified the allowable limit of cadmium (II) and lead (II) concentrations in drinking water to be 3 ppb and 10 ppb respectively [6]. Many industries such

as pulp and paper, batteries, mining, textile, glass and ceramics, paints and pigments, chloro-alkali, petrochemicals and refineries, fertilizers and metal finishing *etc.* discharge cadmium (II) and lead (II) in varied proportions as their effluent into the environment. Hence, it is important that they should be removed before effluent disposal [7]. Major bottleneck for the separation and purification of cadmium (II) and lead (II) from industrial effluent is the fact that they are found in trace quantities. The separation and purification of trace amount of solute from their dilute solutions has been a challenging problem for scientists and engineers since decades [8, 9].

The conventional techniques for separation of heavy metals are available in the literature such as adsorption, precipitation and coagulation, ion exchange, solvent extraction, *etc*. Each of these methods is associated with its inherent merits and demerits. For example, adsorption is an effective, economical (provided the adsorbent has low cost) and simple method used for the removal of pollutants from effluent. It has been reported as a superior technique for treatment of wastewater in terms of initial cost and operation, flexibility and simplicity of design and the quality of treated effluent [10]. However, it suffers the drawbacks such as production of secondary pollutants, loss of adsorbents, expensive regeneration process and the disposal of the used adsorbents. Though coagulation and precipitation techniques are simple, they are often expensive, create sludge disposal problem and give rise to secondary pollution problem due to excessive use of chemicals. High electrical energy requirement and consumption of large amount of chemicals are common problems encountered in such methods [1, 10]. Ion exchange is another efficient method applied for the removal of effluents from industrial wastewater. However, because of expensive resins, this method is commercially unattractive. Solvent extraction or liquid-liquid extraction is a widely used and energy saving process. The major

disadvantages of such processes are the loss of solvent and the problems encountered during recovery of the solvent. And another demerit of solvent extraction is the utilization of large amount of hazardous solvents. On the other hand, in LM based (in particular SLM based) processes very small quantity of solvent is needed. Hence, it is necessary to develop some cost effective yet environment friendly alternatives for recovery of trace quantity of heavy metals from their dilute solutions [11, 12].

The membrane based technology for the separation of heavy metals *viz.* cadmium (II) and lead (II) from industrial effluents is very effective. The advantages of this process are requirement of less energy, its ability to integrate with other processes and also its adjustable characteristics. Membrane based separation processes, in principle, differ based on the size of the membrane and thus classified as microfiltration, ultrafiltration, nanofiltration etc. Other factor such as affinity (*viz.* reverse osmosis, gas separation, pervaporation), charge (*viz.* dialysis, electrodialysis) and chemical nature (*viz.* carrier mediated separation) of the separated particles also play important roles [1, 13]. It also differs based on the membrane materials such as solid membrane and liquid membrane [13]. As the name implies, the membrane in one case is in solid form (*viz.* organic or polymeric and inorganic) and in the other case it is liquid such as organic solvents. Though the separations based on solid membrane such as ultrafiltration, reverse osmosis, electrodialysis, *etc.* are more stable, they face the problems of low selectivity and requirement of large size equipment. The Liquid Membrane (LM) based separation, on the other hand, has been an effective technique for selective transportation and pre-concentration of trace quantity of solutes such as heavy metals. The LM is a homogeneous, thin film of liquid (membrane phase) interposed between two other liquid phases, *viz.* feed (or source) phase and receiving (or strip)

phase [14–16]. The membrane phase is composed of a solvent with/without an additional extractant/carrier agent and it must be immiscible with the feed/receiving phases. Feed phase typically contains solute that needs to be transported across the thin film LM to the receiving phase. The transport of solute across the LM occurs due to the difference in solubility and diffusivity in the liquid film as well as the concentration gradients in the phases. Depending on the type of application, the source/membrane/strip phase combination can have either aqueous/organic/aqueous configuration or organic/aqueous/organic configuration. From the perspective of wastewater treatment, which is the central theme of this thesis, aqueous/organic/aqueous configuration is followed. It has been applied in various fields, such as metallurgy, biotechnology, environmental science and material sciences, *etc*. The principle and salient features of the liquid membrane are elaborated in the subsequent sections [1-3].

In this thesis, the phrases "LM", "membrane phase" and "organic phase" are used interchangeably to refer the same thing. Similarly the phrases "feed phase" and "source phase" are used interchangeably; and the phrases "receiving phase" and "strip phase" are also used interchangeably. The feed phase and strip phase are collectively termed as aqueous phases.

1.1. Liquid membrane (LM)

The concept of LM had been proposed by Nernst and Riesenfeld at 1902. It was developed by the oil layer separating the electrolytic solution [15]. LM techniques are basically two extraction processes in series where selective organic and inorganic species are transported across the phases in pure form [1-3]. LM based transport often functions on "solution diffusion mechanism" which is described in a later subsection. Solubility and diffusion coefficient of solutes in the liquid phases vary from solute to solute. The solution diffusion mechanism is also

observed in some polymer based solid membrane too [12]. Nevertheless, as the diffusion coefficients in liquids are higher than that in polymers, a large flux can be obtained with LMs [7-8]. When the solute is not soluble at all or less soluble in the selected solvent, carrier/extractant is added in the solvent to increase the solubility of the solute by enabling solute-carrier complexation. In this case the membrane phase (*a.k.a* organic phase) is the combination of a solvent and a carrier. The increased solubility is manifested by the enhanced distribution coefficient (DC), defined as the ratio of solute in organic phase and the solute in feed phase after the equilibrium is reached. The carrier itself is not used as the solvent as it is more viscous, and has higher molecular weight and is a more expensive compound. The transport mechanism in LM depends highly on the viscosity of membrane phase as diffusivity according to Stokes-Einstein equation is inversely proportional to viscosity. With increase of concentration of carrier in LM phase, the viscosity of membrane phase increases and hence the diffusion coefficient and the flux reduce [13, 17].

$$D = \frac{kT}{6\pi\eta r} \tag{1.1}$$

where, D is the diffusivity (cm^2/s), k is the Boltzmann constant (J/K), η is the viscosity of the organic phase (cP), T is absolute temperature (K) and r is the molecular radius (cm). Hence, the viscosity of the membrane phase should be low for enabling higher transport. However, if the DC increases manifold with addition of carrier, the overall transport efficiency is increased as well [18]. From the perspective of separation of heavy metals from aqueous extract, which is the central theme of this thesis, aqueous/organic/aqueous configuration of LM is followed.

1.1.1. Mechanism of transport of solute in LM based separation

The organic phase consists of organic diluents which is immiscible in water and has low dielectric constant. A complexing reagent, termed as carrier in LM based operation, is often mixed into the organic phase to increase its extractability of solute from the feed phase. In SLM operation, the organic phase is impregnated into a micro porous polymeric film. The polymeric film may either be hydrophobic or hydrophilic in nature depending on the requirement of the process and its function is to act as a solid support for LM. In practice the SLM is held in between two aqueous solutions. The metal ions are extracted from feed solution to membrane phase. The DC of metal ions between membrane phase and feed solution should be high enough to favor metal ion extraction into membrane phase [1-2]. There are two basic types of principles involved in LM operation *viz.* passive transport and active transport.

1.1.1.1. Passive transport

Passive transport is a movement of ions/atoms/molecules across membranes that is driven by the growth of entropy of the system and does not require any chemical energy. The four main kinds of passive transport are solution diffusion, facilitated diffusion, filtration and osmosis. Solution diffusion is the phenomenon by which components from a high concentration zone moves towards lower concentration zone due to concentration gradient. Diffusion continues until this gradient is eliminated [12]. Separation of component A (solute) from feed phase to membrane phase occurs by higher solubility or diffusivity of solute A in the membrane phase as shown in Fig. 1.1. The rate of mass transfer in this case is low and depends on the solubility of solute in the LM as well as strip phase.

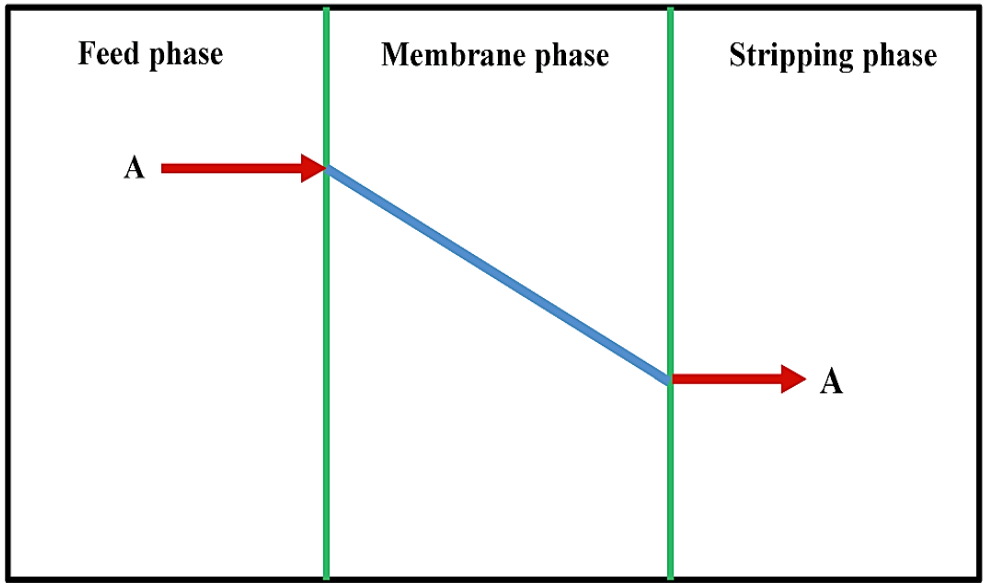


Figure 1.1: Ordinary diffusive transport of component, A through LM.

Facilitated diffusion (or carrier-mediated diffusion) is the movement of molecules across the cell membrane *viz.* special carrier agents embedded within the LM. The carrier C dissolved in membrane phase reacts with the solute A of the feed phase at the feed/membrane interface and forms a complex AC. The component AC diffuses through the membrane, dissociates at the membrane/strip interface and releases the solute A in the stripping phase. The carrier C diffuses back to the feed phase, and becomes ready to form another complex. Transport of as many molecules of A is possible in this fashion until the feed phase is depleted of and/or stripping phase is saturated with solute. The mechanism is represented schematically through Fig. 1.2.

The transport of A is no longer a function of only the gradient of A, but also depends on the concentration of the carrier.

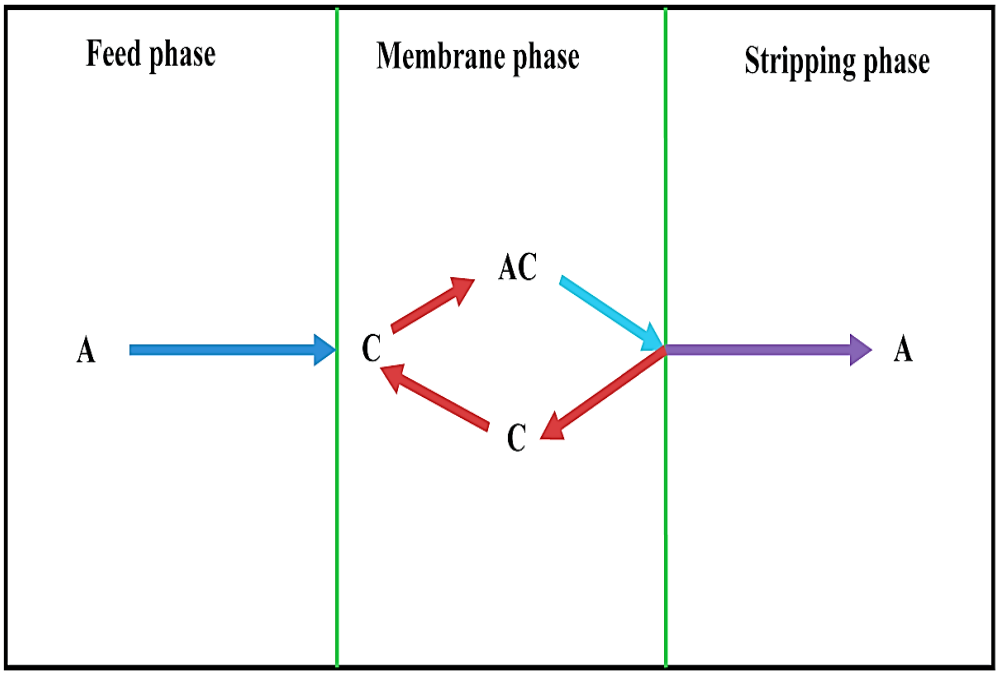
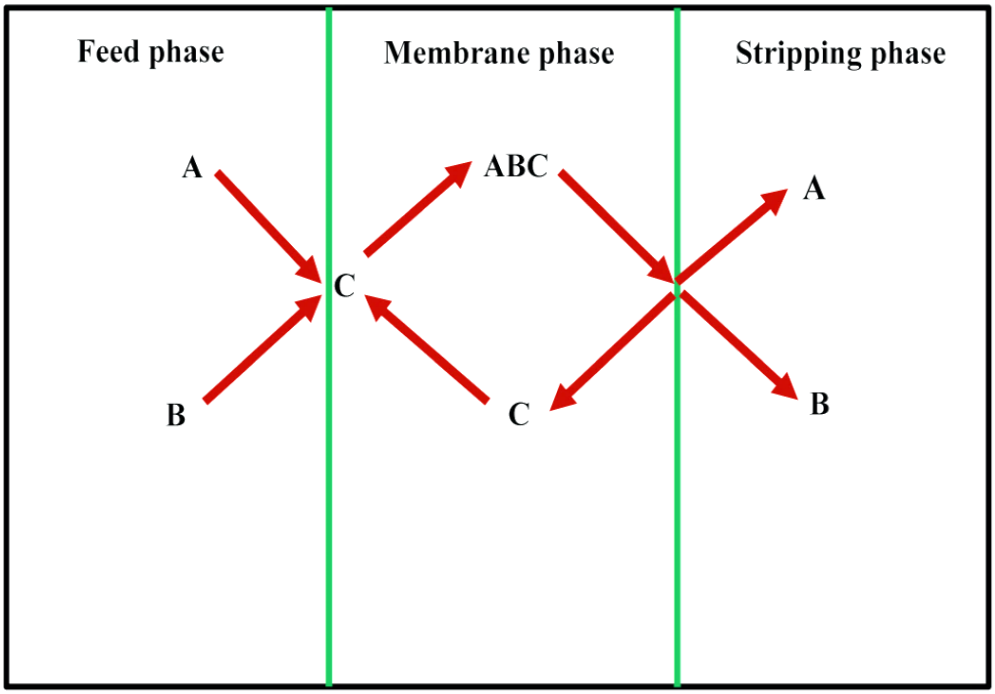
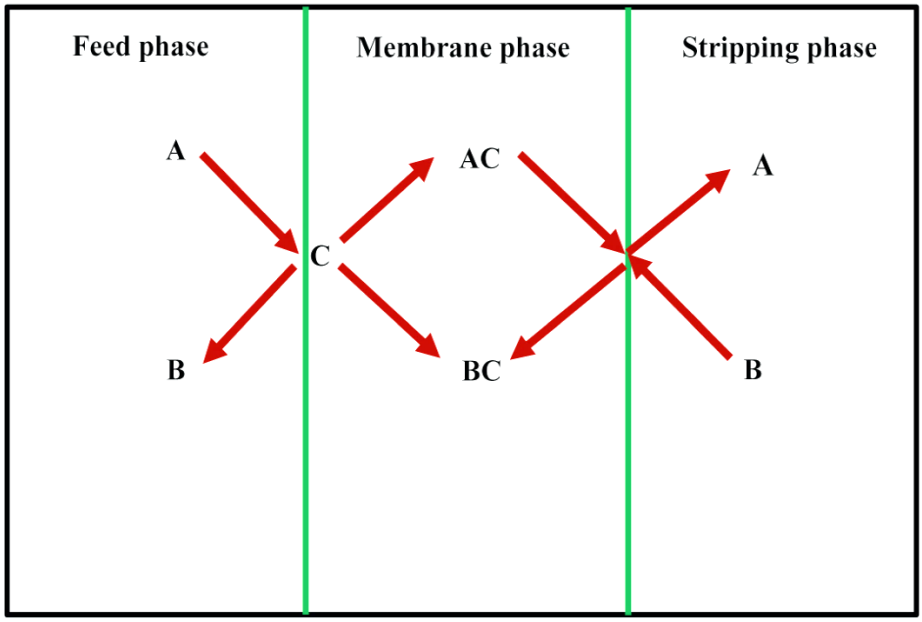


Figure 1.2: Mechanism of carrier mediated (or facilitated) transport in LM.

In the case of coupled transport (Fig. 1.3), the membrane contains a carrier which can only lead to transport when two different species are present at the same time (Fig. 1.3 (a)). If transport of the two species occurs in the same direction it's termed as co-transport, and if it occurs in opposite directions it is called counter transport (Fig. 1.3 (b)). A and B are transported in one direction, and the unchanged carrier C diffuses back. If B is present in excess on stripping side, A can still be transported through the membrane if the concentration of A on the stripping side is larger than on feed side. This process of transporting mass against its concentration gradients is termed 'pumping'. In addition, if it is possible to bring the concentration of B on the stripping side to zero by means of a suitable auxiliary reaction, then A can be transported almost quantitatively from feed to strip phase. The driving force for this transport is the concentration difference of B [1-4, 8, 13].



(a)



(b)

Figure 1.3: Mechanism of coupled transport in LM: (a) Co-transport and (b) Counter transport.

1.1.1.2. Active transport

In active transport, the movement of a substance across a membrane occurs against its concentration gradient (from low to high concentration). This is known as uphill transport [12]. In the case of active transport, two chemical reactions (redox reaction) occur as shown in Fig. 1.4. These oxidation and reduction reactions provide the pumping energy for the process. No other species are transported in this type of transport, as it is highly selective transport. In active transport, chemical reactions are irreversible in LM [1, 8].

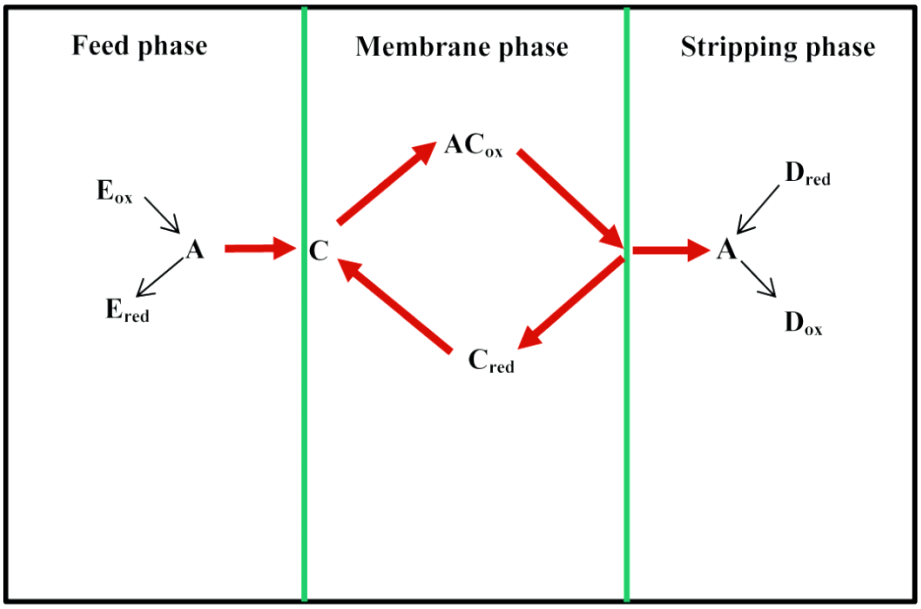


Figure 1.4: Mechanism of active transport in LM

1.1.2. Carrier

Carrier is one of the most important reagents in a LM based separation process. It acts as a catalyst. Carrier is basically an extractant that enables complex formation with solutes at the feed/membrane interface. The solute itself may not be highly soluble in organic phase, but the complex is. A higher solubility leads to higher diffusivity. A few examples of such carriers are *N*,*N*-Dimethyloctylamine (DMOA), Di(2-ethylhexyl)phosphoric acid (D2EHPA), Tri-*n*-

octylamine (TOA), Aliquat 336 *etc*. These carriers are mixed with solvents to form the desired organic phase. Small amount of carrier is sufficient for such purpose. The complex is diffused across the organic (membrane) phase. However, high concentration of carrier leads to increase in viscosity in the organic phase that adversely affects the diffusivity. Carriers are mainly of three types *viz.* acidic, basic and neutral (Table 1.1), depending on the functional groups of their molecules. A suitable carrier should possess the following properties [15]:

Table 1.1: List of carriers used in various LM processes

Type	Name of carrier agent	Application in the extraction of metals	Ref.
Acidic	Di(2-ethylhexyl)phosphoric acid [D2EHPA] ($C_{16}H_{35}PO_4$ – 322.4)	Ni, Ag, Cu, Pb, Cd, and Hg.	[18]
,,	Trioctylphosphine oxide [TOPO] ($C_{24}H_{51}OP$ – 386.63)	Cd, Cr and pt.	[19]
Basic	Trioctylamine [TOA] [$(C_8H_{17})_3N$ – 353.67]	Hg	[1]
,,	Trioctylmethylammonium chloride **[**Aliquat 336] [$CH_3N[(CH_2)_7CH_3]_3Cl$ – 404.16]	Cd	[20]
,,	N,N-Dimethyloctylamine [DMOA] [$C_{10}H_{23}N$ –157.3]	Cd	[21]
Neutral	Di-benzo-18-crown-6 [DB18C6] [$C_{20}H_{24}O_6$ – 360.4]	Ag and U.	[1]
,,	Tributyl phosphate [TBP] [$C_{12}H_{27}O_4P$ – 266.31]	Rare earth U.	[18]

- Selectivity to the solute and reversibility of binding with the solute
- Moderate binding energy
- Non-binding with a solvent
- Moderate viscosity

- Lack of ability to coalesce and
- Non-toxicity

1.1.3. Types of LM

Based on the configuration, LM can be generally categorized as shown in Fig. 1.5. In terms of the application, LM based separations are mainly of three types, *viz.* Bulk Liquid Membrane (BLM), Supported Liquid Membrane (SLM) and Emulsion Liquid Membrane (ELM) [22]. According to the geometry SLM is again of three types, flat sheet, hollow fiber and spiral wound membranes. The other types of LMs are electrostatic pseudo LM and contained liquid membrane. Fig. 1.5 shows the various configurations of LM.

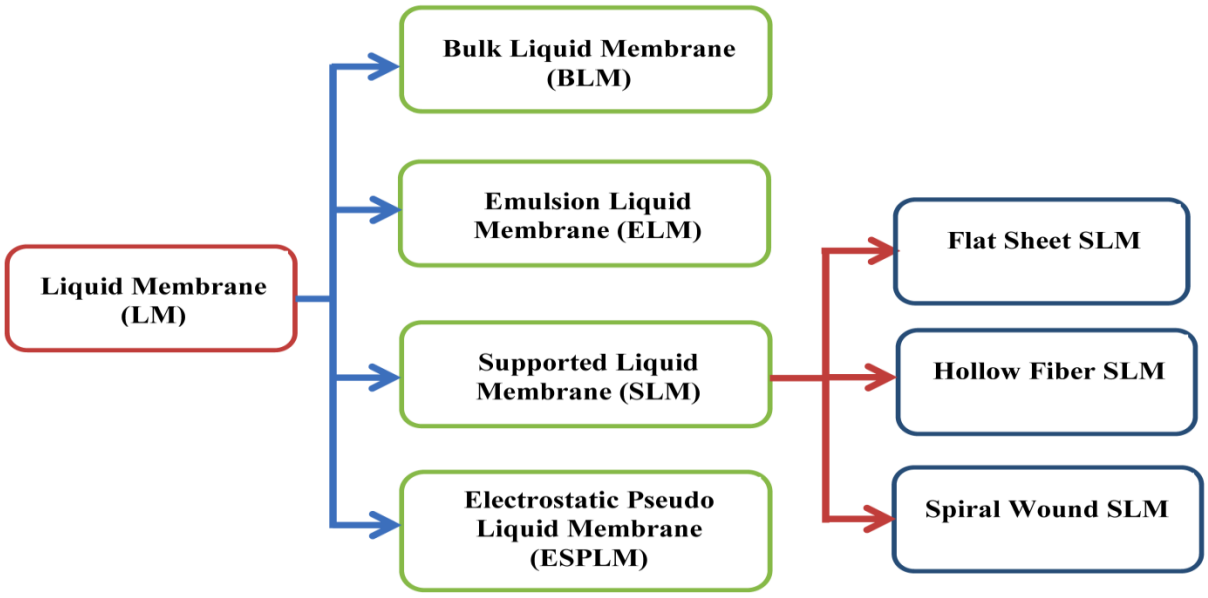


Figure 1.5: Family of liquid membranes

This research work is more concerned with BLM and FS-SLM. BLM is studied for initial estimation of the various parameters related to mass transfer and transport feasibility of solute.

As SLM is the most promising for commercial applications, it is studied in detail. In the following sub-sections, BLM and SLMs have been introduced in brief.

1.1.3.1. Bulk liquid membrane (BLM)

A schematic of BLM is given in Fig. 1.6. The membrane phase is interposed between the feed and stripping solutions, separated with a solid barrier (*e.g.* a glass wall), thus being in contact with both of these solutions. Depending on the density of the membrane phase, two different types of BLM can be formed as shown in Fig. 1.6(a) and (b). The Fig. 1.6(a) shows the case when the density of the LM phase is lower than feed and strip phases and Fig. 1.6(b) shows the other case when LM phase is heavier than feed and strip phases. The fluxes obtained are too low to make this process competitive with conventional separation processes because of the large thickness of the LM phase. BLMs are often used to study the transport properties of novel carrier and selection of suitable stripping solution. However, it is the simplest of all configurations of LM and it provides the understanding of the separation feasibility of an LM for any system of concern. However, up-gradation of the laboratory scale BLM to a commercial scale is difficult. It happens to be practically ineffective, mainly due to very low mass transfer area per unit volume as well as for the longer diffusion path of the solute or solute-carrier complex [1].

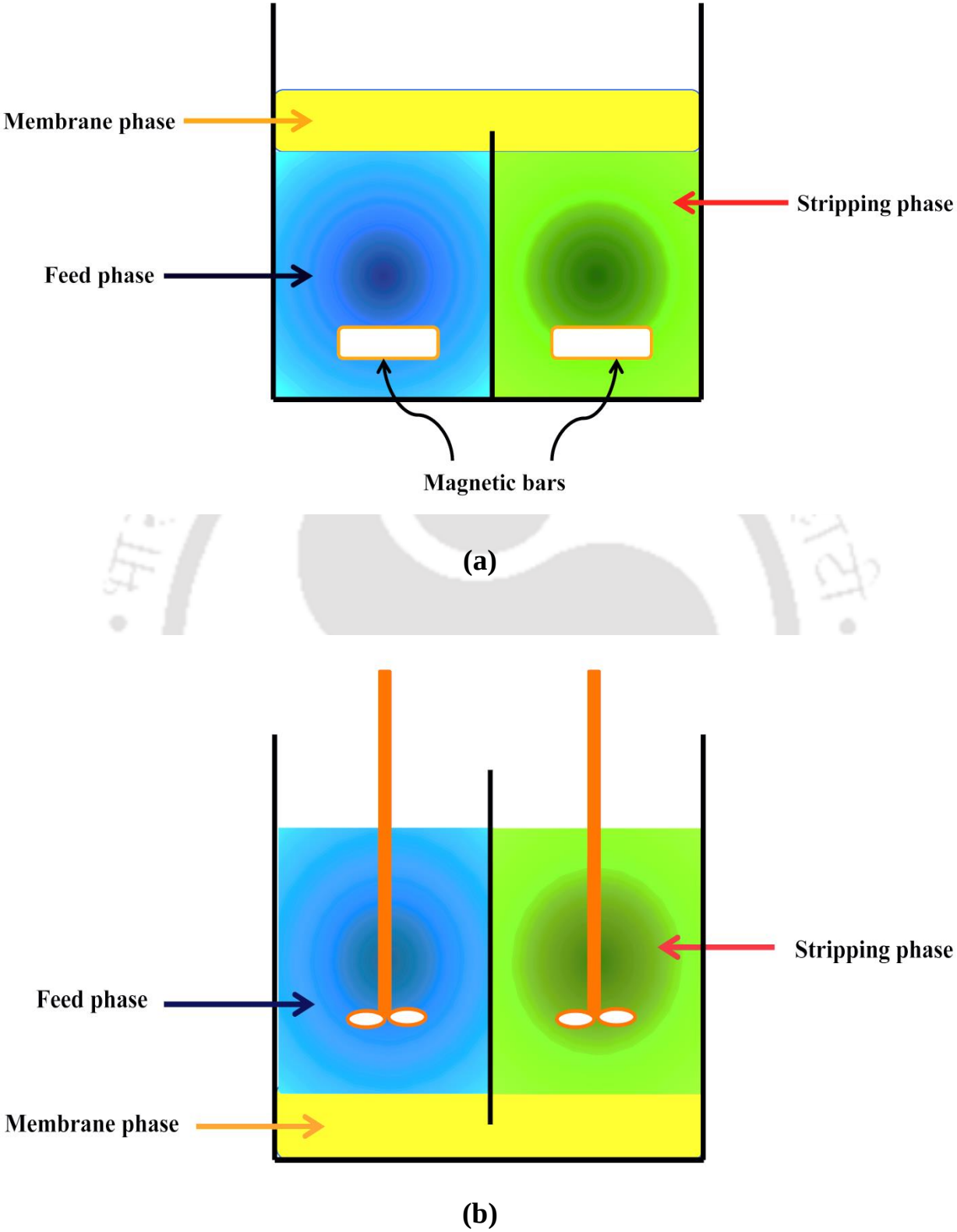


Figure 1.6: Schematic of BLM: (a) for lighter organic phase (b) for heavier organic phase.

1.1.3.2. Supported liquid membrane (SLM)

The SLMs, which consists of a micro porous polymeric support with an organic solution held within its pores by capillary forces. The hydrophobic organic solution (mixer of solvent and organic carrier) is immobilized in a porous solid support separating the feed and stripping solutions [8]. The novelty of the SLM techniques lies in the fact that the diffusion path (L) of the solute can be designed to be very small provided that the stability of membrane is not compromised. The rate of diffusion of a solute through a medium (liquid) is inversely proportional to the diffusion path (by Fick's law of diffusion). Hence, to increase the rate of solute diffusion, thickness of the LM should be kept as minimum as possible. All these factors result in the increase in the solute flux [13-16]. However, the success of SLM techniques depends on the judicious selection of support, solvent, carrier and the stripping agent for solute of interest. Important properties of membrane phase in view of membrane stability are viscosity of membrane phase, interfacial tension between membrane phase and the aqueous phases, solubility of membrane phase in aqueous phases, *etc*. In addition, the support material needs to be compatible with the membrane phase. The compatibility is of two types, *viz.* physical and chemical. Physical compatibility includes thickness, pore size, shape of the pores, tortuosity *etc.* On the other hand, relative hydrophobicity of membrane phase and the support material falls in the category of chemical compatibility.

Ideally, the pores should be of identical in size and cylindrical in shape. But, very often, they are away from this uniqueness and regular shape. Moreover, the supports need to be of higher porosity so that the effective surface area for the solute diffusion is high. Therefore, the porosity, thickness, shapes and sizes of the pores of the supports as a whole contribute to the performance

of solute transportation. The effective characteristic is measured as the tortuosity (τ) of the support which is defined as follows [1]:

$$\tau = \frac{1 + V_p}{1 - V_p} \tag{1.2}$$

where V_p is the volume fraction of the polymeric framework and again defined as: $V_p = 1 - \varepsilon$, where ε is porosity of the support membrane.

Based on the geometry of the supports, SLM is of three types *viz*. Flat Sheet-SLM (FS-SLM), Hollow Fiber-LM (HF-SLM) and spiral wound-SLM. FS-SLM, as the name implies, uses support material in form of a flat sheet. It is simple in structure and of low cost but has very low mass transfer area per unit volume as well. A schematic of FS-SLM is shown in Fig. 1.7.

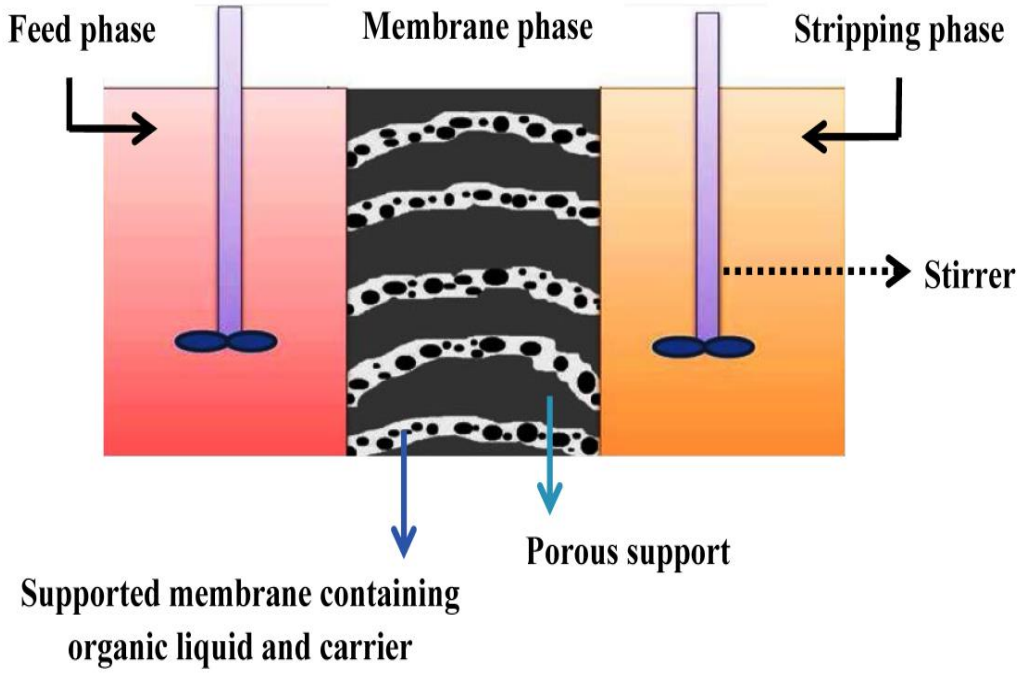


Figure 1.7: Schematic of FS-SLM

There are other advantages of using the SLM's such as

- Simpler process than ELM.
- Low operating cost and energy consumed.
- A very little amount of carrier is sufficient.
- Easy to erect and operate.
- Highly selective transport.
- Extraction and recovery of solute in single step operation.

The main problem of the SLM technology is the stability, viz. the chemical stability of the organic carrier, the mechanical stability and limited membrane lifetime.

The following are the reasons of instability of SLMs

- Effect of solubility of LM phase into the aqueous phases, and the loss of organics from the pores of SLM
- Effect of trans-membrane pressure
- Effect of osmotic pressure
- Shear-induced emulsion of the LM phase
- Contamination and pore-blockage

They have been discussed in details elsewhere [17].

1.2. Pollutants studied

Transport of solute occurs in LM in the form of salt through diffusion mechanism. Various physical and chemical properties (*viz.* size, affinity, charge and chemical nature) of solute influence the transport process through LM. The size of the solute is also an important criterion

for mass transfer. In order to assess the competence of the LM, two different pollutants of wide difference in molecular size have been chosen for the present study, *viz*. cadmium (II) and lead (II). Moreover these pollutants co-exist in various industrial effluents such as pulp and paper, chloro-alkali, battery, fertilizer, alloy and steel, paints and pigments, petrochemicals, and mining activities [1-3]. The sources, properties and impacts of these pollutants on the environment have been discussed in this section.

1.2.1. Cadmium (II)

Elemental Cadmium and various compounds of it are water soluble. Hence, the cadmium is carried away and spreaded by the aqueous streams. Owing to its nature of non-biodegradability, the concentration of cadmium in the form of both elemental and compounds increases with time [23]. The major sources of cadmium are corrosion of galvanised pipes, mining, smelting and refining of non-ferrous metals, cigarette smoke, copper refineries, electroplating, fertilizers, rubber and plastic industries, *etc*. The toxicological properties of Cd(II) are comparable with zinc which is one of the major nutrient of plants. [24, 25].

Cadmium is consumed by the human and other animals through potable water and food materials. Consumed cadmium remains in the organisms for a long time and causes various health problems. The adverse effects of cadmium in the organisms for longer time are reported elsewhere [26]. The low levels but prolonged exposure of cadmium in the human body causes disorder in renal system, whereas high level of exposure causes even death. The allowable limit of Cd(II) in drinking water is 3 ppb. This limit of permissibility of Cd(II) has been set by both WHO and US-EPA [6, 27]. The US-EPA has also set the permissible limit of Cd(II)

concentration as 2 ppm that can be discharged to a wastewater body. As per the Indian standard code IS 10500, the maximum permissible limit of Cd in effluents is 2 ppm while discharging them to inland surface waters and the same is only 1 ppm while discharging them to public sewers [28].

1.2.2. Lead (II)

Lead (II) and its compounds are obtained from both natural and anthropogenic sources. The presence of Pb(II) in the earth crust has been detected up to 13 ppm (w/w) [29]. Exposure and consequent health hazard are ensued by the consumption of food and drinks, and is also caused by air polluted by the lead bearing paints. The aquatic environment is contaminated by the Pb(II) from use of gasoline, paints, waste from battery industry, manufacturing of explosive, photography industry and anthropogenic activities [30]. The excessive consumption in the human body causes damage of central nervous system, kidney, liver, reproduction system, brain and basic cellular processes and causes high blood pressure [31, 32]. Considering its acute health hazard, the maximum level of lead (II) that can be present in potable water and wastewater are 10 ppb and 20 ppb, respectively [33]. Hence, it is evident that removal of lead (II) from potable water as well as from wastewater is of sheer importance. An effort is made in this research to study the feasibility of LM techniques for the removal of cadmium (II) and lead (II) simultaneously from wastewater.

1.3. Literature review

LM based technique has been advocated as the need of the hour. As a result there have been numerous reports on the studies of LM based separation. This section presents a thorough review

of these literatures, which is presented under four sub-sections *viz.* LM for general applications, LM for recovery of cadmium (II), LM for recovery of lead (II) and LM based separation for industrial applications.

1.3.1. LM for general applications

Since N.N. Li invented Emulsion Liquid Membrane (ELM) as separation technique in 1968, it is considered as an effective tool for a wide variety of applications [34]. Thereafter a number of researchers applied this technology in diverse areas such as separation of gases, wastewater treatment, separation of chemical compounds *etc*. Richard D. Noble and his co-workers have summarized these works elsewhere [35]. The review of the literature in the past two decades shows that LMs have been used for separation of metals such as Cu, Cd, Fe, Pt, Ag, Au, Ni, Sr, As, Hg, Cr, Co, Pb, Zn *etc.*[36-43], alkali metals such as sodium, lithium, cesium *etc.* [44], organic and inorganic acids such as acetic acid, nitric acid *etc*., biochemical compounds such as amino acid, antibiotics *etc*. [45, 46], aromatics such as benzene, toluene *etc.* [47, 48], pharmaceutical products such as diclofenac, penicillin-G, cephalosporin-C *etc*. [49-51] and for removal of phenols from wastewater [52-54]. Matsumoto *et al.* [47] presented a SLM separation method for the selective separation of aromatic hydrocarbons (*viz*. benzene, toluene and xylene) using room temperature ionic liquid (IL) (imidazolium based) as the membrane phase. They observed that benzene, toluene and *p*-xylene were successfully transported through SLM. The selectivity of aromatic hydrocarbons was greatly improved by the use of IL.

Strict environmental regulations have recently shifted the research activities towards the development of efficient LM based on environment friendly solvents. The conventionally used solvents in LM techniques are toxic, flammable and volatile in nature [55]. The solubility of

these solvents in water leads to health hazards. Hence, environmentally as well as physiologically benign solvents are preferred to be used in LM as a green solvent for separation of wastewater treatment. Vegetable oils are good alternatives to conventional organic solvents though they are comparatively more expensive and they are basically food items. Nevertheless, very less quantity of such vegetable oils would be sufficient to run such LM based operations. Venkateswaran *et al.* [56] reported SLM based separation of copper using vegetable oil such as coconut oil as diluent. They reported coconut oil as a novel and stable diluent for the separation of Cu^{2+} from copper plating wastewater. The removal of copper was about 70%. The extraction was less than that reported by Lazarova *et al.* [57] (99%) and Castro *et al.* (100%) [37]. Muthuraman and Palanivelu [58] studied the transport of textile dyes through vegetable oil based SLM. They investigated the efficiency of various vegetable oils such as sunflower oil, palm oil and coconut oil as diluent for the separation of dyes from wastewater. Among them, they have found coconut oil as the best green solvent. Mahmoud *et al.* [59] also extracted textile dye from wastewater in similar manner. Chakraborty *et al.* [60], separated Hg(II) using coconut oil as the solvent and reported 93.2% extraction. The SLM comprising coconut oil as solvent was quite stable (up to 98 h) in regard of flux. This is because coconut oil has high viscosity, high boiling point, high chemical stability and its physical compatibility with support material PVDF is also high. Manna [61] *et al.* studied the transportation of bioactive polar solute, catechin through LM comprising 0.55 M Trybutyl phosphate (TBP) as extractant in sunflower oil (SFO) in BLM. They observed 70% extraction of catechin while the initial concentration of solute in the feed phase was 100 ppm and the pH of feed solution was 4.0; they also obtained simultaneous recovery of 44% in 0.2 M aqueous ethanol solution.

1.3.2. LM based separation of Cd(II) and Pb(II)

Various research groups have studied the LM based extraction and recovery of several heavy metals from aqueous solution. EDTA is a well-known metal chelator and it re-extracts metal ions from the membrane-strip interface and forms metal-EDTA complex. Castro *et al.* [39] used the BLM configuration for separation and pre-concentration of Cd(II) ions in natural water using 2-acetylpyridine benzoylhydrazone as the mobile carrier, toluene as the organic solvent and nitric acid as the stripping agent [39]. The kinetics of transport of Cd through BLM was studied by He *et al.* [62]. It employed tricaprylamine as the carrier, xylene as the solvent and 0.5 M ammonium acetate as stripping agent. The performances of acidic carriers, *viz*. TOPS-99 (or di-2-ethylhexylphosphoric acid) for separation of cadmium were studied by various group of researchers [63-67]. Tripathy *et al.* [65] used H_2SO_4 as a stripping agent. They achieved the maximum flux of cadmium with 0.1 M carrier in the membrane phase. Bidari *et al*. [66] investigated the influence of acetate ions as stripping agent on the extraction of cadmium ions with kerosene as the solvent and D2EHPA as the acidic carrier. They found that the presence of acetate ions can increase the efficiency of extraction of cadmium to a great extent. On the other hand, Grudpan *et al*. [67] used the alkaline carrier, Aliquat 336, for the extraction of cadmium from aqueous sulfate solution using aqueous perchloric acid as the stripping agent and carbon tetrachloride as the solvent. McDonald *et al.* [68] also studied the performance of Aliquat 336 for the separation of lead using EDTA as stripping agent and achieved 80% extraction. Altin *et al*. [69] used 0.06 M EDTA as stripping solution with 0.1 M Aliquat 336 as carrier and toluene as a solvent for transportation of cadmium through SLM and achieved 82% transportation efficiency. Ashraf *et al.* [10] studied the separation of Cd(II) through SLM and reported the role of concentration of proton in the feed solution as well as the carrier agent, *viz.* tri-ethanolamine

(TEA). They observed the optimal concentrations of proton and carrier as 2.0 M HCl in feed solution and 3.0 M in membrane phase, respectively. They achieved the maximum flux at 8.4 x 10^{-7} mol.cm^{-2}.s^{-1} using 0.1 M NaOH as strip solution. Separation of Pb(II) ions was also reported by Gill *et al.* [70] who used SLM with TEA in cyclohexanone supported in microporous polypropylene films. A comparative study of transportation of Cd(II) and Pb(II) through the SLM and polymer inclusion membrane (PIM) was carried out using 7-(4-Ethyl-1-methylocty)-8-hydroxyquinoline (Kelex 100) as carrier agent and kerosene as solvent [71]. A chemical model for the transportation of metals was proposed and a very high separation of metal ions was obtained in terms of flux and stability. Anupama *et al.* [72] studied the separation of Pb(II) in SLM process with neutral carrier, tributyl phosphate (TBP) as extractant and NaOH as stripping agent. The initial concentration of feed phase was 25 ppm and the transportation was successfully completed within 4 h. A permeability coefficient of 1.146 x 10^{-5} was obtained. Although, some studies on separation of cadmium and lead have been conducted with acidic carrier [69] as well as with neutral carrier [72] with corresponding and compatible stripping agents, majority of the researchers have reported the alkaline Aliquat 336 as the suitable carrier combined with EDTA as stripping agent for transportation of both lead (II) and cadmium (II). All these studies were reported for transportation of a single metal (either Cd or Pb) with a few exceptions as well *viz.* Aguilar et al. [71] and Rounaghi *et al.* [73]. The selective separation of lead (II) cation from aqueous solutions containing other interfering cations was carried out by Rounaghi *et al.* [73]. They used BLM which was composed of dicyclohexano-18-crown-6 (DC18C6) as carrier agent in chloroform as a solvent.

The generation of the solid waste from the liquid ones is an important issue in the waste management because volume of waste is grossly reduced which eventually leads to easier waste management. The use of a precipitating agent in the stripping section recovers the hazardous heavy metals (Pb(II) and Cd(II)) as solid precipitate which reduces the load of downstream processing. Selective removal of Pb(II) across LM consisting of aza-18–crown-6 and palmitic acid in chloroform as solvent was performed by Akhond *et al* [74]. The combination of solvent with carrier agent in membrane phase and nature of the stripping agent in strip phase played an important role for the selective separation of Pb(II) ions, as compared to the other metals such as Zn(II), Cu(II), Ni(II), Co(II), Fe(II), Pd(II) and Ag(II). Use of pyrophosphate as stripping agent for the transportation of Pb(II) across the membrane phase caused 89.1% separation. Rehman *et al.* [33] have studied the separation of lead (II) through SLM with Carrier-Solvent-Support (CSS) combination: tri-*n*-octylamine (TOA)-xylene-polypropylene. They have studied various process parameters, *viz.* concentration of Pb(II) and HNO_3 in source phase, concentration of stripping agent (NaOH) in strip phase and concentration of carrier agent (TOA) in membrane phase. In the optimized operating condition, the 99% separation of Pb(II) was achieved from wastewater from paint industry. However industrial effluents usually contain multiple heavy metals in various proportions. Researchers are now showing interest to establish a technique for the treatment of effluent that contains multiple metals. Canet *et al.* [75] performed competitive metal transport experiments using combinations of two metals (*a.k.a.* binary metals) such as Cd(II) and Zn(II), Cd(II) and Pb(II) and Ag(II) and Pb(II). It was observed that Pb(II) is favorably transported through FS-SLM in comparison to other metals *i.e*. Cd(II) and Zn(II). Chang *et al.* [76] employed D2EHPA as carrier in a vegetable oil (soybean oil) for studying the kinetics of transportation of Cu(II) through bulk liquid membrane (BLM). The effects of different process

parameters, such as initial solute concentration in feed solution, temperature and comparison of kinetics between soybean oil and kerosene on separation of lead (II) were evaluated. It was observed that soybean oil based BLM showed slightly higher rate constant (k_1=1.94 h^{-1}) than that of kerosene based BLM (k_1=1.73 h^{-1}). Suren *et al.* [77] studied high selective transportation of lead (II) and mercury (II) ions through a double module HF-SLM. The selective separation of ions from their chloride salts in aqueous source phase depended on different type of carrier and stripping agents. The maximum separation of 98% was achieved for Pb(II) ions with the help of 0.03 M D2EHPA (carrier) and 0.9 M HCl (stripper). And similarly ~100% separation of Hg(II) ions was achieved with the help of 0.06 M Aliquat 336 (carrier) and 0.1 M thiourea (stripper). Rathore *et al.* [78] studied the impact of acid and concentration (ionic strength) of chloride ion on the transport of Cd(II) and observed the appearance of a 'third phase' in highly acidic concentration in feed phase. It could be avoided by using an aromatic diluent instead of an aliphatic one. However, none of them have studied combinatorial separation of Pb(II) and Cd(II) in such low concentration using environmentally benign solvents. The treatment is needed for such effluents where both the pollutants are present.

1.3.3. LM Based on industrial applications

In recent years, LM have gained considerable interest in separation and recovery of trace amount of heavy metals from the industrial effluents. For separation of metals, co-transport is better than counter transport [1]. Studies have been carried out for the separation, process kinetics, mass transfer modeling and engineering evaluation of heavy metals such as mercury, lead, cadmium, copper, cobalt, zinc, nickel, chromium and several others including noble metals like silver, gold, lanthanides and rare earth elements [8]. LM offers large scope for selective extraction and

recovery of solute in trace concentration of pollutants from industrial effluents, resulting in high treatment efficiencies. By LM process, it is possible to carry out wastewater treatment as well as recovery of some value added products simultaneously. Mineral acids as well as organics may be removed from wastewater using LM based technology [1-3].

Some investigators have worked on separation of gases by using supported Ionic liquid membranes (SILM). CO_2 and CH_4 were separated from their mixture by using SILM containing mono ethanol amine (MEA) and di ethanol amine (DEA). DEA supported membranes showed greater permeation rates compared to MEA supported membranes [79]. The mechanism of transport was mediation facilitated transport. Some of the areas in which this technique has been applied include removal of CO_2 and CO. LMs can also be used as chemical reactors for the reaction between two gases in a heterogeneous catalysis system. SLM can also act as selective separation barrier for pharmaceutical compounds (example penicillin G) [8]. Kaminski *et al* [15] argued that there are three major industries in the world that remove zinc metal from wastewater from textile industry using ELM method. The capacity of those industries are the following: Glanzstoff (Austria) 0.7 m^3/h, CFK Schwarz (Germany) 0.2 m^3/h, AKZO/Ede (the Netherlands) 0.2 m^3/h. Another industrial application of ELM is removal of phenol from wastewater of plastic industry in China [1, 55]. This plant separates 0.5 tons of solution containing 1000 ppm of phenol per hour and reduces their concentration to 0.5 ppm after treatment. Several pilot plants are installed in metallurgical industries to treat effluent for recovery of metals, such as zinc, cadmium, lead, iron, copper, cobalt, nickel, manganese, magnesium, calcium and sodium [8, 20]. ELMs were also field tested for separation of copper from run of mine wastewater [80]. Considerable potential for large scale applications of LM based systems are there in many

applications such as wastewater treatment, biotechnological and biomedical applications, hydrometallurgy and separation of organic acids.

1.4. State of the art issues with LM and their lacunae

Based on the experience gathered as above and also from the literature survey therewith, following lacunae were observed in the field of research with LM.

- SLM based separation has high potential in the industrial application, yet very few industries have accepted this technology in large scale.
- Environmentally benign solvents should have been automatic choice for LM based applications for obvious reasons, yet the majority of research works undertaken so far have not considered this option at all.
- Environmental pollution due to heavy metals in industrial wastewater has been a long standing problem and LM based application has huge unexplored potential with respect to the above.
- In the industrial effluent, the concentration of Cd(II) and Pb(II) varies. None of the research work has been done for combinatorial separation of trace amount of Cd(II) and Pb(II) from wastewater using environmentally benign solvents.
- Till date no research work has been reported for LM based separation of heavy metals for the transformation of liquid waste to solid waste and the recovery of metals in the pure value-added form.

This research work targets all the above issues with a holistic approach of wastewater treatment.

1.5. Importance and objective of the research work

In spite of having huge potential for commercial application on wastewater treatment, the LM based separation technique finds itself within a narrow bound of a few research papers and even fewer applications in industries. The key to its wider acceptability is to make it more industry-friendly such as faster transport, continuous mode of operation, less solvent loss, reliable scalability, less energy expenditure, environment-friendliness, minimum maintenance, easy disposal of waste and possibility of recovery of value-added components.

If the heavy metals recovered from the wastewater can be converted into solid waste, it would be highly beneficial with respect to their easy disposal. An option for precipitation of metal salts in the stripping phase may perhaps be a reasonable objective.

Further, if the heavy metals recovered from the wastewater can be converted into some value-added product, it would be the most desirable solution to the problem of their mitigation. The electrodeposition of heavy metals on a metal electrode (cathode) placed inside the stripping phase of the LM setup is a technical novelty with the perspective of LM based separation that has been suggested and implemented in this thesis. Heavy metals can be separated from waste and recovered as pure metal through metal deposition on the surface of cathode on applying an electric potential. The recovered pure metal can be used in different industrial applications. The LM based separation step prior to electro-deposition is necessary instead of direct electroplating as the two steps in sequence provides the selectivity and electro-deposition of metals, respectively. The electrodes are exposed to the selective and transported solute in the strip phase only and not contaminated by the other pollutants present in the industrial effluents. Hence the

recovery of target metals on cathode plate is in its purest form. The electroplated cathode is a salable item and is thus a value-added product.

Moreover, simultaneous stripping and precipitating/electroplating yields an "ever-unsaturated" condition of the stripping phase which in turn leads to higher and faster separation of heavy metals from wastewater. Hence, this is a case of process integration whereby SLM based separation technique is integrated with precipitation/electrodeposition process for serving dual purpose, *i.e.* higher and faster purification of wastewater as well as easy disposal of waste/production of value-added product.

The overall aim of the proposed research work is to study the merits of LM based extraction and recovery of trace amount of Cd(II) and Pb(II) from the industrial effluents in the context of above key issues. This aim can be achieved through the following measurable objectives.

- Identification of low cost, easily available and yet environmentally benign solvents that can extract solutes (heavy metals) from their aqueous solution by two phase equilibrium study. Potential candidate can be found among the vegetable oils such a coconut oil, mustard oil, soybean oil, sunflower oil *etc*.
- Identification of suitable carrier compounds (*i.e.* extractant) or more precisely a suitable solvent-carrier combination that enhances the extraction of solute from the source phase
- Identification of the best operating condition in terms of feed phase pH, initial concentrations of feed phase, concentration of extractant and operating temperature which would yield best extraction of solute(s) in two phase extraction study.

- Identification of suitable stripping agent that ensures re-extraction of solute from the membrane phase to the aqueous strip phase through a three phase BLM study.
- Identification of the best operating condition in terms of feed phase pH, initial concentrations of feed phase, concentration of strip phase, concentration of carrier and operating temperature which would yield best separation of solute(s) in a BLM unit.
- Verifying of the above conditions for application for separation of cadmium and lead by using FS-SLM and selection of support material for a stable FS-SLM configuration.
- A comparative study of separation of cadmium (II) and lead (II) in "binary pollutant" condition.
- The Development of efficient recovery strategies and stripping conditions so as to enhance the extraction and recovery of the selected metals, such as
  - ✓ Precipitation of metal in stripping solution by chemical process
  - ✓ Electrodeposition of metals in stripping solution by employing electric potential

CHAPTER-II

Materials and Methods

CHAPTER-II

Materials and Methods

This chapter describes two types of LM set-ups (BLM and FS-SLM) used in this work. The detailed experimental procedures of metal transportation studies in both configurations of LM are elaborated thoroughly. It also describes the chemicals and reagents used in various experiments to carry out this work. A brief discussion of analytical instruments and characterization techniques used for this research work are included here. The specifications of chemicals and reagents and the working conditions of instruments are also described.

2.1. Chemicals and reagents

Various materials used in the extraction and recovery of cadmium (II) and lead (II) along with their sources are summarized in this section. All the chemicals and reagents used in this work were of Guaranteed Reagent (GR) grade. Aqueous solutions were prepared by using Milli-Q® (Millipore, USA) deionized water. $PbCl_2$ was obtained from Loba Chemie Pvt. Ltd. (India), $Pb(NO_3)_2$ was obtained from Qualigens Fine Chemicals Pvt. Ltd. (India), Aliquat 336 (methyl-tri-caprylyl ammonium chloride) was procured from Sigma Aldrich (India) and D2EHPA was procured from Spectrochem Pvt. Ltd. (India). All other chemicals such as cadmium chloride ($CdCl_2 \cdot H_2O$), sodium carbonate (Na_2CO_3), Disodium ethylenediaminetetraacetate (Na_2–EDTA), HCl (35%), ammonia solution (25%), HNO_3 (69%), toluene, 1, 2-dichloroethane, chloroform, *n*-heptane and isooctane were obtained from Merck (India). Parachute® coconut oil (Marico India limited, India), Refined sunflower oil, Dhara® refined mustard oil (Mother Dairy Fruit & Vegetable Pvt. Ltd., India) and refined

soybean oil (Adani Wilmar limited, India) were purchased from local market. Polyvinylidene Fluoride (PVDF) membrane (Hydrophobic, pore size 0.2 µm and thickness 127 µm) was procured from Pall Corporation Pvt. Ltd. (India). Accutrace® reference standard lead (II) solution (1000 ppm) and cadmium solutions (1000 ppm) were procured from AccuStandard (USA) for AAS analysis.

2.1.1. Working solutions for cadmium (II)

The stock solution of cadmium (II) (1000 ppm) was prepared by dissolving 1.6308 g of cadmium chloride ($CdCl_2 \cdot H_2O$) in sufficient quantity of Milli-Q® deionized water in one liter volumetric flask. The solution was shaken well and required amount of the concentrated solution (1000 ppm) was taken in 1000 mL volumetric flask and diluted with Milli-Q® deionized water. Feed phase with different initial concentrations were then prepared from this stock solution by proper dilution with Milli-Q® de-ionized water. The membrane phase was prepared by dissolving an appropriate amount of carrier agent in coconut oil. Concentration of carrier (% v/v) is defined as the ratio of the volume of carrier to volume of membrane phase without carrier. The stripping phase was prepared by dissolving the required amount of stripping agent in 500 mL of Milli-Q® deionized water.

2.1.2. Working solutions for lead (II)

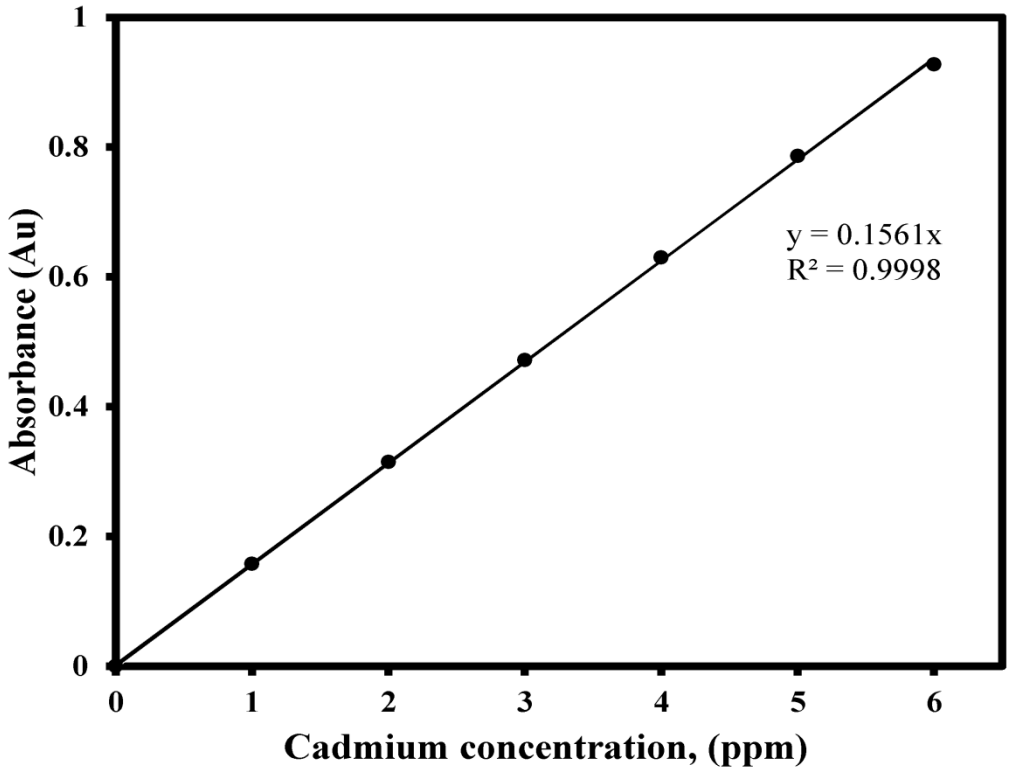
The stock solution (1000 ppm) of Pb(II) was prepared by dissolving 1.342 g of $PbCl_2$ in one liter volumetric flask. The solution was shaken well and required amount of the concentrated solution (1000 ppm) was taken in 1000 mL volumetric flask and diluted with Milli-Q® deionized water. The feed phases were prepared by diluting a quantity of the stock solution with water up to the desired concentration. Similarly 1.598 g of $Pb(NO_3)_2$ was dissolved in

sufficient quantity of Milli-Q® deionized water in one liter volumetric flask. The stripping phase was prepared by dissolving the required amount of stripping agent in 500 ml of Milli-Q® deionized water. The organic phase in equilibrium studies and LM in three phase studies were prepared by dissolving appropriate amount of the carrier in various pure solvent.

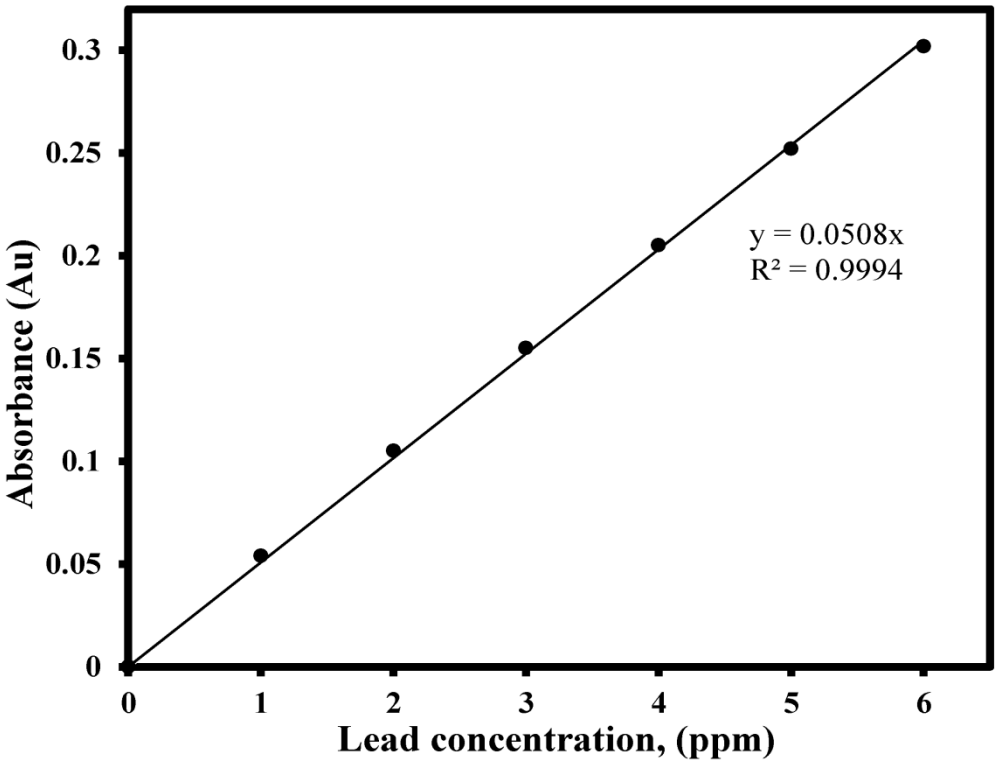
2.2. Analytical instruments

2.2.1. AAS

The concentration of lead (II) and cadmium (II) ions in the feed and stripping solutions were determined by Atomic Absorption Spectrometer (AAS) (Make: Varian Australia, Model: AA240FS) equipped with photon make hollow cathode lamps for cadmium (II) and lead (II) using flame mode. The instrument was fully computer controlled using software SpectrAA Base and PRO software versions. The optimized instrument parameters for measurement of targeted metal ions are for cadmium: lamp current 4 mA, wave length 228.8 nm, slit width 0.5 nm, fuel is acetylene, support is air and for analysis delay time 10 seconds. Similarly for lead as follows, lamp current 5 mA, wave length 283.3 nm, slit width 0.5 nm, fuel is acetylene, support is air and for analysis delay time 10 seconds [81]. The calibration curves and its equations for standardization of cadmium (II) and lead (II) by AAS analysis were reported in Fig. 2.1. Ratio method was preferred for curve fitting. The samples of the experimental runs were collected from aqueous phases then analyzed directly, *i.e*. no further processing of the sample is required for analysis in AAS. All the individual experiments were repeated thrice.



(a)



(b)

Figure 2.1: Calibration curves for analysis of (a) cadmium (II) and (b) lead (II) in AAS

2.2.2. Other analytical instruments

A digital pH meter (Eutech Instruments, EUTECH 510) was used for the measurement of pH. A rheometer (Thermo Electron Corporation, HAAKE Rheostress RS1) was used for the measurement of viscosity. Shaking incubator (Daihan Labtech Co. Ltd, LSI 3016R) was used to provide proper mixing of aqueous and organic phases in two phase equilibrium study. A tensiometer (Kruss Germany, K9) was used to measure the surface tension and interfacial tension. The morphology of supporting polymeric membrane was done by using Field Emission Scanning Electron Microscope (FESEM) (Zeiss, Sigma). Scanning electron microscopic (SEM) and Energy Dispersive X-ray (EDX) analysis in order to characterize the surface morphology and examine global chemical composition of the cathode confirmed the deposition of pure metals on the copper surface.

2.2.3. Physical properties of vegetable oils

Viscosity of a vegetable oil is an important parameter that influences the solute diffusivity through LM. The viscosity of vegetable oils at various temperatures was determined using rheometer in the working temperature range of 25–50 ^{o}C. The variation of viscosity was found almost linear. From the Fig. 2.2, a relationship is developed between viscosity and temperature (Eq. (2.1)) for the different vegetable oils as:

$$\mu_T = m\Delta T + \mu_0 \tag{2.1}$$

where μ_T is viscosity (Pa.s) of vegetable oils at temperature T, μ_0 is viscosity at 0 ^{o}C, m is slope of the above equation and ΔT is temperature difference (^{o}C). The magnitudes of viscosity of the oils, as found in the Fig. 2.2, are in the decreasing order of Mustered oil > Soybean oil > Sunflower oil > Coconut oil [21].

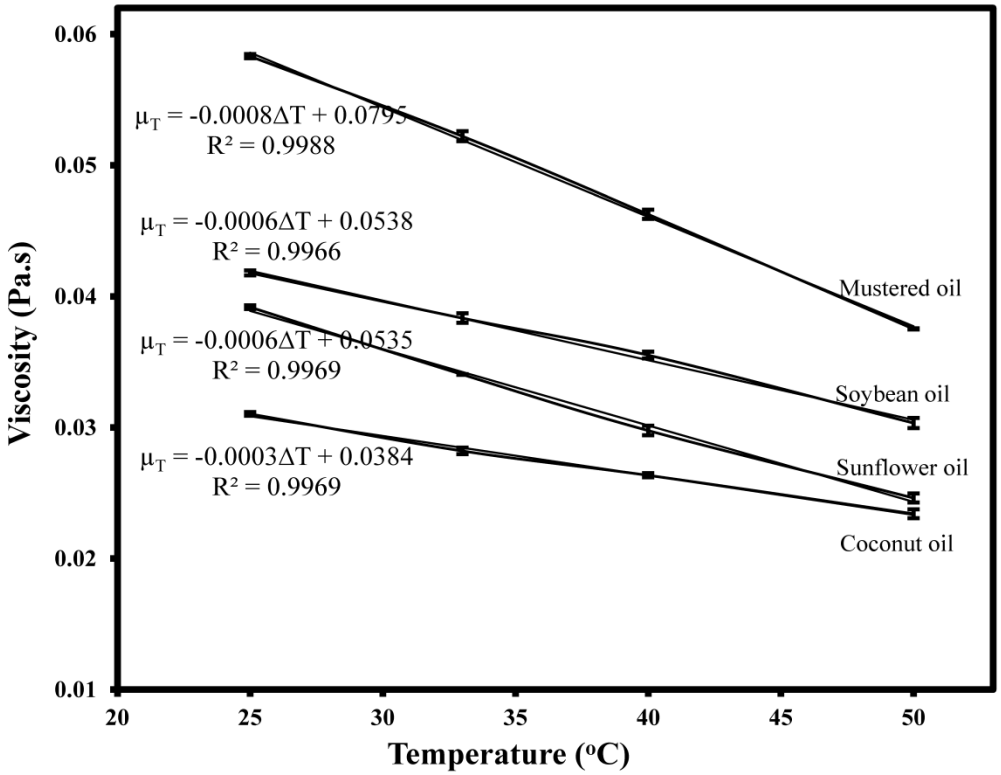


Figure 2.2: Effect of change of temperature on viscosity in various vegetable oils

Surface tension and interfacial tension of vegetable oils and Milli-Q® deionized water are important properties to consider in LM based separation. They are measured using tensiometer at 25 °C and reported in Table 2.1. It may be seen that the coconut oil - water system has significantly lower interfacial tension than the other oil-water systems reported in the table.

Table 2.1: Surface tension and interfacial tension of various vegetables oils

Name of the sample	Surface tension at 25 ^{o}C, mN.m^{-1}	Interfacial tension (oil and water), mN.m^{-1}
Water (Milli-Q® deionized water)	72.8	-
Coconut oil	31.5	13.9
Sunflower oil	33.5	24.8
Soybean oil	32.9	22.1
Mustered oil	35.7	24.8

2.3. Two phase equilibrium set-up and procedure

The objective of the work is to establish the applicability of the LM-based separation technique for industrial wastewater. Hence, an effluents that contains high level of Cd(II) and Pb(II) concentrations are targeted. The major industries that emanate these pollutants are battery, paint and chloro-alkali. The concentrations of cadmium and lead in the effluents of these industries are shown in Table 2.2 and they vary in the range of 0.11–4.0 ppm. Hence, an initial concentrations of Cd(II) and Pb(II) as 5 ppm was selected for experimentation purpose [3, 21]. The two phase equilibrium distribution studies were carried out by mixing an equal volume (20 mL) of stock solution (5 ppm) of cadmium (II) (aqueous) and organic solution in a conical flask (100 mL). The mixture was agitated continuously by using a mechanical shaker with constant stirring rate of 200 rpm for a period of 6 h. The mixture was then kept undisturbed for some time until the phase separation takes place. The aqueous phase was carefully separated from organic phase. The samples were collected from aqueous solution. The concentration of Cd(II) in the aqueous phase after extraction was measured by using AAS. The inaccuracy of the instrument is less than 0.8% in terms of Relative Standard

Deviation (RSD) in ppm level. The concentration of Cd(II) extracted in the organic phase is calculated based on mass balance. All the experiments were carried out at room temperature (25 ^{o}C).

Table 2.2: Various industries releasing Cd and Pb in their effluents

Name of the industry	Cd (ppm)	Pb (ppm)	Reference
Chlor-alkali	1.1	2.2	[9]
Battery	4.01	0.12	[82]
Paint	0.23	0.11	[82]

2.4. Three phase experimental studies with BLM

The BLM configuration consists of a cubical shaped glass container (73 mm x 73 mm x 65 mm), divided into two leak-proof compartments by fixing a thin glass plate of thickness 5 mm in the middle. A dye test was done in order to ensure the leak-proof nature of the compartments. Feed and strip phases (both 65 mL) were poured in those compartments up to well below the upper end of the divider plate, so that procedural stirring in these compartments does not risk an accidental mixing between the two. The membrane phase organic solution (30 mL), being lighter than water, was floated on these aqueous solutions up to well above the upper end of the divider plate, so that a connection between two aqueous/membrane interfaces was established for the diffusion to take place. Area of membrane-aqueous phase interfaces at both sides of the BLM setup was about 19.5 cm^2. Stirring was provided to the feed and stripping solutions by using the magnetic stirrer (Fig. 2.3). Experiments were performed in order to study the effects of operating conditions (such as feed phase pH, initial concentrations of feed phase, concentration and pH of strip phase

and concentration of carrier) on extraction and recovery of Cd(II). Experimental samples were collected at regular time intervals from both feed and strip side and Cd(II) concentration was measured by using AAS.

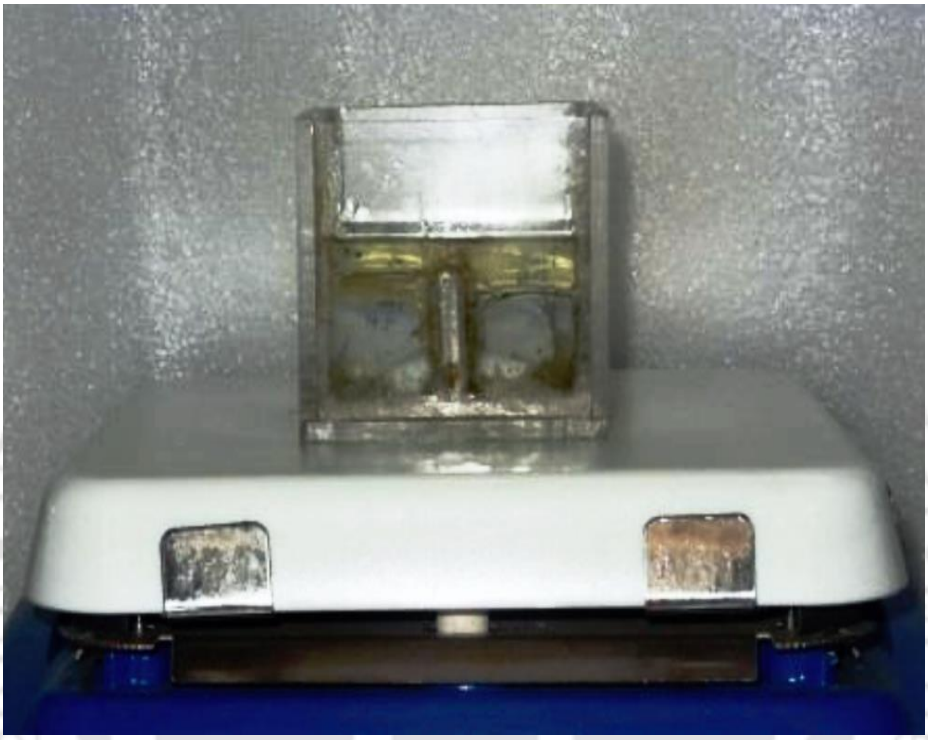


Figure 2.3: Photograph of the BLM set-up

The performance of the two phase equilibrium distribution and three phase transport results were obtained in terms of % extraction and % recovery, calculated by following Eq. (2.2) and Eq. (2.3).

$$\%\, Extraction = \frac{C_{fin} - C_f}{C_{fin}} \times 100 \tag{2.2}$$

$$\%\, Recovery = \frac{C_s - C_{S_{in}}}{C_{f_{in}}} \times 100 \tag{2.3}$$

where, $C_{f_{in}}$ is initial concentration in feed phase (ppm), C_f is concentration in feed phase after transportation (ppm) respectively and $C_{S_{in}}$ and C_S is the initial and final concentrations in stripping phase (ppm) respectively. As the stripping phase is initially solute-free in normal circumstances, $C_{S_{in}} = 0$ can be a reasonable assumption. Hence Eq. (2.3) can be written as

$$\% \, Recovery = \frac{C_s}{C_{f_{in}}} \times 100 \tag{2.3a}$$

2.5. Three phase experimental studies with FS-SLM

Various types of SLM modules such as flat sheet, hollow fiber, spiral wound, *etc.* are discussed in the previous chapter. Among these the simplest one, *i.e.* the Flat Sheet Supported Liquid Membrane (FS-SEM), is considered for this research work. The SLM set-up and its working procedure are described in the next sections.

2.5.1. FS-SLM setup and experimental procedure

The three-phase experiments were carried out in an FS-SLM setup. It consists of two equal volumes of rectangular shaped containers (50 mm x 65 mm x 80 mm) made with perspex sheet (*a.k.a* half cells). The containers are joined by flanges (ID 42 mm). The solid polymeric (PVDF) support, impregnated with organic solution, was placed in between the flanges of two cells of the apparatus. Preparation of organic solution and its immobilization inside the pores of PVDF support have been carried out in the manner shown in Fig. 2.4. The aqueous feed and strip solutions were poured into two different containers of half cells, each having maximum capacity of 250 mL. The effective surface area of membrane contact is 804.2 mm^2. Solutions in the two compartments were agitated with the help of vertical mechanical stirrers (Make: Remi, Model: RGQ 121/D). Samples were collected from the feed and strip side at regular intervals during the experimentation. The concentrations of Pb(II) and Cd(II) were

measured by using AAS. All the experiments were performed at least thrice in order to ensure the repeatability of the experimental results. All experiments were carried out at room temperature i.e. 25.0 ± 1ºC and in batch mode [83].

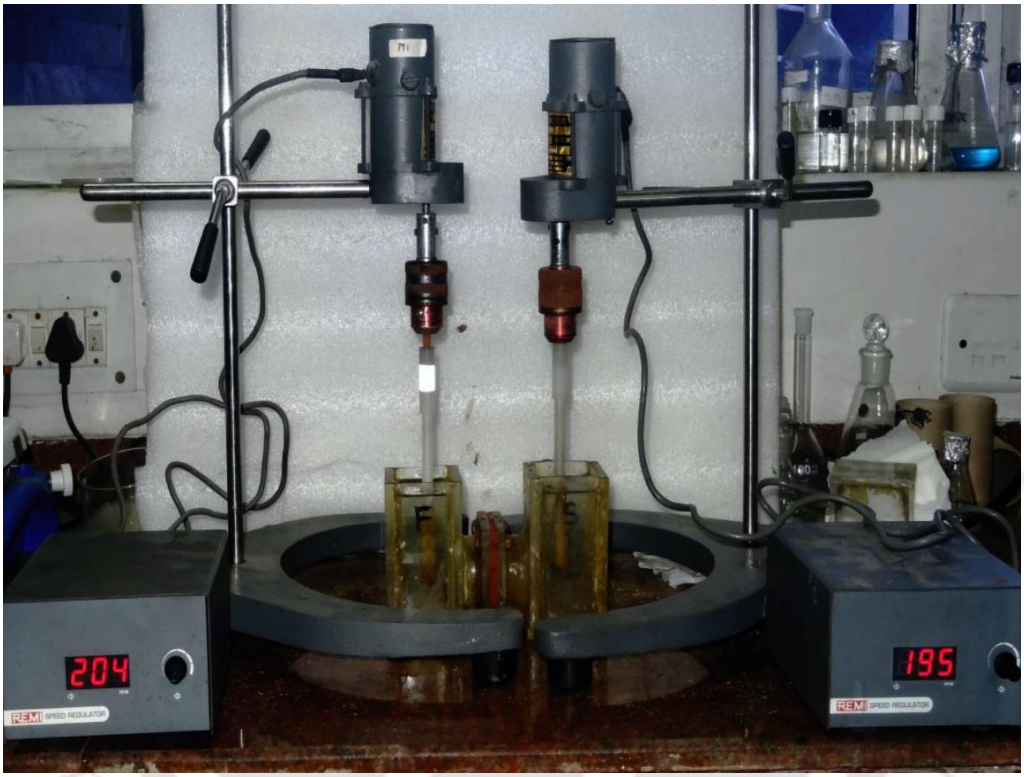


Figure 2.4: Photograph of the FS-SLM set-up

2.5.2. Solid membrane support

The polymeric membrane (PVDF) was used as support for the organic phase. The porosity of the support materials was detected through SEM analysis. The thickness of the support materials was estimated from the SEM pictures. A mean value of the thickness was calculated by measuring the thickness at various points. The value of the tortuosity (τ) was calculated from the Eq. (1.2).

The porosity and tortuosity of the PVDF membrane were 0.45 and 3.44 respectively. The thickness of the support membrane before and after impregnation by LM were measured by SEM analysis and found as 127μm and 133.6 μm respectively.

2.5.3. Preparation of FS-SLM

Solid polymeric support (PVDF membrane) was impregnated with the organic solution into its pores by dipping it in the LM for 24 h. The impregnated support was removed from the organic solution and kept in vacuum desiccator for 1 h duration. The support was taken out from the desiccator and the excess amount of organic solution in membrane surface was gently wiped out with good quality tissue paper. The prepared SLM was placed between the two flanges that connect two compartments of FS-SLM setup [3].

2.6. Three phase experimental studies with FS-SLM based simultaneous separation and electro-deposition

2.6.1. Set-up and experimental procedure

The FS-SLM cell along with the arrangement of electroplating is shown in Fig. 2.5. It consists of two equal volume rectangular shaped containers (50 mm x 65 mm x 80 mm) made of Perspex sheet and connected by a flanged cylindrical pipe (ID 42 mm). The working volume of each compartment (feed and strip) is 250 mL. The pipes are bolted together while a porous support (solid membrane) is sandwiched between the flanges at the end of the pipes. The pores of support are filled with organic phase (*i.e.* combination of organic solvent and carrier at desired ratio). The tanks are filled with aqueous solutions *i.e.* feed and strip phases. The phases are continuously stirred by stirrers (Make: Remi, Model: RGQ121/D) whose speeds (rpm) are controlled by voltage regulators. During this process, solute is transferred

from feed phase to the strip phase across the membrane. The effective membrane contacting area is 804.2 mm^2. Electrodes are kept inside the stripping chamber and they are 3.5 cm apart from each other. One D.C. power (0-30 V) supply is used to supply the current across the stripping solution through the electrodes. All experiments were carried out at room temperature *i.e.* 25 ± 1 °C and in batch mode. Individual experiments were performed thrice in order to ensure the repeatability of the experimental results.

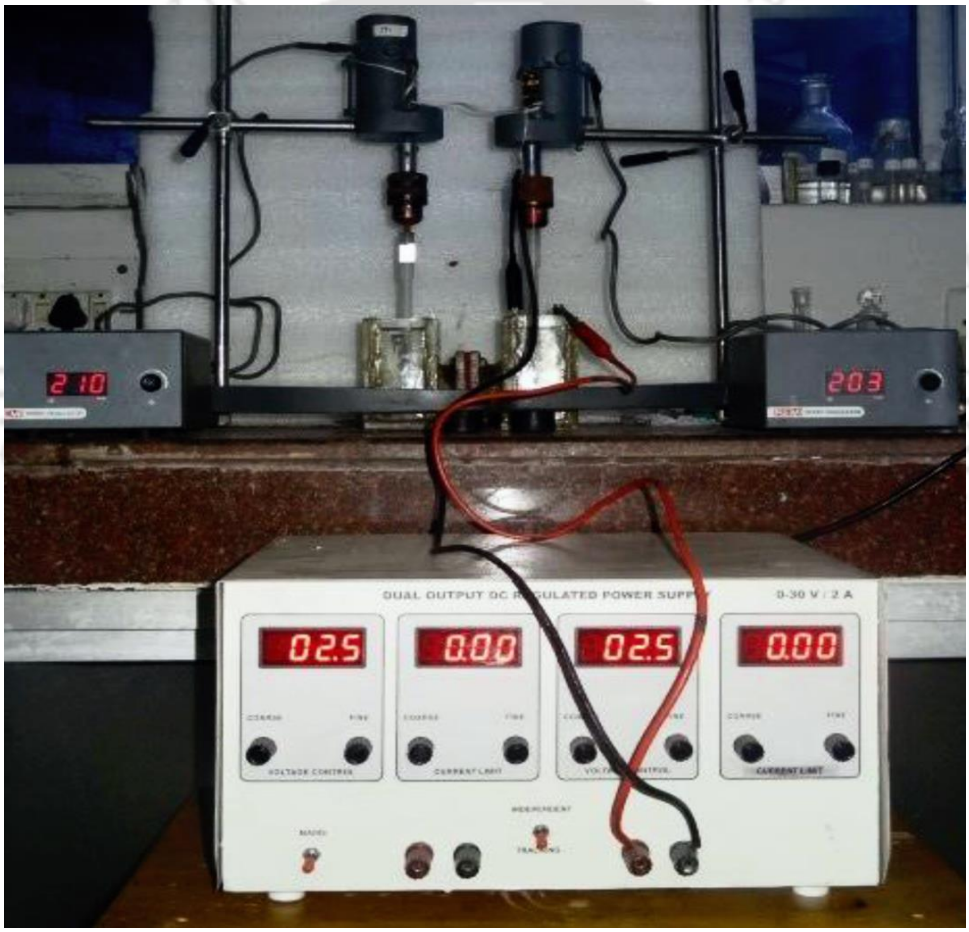


Figure 2.5: Photograph of FS-SLM with electro-deposition experimental set-up

The performance of the three phase transport study as well as metal deposition were reported in terms of % extraction and % recovery directly from the measurement of cadmium (II) and lead (II) concentrations in feed phase (Eq. 2.2) and stripping phase (Eq. 2.3).

Direct measurement of % deposition of metals on the cathode plate by weighing method is difficult. Hence, it was measured indirectly from the measured concentrations of metals both in feed and the stripping phases with the fare assumption that no metal will be trapped in the membrane phase during the experimentation. This assumption is quite acceptable because very little quantity of solvent is used in any SLM process compared to the quantity of aqueous phases. Following equation indicates the extent of deposition of metal on the cathode plate:

$$\%\ Deposition = \frac{\left(C_{f\,in} - C_f\right)_{feed} - C_s}{C_{f\,in}} \times 100 \qquad (2.5)$$

where, $C_{f\,in}$ and C_f are the initial and final concentrations of feed phase respectively whereas C_S is the final concentration of stripping phase.

CHAPTER-III

BLM based separation of Cd(II) *and* Pb(II)

CHAPTER-III

BLM based separation of Cd(II) *and* Pb(II)

This chapter presents an experimental investigation for extraction and recovery of harmful heavy metals from the industrial wastewater through BLM based technology. The selective extraction and stripping are achieved through the transportation of two such heavy metals viz. lead (II) and cadmium (II). The environmentally benign coconut oil is selected as solvent of the LM through two phase equilibrium studies. Experiments are performed in order to optimize various physico-chemical parameters, such as pH and concentration of aqueous phase, temperature and speed of stirring of mixture, run time of experiment, on the extraction of cadmium (II). The performance of extraction is enhanced with respect to its run time by the use of a suitable extracting agent i.e. carrier. Optimal concentration of carrier has been detected through the two phase study. Three phase transportation studies are thereby conducted through BLM at the same optimized operating parameters obtained in two phase studies. Initially selection of the carrier was carried out based on their capability of extracting the target metals. DMOA was found to be the best carrier in two phase equilibrium studies. Hence, the three phase transportation studies were performed using DMOA as carrier. However, it was observed that the efficiency of stripping of metals into the recovery phase was too low (13% only) for the SLM to be commercially viable. Consequently, the second best performing carrier, viz. Aliquat 336, was used as a carrier agent and the three phase experimental studies were repeated and the optimum operating conditions were re-tuned. The stripping efficiency was found to be very satisfactory. The extraction and recovery were found to be 72% and 64%, respectively. Further experimentations through BLM were conducted for transportation of lead (II) with the same set of operating parameters. Both the

extraction (82%) and recovery (77%) are found comparatively higher for lead (II) as compared to that of cadmium (II).

3.1. Results and discussion

The carrier agent in three phase LM study is more appropriately referred to as extractant in two phase study. Also it is more appropriate to refer the LM as organic phase.

3.1.1. Two phase equilibrium study

The two phase studies were carried out in order to measure the extent of solute extraction capability of organic phase (solvent mixed with extractant) at various physico-chemical conditions of aqueous phase. The operating parameters for extraction were optimized prior to the BLM study.

3.1.1.1. Selection of solvents

Solvent plays a key role in LM based separation process. Ideally, solvents should have low volatility, low viscosity, immiscibility with the aqueous phases and high extractability. In this work, both conventional hazardous organic solvents and environmentally benign vegetable oils were tested. The extraction capacity of each pure solvent (without adding any extractant in organic phase) was measured as % extraction (Table 3.1). It was observed that negligible transfer of solute Cd(II) took place when *n*-heptane and mustard oil were used as the solvent. On the other hand, maximum extraction (92%) was observed with Parachute® coconut oil. Other organic solvents such as chloroform, toluene, *iso*-octane, dichloroethane and vegetable oils such as soybean oil and sunflower oil showed the extraction as 63.90%, 5.33%, 3.61%, 2.76%, 19.50% and 17.92%, respectively [21].

Table 3.1: Performance of various solvents for extracting Cd(II) in absence of any extractant in two phase study *(pH of aqueous phase = 6.5, time of stirring = 6 h)*

Solvent	% Saturated fatty acids	Extraction (%)
Coconut oil	92.4	92.10
Soybean oil	14.4	19.50
Sunflower oil	5−16	17.92
Mustered oil	10−12	0.79
Chloroform	−	63.90
Toluene	−	5.33
Iso-octane	−	3.61
Dichloroethane	−	2.76
n-heptane	−	0.060

High extraction capacity of coconut oil, even in absence of any extractant, is not surprising. Coconut oil contains maximum amount of saturated fatty acids as compared to other vegetable oils [1, 84]. The chemical composition of common coconut oil was reported in Appendix-I. It has 45.9%–50.3% lauric acid ($CH_3(CH_2)_{10}COOH$). Chen *et al*. [85] described the mechanism of metal ion complexation with fatty acid by the following equation:

$$M^{++} + 2CH_3(CH_2)_{10}COOH \leftrightharpoons M[CH_3(CH_2)_{10}COO]_2 + 2H^+ \quad (3.1)$$

In other words, fatty acid itself serves the purpose of an extractant in this case.

Moreover the interfacial tension of coconut oil (with Milli-Q® deionized water) is minimum too (Table 2.2). The lower interfacial tension (13.9 $mN.m^{-1}$) favored the interphase mass transfer of solute. Coconut oil showed highest extraction and it is environmentally benign too. Hence, Parachute® coconut oil was chosen as the suitable solvent for further studies.

3.1.1.2. Effect of pH of feed phase

In order to study the effect of pH of feed phase, two phase equilibrium study was carried out at different pH ranging from 3 to 8. The extraction of cadmium (II) increases with increase in pH up to 6.5 and decreases thereafter as shown in Fig. 3.1. The experiments were performed in absence of any extractant in organic phase. In the mildly acidic condition (pH = 6.5), cadmium is ionized and cations (Cd^{++}) are available in the feed phase for subsequent complexation at aqueous–organic interface. The saturated fatty acids of carbon chain C_{10} to C_{14} (*viz.*, lauric, myristic, caprylic acids) present in coconut oil act as good extractant of Cd^{++} as described in Section 3.1.1.1. The extraction of cadmium (II) increased at higher pH since cadmium (II) stays in cationic form at mild acidic condition [21].

In higher acidic condition of aqueous phase, extraction decreases because cadmium forms H_2CdCl_4 complex at higher acidic condition (low value of pH) and this complex in turn forms a co-ordination complex with some components of coconut oil at the aqueous-organic interface [1]. Formation of cation ceases towards the neutrality and/or alkalinity of feed phase solution. Hence, pH of aqueous phase was maintained at 6.5 in the subsequent experiments.

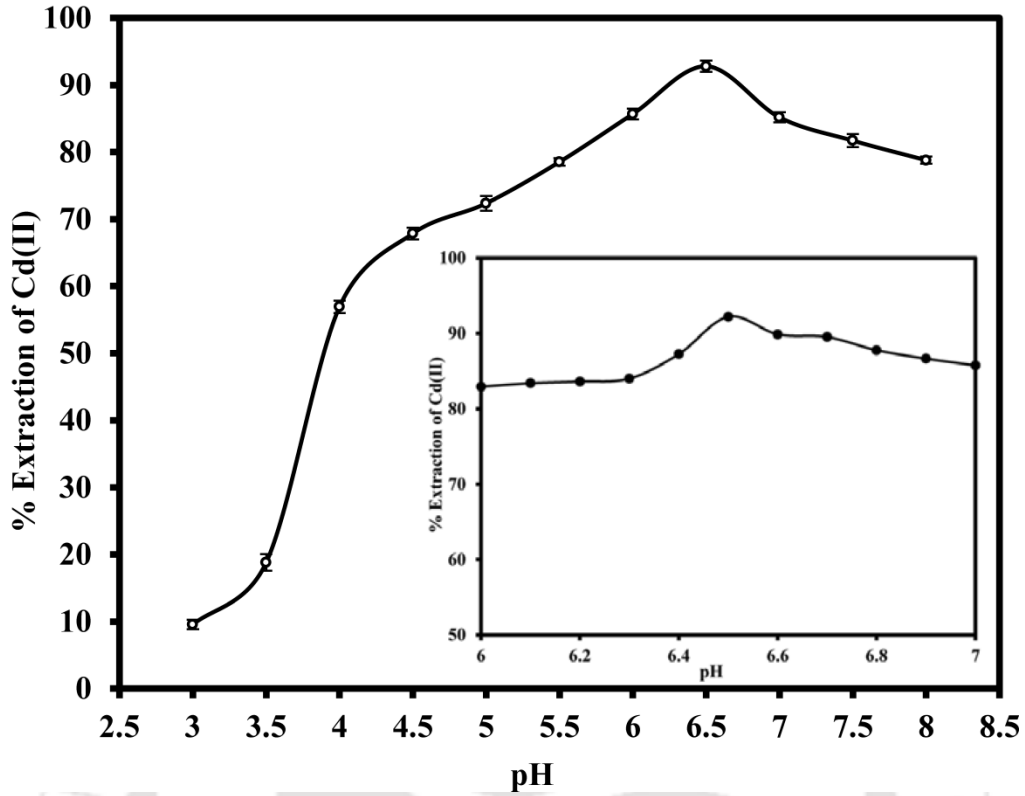


Figure 3.1: Effect of pH on the equilibrium distribution of Cd(II) in absence of extractant: (*initial concentration of aqueous phase = 5 ppm, V_F = V_{Org} = 20 mL, stirring speed = 200 rpm, duration of extraction = 6 h and T = 25 ^oC).*

3.1.1.3. Effect of initial feed concentration

The effect of initial feed concentration on the extraction of Cd(II) was studied by varying the feed concentration in the range of 1 to 9 ppm in absence of any extractant in the organic phase. The experimental results are shown in Fig. 3.2. At 5 ppm initial feed conc. of Cd(II) for the extraction efficiency was about 92%. Since most of the experiments attained equilibrium within 6 h, experiments were terminated at 6 h only. For example, the equilibrium was not reached in 6 h when the initial feed concentration was decreased to 1 ppm; the extent of extraction was the lowest in this case too. At a lower initial feed concentration, the driving force for the solute transportation between the aqueous and organic phases remains low too [86].

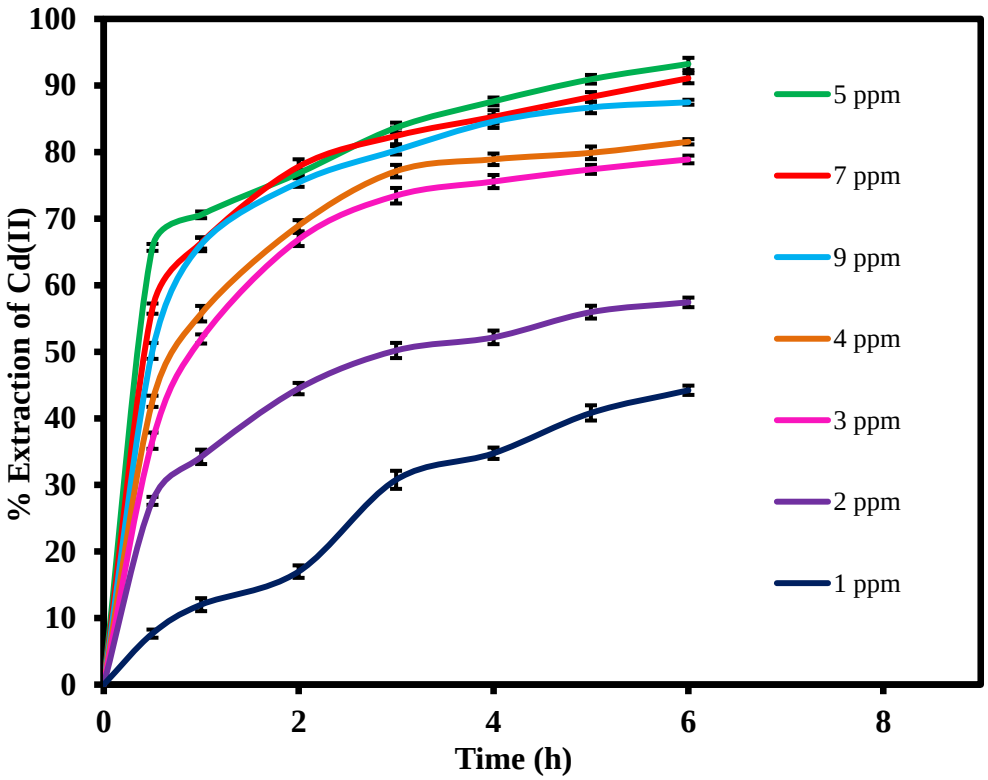


Figure 3.2: Effect of initial feed concentration of Cd(II) in absence of extractant on the two phase equilibrium distribution: *(V_F = V_{Org} = 20 mL, pH_F = 6.5, stirring speed = 200 rpm, t = 6 h and T = 25 ^oC).*

3.1.1.4. Selection of extractant

The effects of various extractants (DMOA, D2EHPA, Aliquat 336, TOA, and TBP) and their concentrations in the organic phase (coconut oil as a solvent) on the equilibrium distribution of cadmium (II) have been studied, with concentration varying in the range of 0 to 2% (v/v). Concentration of extractant is defined as (volume of extractant)/(volume of membrane phase without extractant) or in short (v/v). The results are reported in Fig. 3.3. When the extractant is present in the membrane phase, the formation of cadmium-amine complex in the feed-membrane interface takes place which increases the mass transfer through the feed/membrane interface and eventually yields higher distribution coefficient (henceforth termed as DC). Detailed mechanism can be seen in section discussing three phase experimental results. Fig. 3.3, shows that DMOA yields better extraction of Cd(II) from aqueous solution. The

experiments were conducted for various concentrations of extractant *viz.* 0, 0.01, 0.05 and 0.1% (v/v) DMOA in the organic phase. The experimental results were reported in Fig. 3.4. The optimality in the DC at 0.1% (v/v) DMOA indicates the membrane phase has reached its saturation for the complex. It is also observed that the saturation capacity reduces due to the presence of excess amount of extractant. This reduction is reflected from the lower DC obtained at higher extractant concentration.

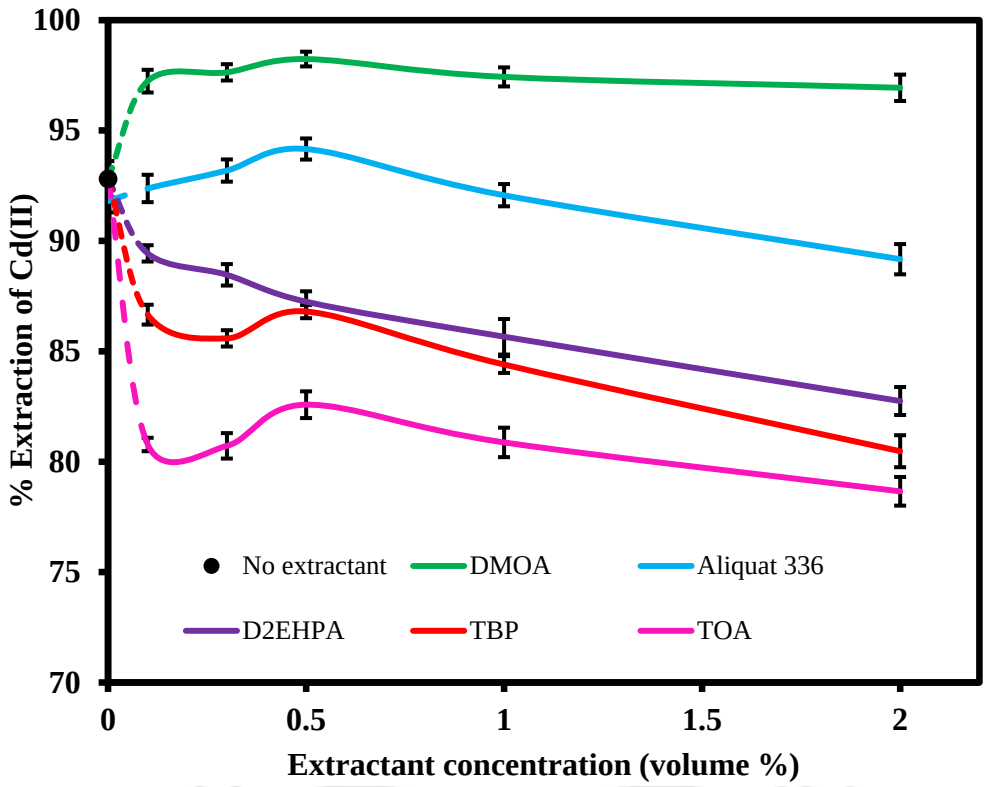


Figure 3.3: Effect of extractant concentration on the equilibrium distribution of Cd(II): *(initial feed sol. conc. = 5 ppm, V_F = V_{Org} = 20 mL, pH_F = 6.5, duration of extraction (t) = 6 h, stirring speed = 200 rpm, T = 25 ^oC).*

However, the optimum concentration of extractant should also depend upon the ratio of volume of membrane phase to volume of feed phase and the initial concentration of feed phase. It is observed that in presence of extractant (0.1% (v/v) DMOA), extraction of Cd(II)

reached 97% within 1 h and in absence of extractant it was only 65.27% within the same period of time (Fig. 3.4).

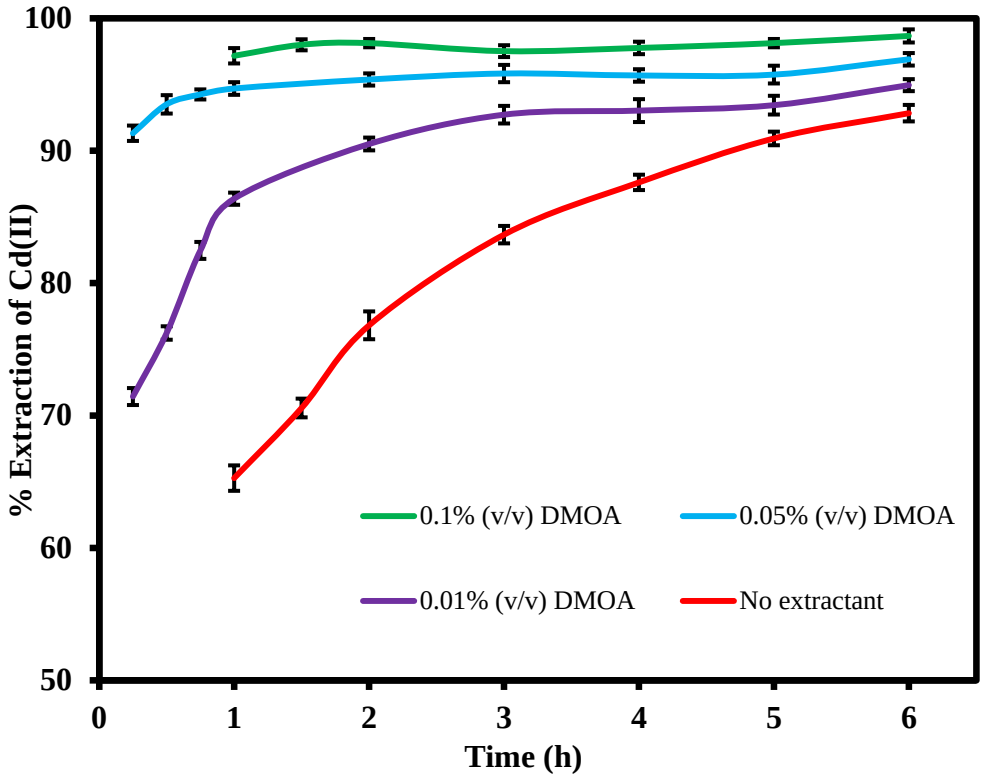


Figure 3.4: Effect of extractant concentration on the extraction time of Cd(II): *(initial feed sol. conc., = 5 ppm, V_F = V_{Org} = 20 mL, pH_F = 6.5, extractant conc., (DMOA) = 0, 0.01, 0.05 and 0.1% (v/v), stirring speed = 200 rpm, T = 25 ^oC).*

3.1.1.5. Selection of stirring condition

Stirring is an important operation that dictates how quickly the system approaches the equilibrium. The effect of stirring speed on the extraction of Cd(II) in two phase study was carried out in the range of 50 to 250 rpm, while keeping all other parameters constant. The effect of stirring speed was measured in two cases: Case I - with 0.1% (v/v) DMOA (for 1 h duration) and Case II - without extractant (for 6 h duration). Increased stirring speed enhanced Cd(II) extraction. This increase is marginal in Case I but it is very significant in the Case II (Fig. 3.5). The effect was negligible for stirring speed beyond stirring speed of 200

rpm. Thus, the optimum stirring speed was observed at 200 rpm under given conditions. From the results of various experiments it was evident that a stirring time of 1 h is enough to attain almost an equilibrium distribution in the two phase study in presence of extractant. Hence the stirring time of 1 h was adopted for further experimentation.

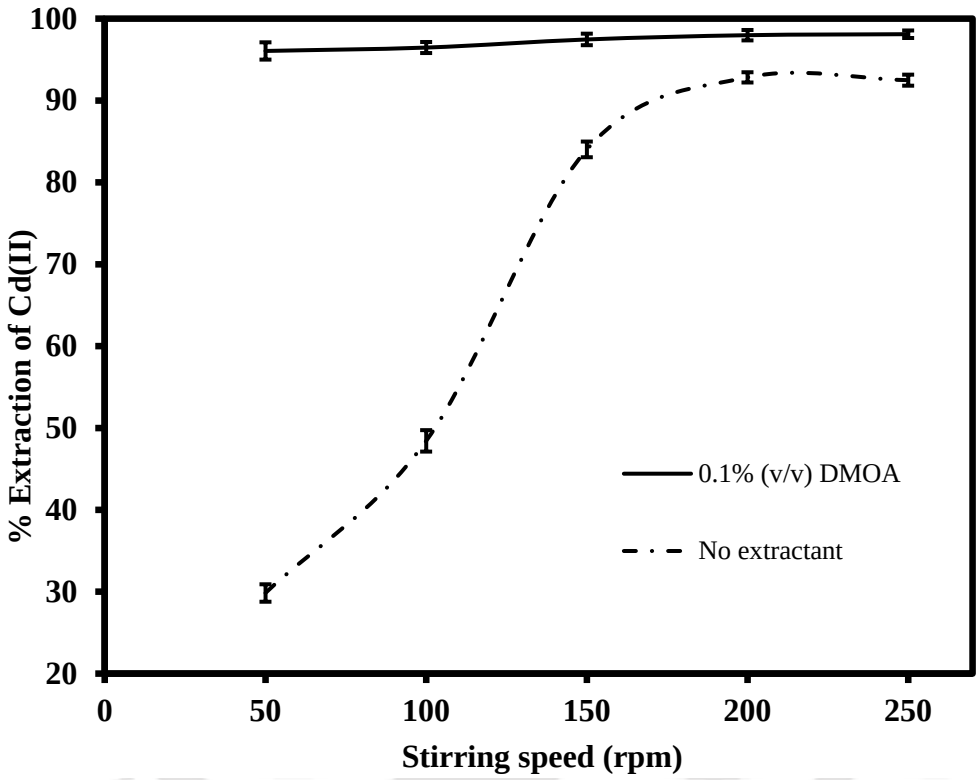


Figure 3.5: Effect of stirring speed for extraction of Cd(II) in the two phase equilibrium distribution: (*V_F = V_{Org} = 20 mL, pH_F = 6.5, concentration of extractant = 0.1% (v/v) DMOA, t = 1 h and T = 25 ^oC).*

3.1.1.6. Effect of temperature

The effect of temperature, on the % extraction of Cd(II) in the two phase study, was examined at 25, 30, 35, 40, 45 and 50 ^oC. The effect of temperature was measured with and without extractant in organic phase. It is observed (Fig. 3.6) that increase of temperature enhances the distribution coefficient of Cd(II) when no extractant is added in the organic phase and an optimum condition is achieved at 35 ^oC. However, the distribution coefficient

drops sharply above 35 ^{o}C. Such behavior is due to combination of various facts such as different feed/membrane interfacial reactions in absence of an extractant as mentioned in section discussing effect of feed phase pH [86]. The effect of temperature in presence 0.1% (v/v) DMOA is almost negligible for the extraction of Cd(II) in the range of temperature studied.

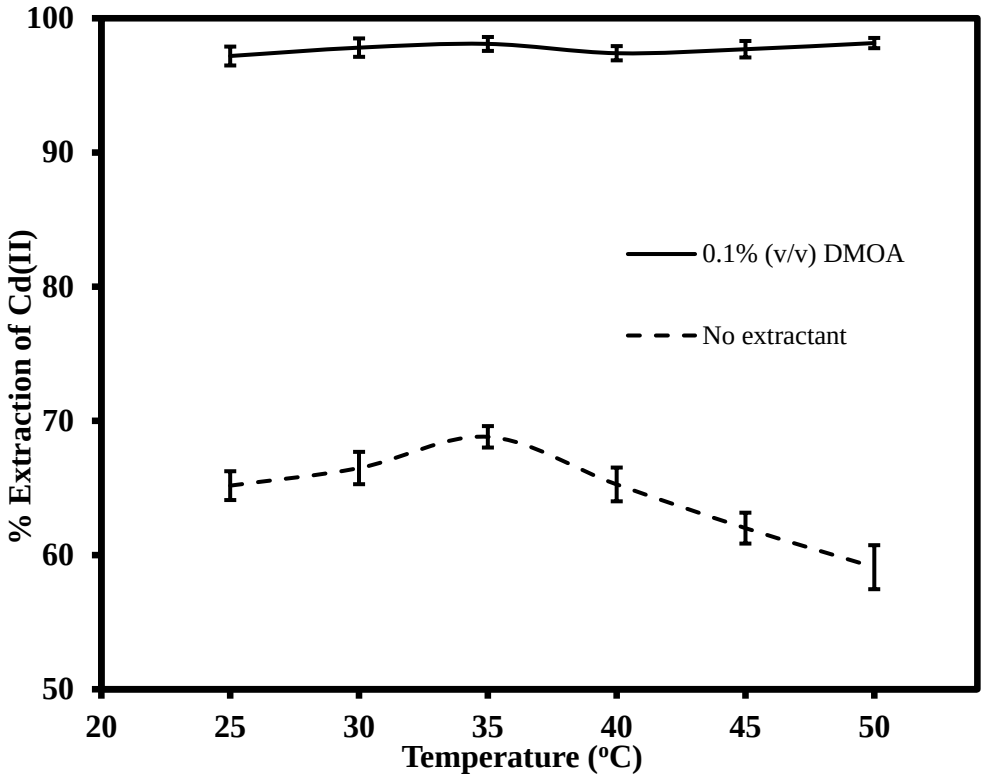


Figure 3.6: Effect of temperature on the separation of Cd(II) in two phase study: *(V_F = V_{Org} = 20 mL, pH of aqueous phase = 6.5, stirring speed = 200 rpm and t = 1 h).*

3.1.2. BLM study with organic phase comprising DMOA as carrier

Based on results of two phase equilibrium study, three phase studies were performed through the BLM configuration. Na_2 – EDTA was selected as the stripping agent as it is found to be very good metal chelating agent [69, 87, 88]. Stripping phase concentration was optimized for efficient stripping. Subsequently, the effects of other parameters such as pH of feed phase,

carrier concentration and concentration of stripping phase were re-optimized for maximum possible yield from the process in terms of extraction (Eq. (2.2)) and recovery (Eq. (2.3)).

At acidic pH, an increase in concentration of H^+ in the feed solution forms H_2CdCl_4 and it does not dissociate enough to form enough quantity of $CdCl_4^{2-}$ that would form the complex with the cation $(R_1^2R_2NH^+)$. So, extraction is not favorable at very low pH. On the other hand, protonation of DMOA is inadequate at much higher pH and $R_1^2R_2NH^+$ does not form that would make complex with $CdCl_4^{2-}$. Thus there must be an optimum pH of operation which has been discussed later in section. The schematic diagram of co-transport mode for Cd(II) extraction has been reported in Fig. 3.7.

Reaction mechanism for the separation of cadmium is as follows.

Complexation of Cd(II) by chloride ions in the feed solution

$$Cd^{2+} + 4Cl^- \rightleftharpoons CdCl_4^{2-} \quad (3.2)$$

Reaction of DMOA (denoted as $R_1^2R_2N$) at the feed/membrane interface with HCl in the feed solution

$$R_1^2R_2N\,(org) + H^+Cl^-\,(aq) \leftrightharpoons R_1^2R_2NH^+Cl^-\,(org) \quad (3.3)$$

In the feed, $CdCl_4^{2-}$ is exchanged with Cl^- of $R_1^2R_2NH^+Cl^-$ in the membrane phase

$$2R_1^2R_2NH^+Cl^-\,(org) + CdCl_4^{2-}\,(aq) \leftrightharpoons (R_2NH^+)_2\,CdCl_4^{2-}\,(org) + 2Cl^-\,(aq) \quad (3.4)$$

The stripping reaction

$$(R_1^2R_2NH^+)_2\,CdCl_4^{-2}\,(org) + Na_2 - EDTA\,(aq) \leftrightharpoons R_1^2R_2NH^+Cl^-\,(org) + Cd(EDTA)\,(aq) + 2NaCl\,(aq) \quad (3.5)$$

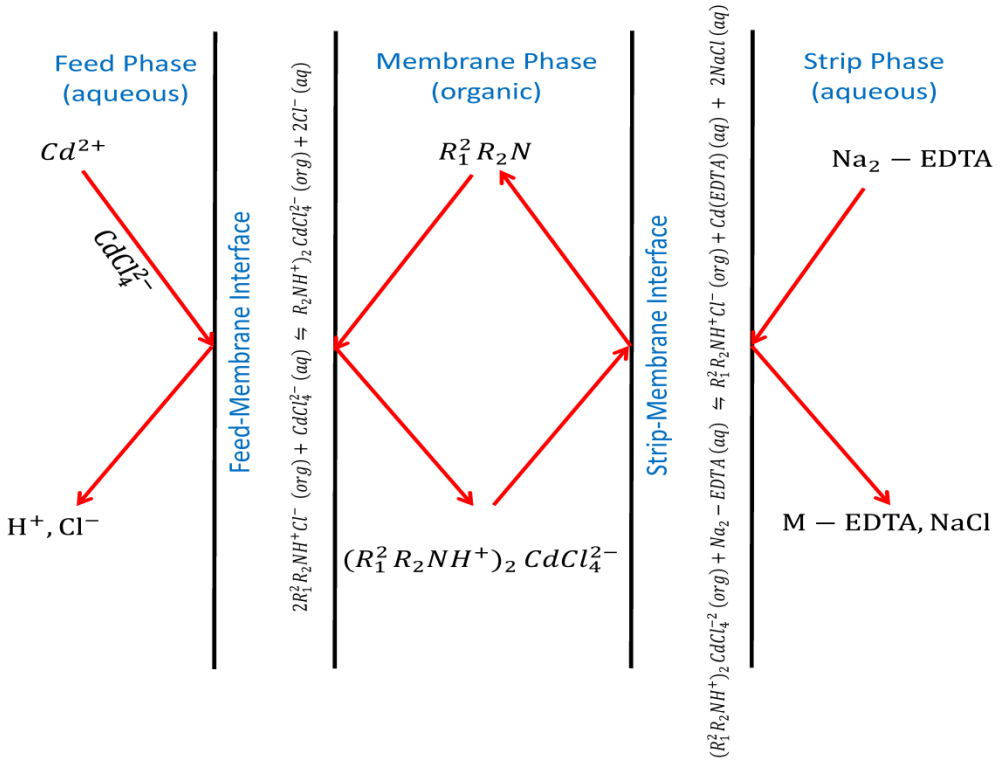


Figure 3.7: Schematic diagram of co-transport mode for Cd(II) extraction.

3.1.2.1. Effect of strip phase concentration

The choice of the stripping agent is a key factor in facilitated transport by LM. The high transport efficiencies are obtained from the suitable stripping agent. The present work was carried out by using Na_2–EDTA as a stripping agent after referring to literature in the similar research field [69]. The effect of Na_2–EDTA concentration on the transport of Cd(II) was studied in the range of 0.005–0.04 M Na_2–EDTA. The results of both extraction and recovery are shown in Fig. 3.8. It was observed that the separation increases with the increase in stripping agent concentration up to 0.015 M Na_2–EDTA, followed by a decrease in extraction. The optimum stripping agent concentration was attained at 0.015 M Na_2–EDTA. The stripping agent should re-extract the Cd(II) at the strip-membrane interface to form Cd-EDTA complex [69, 88, 89]. However, the recovery, though maximum at 0.015 M Na_2–EDTA, is very low. This is possibly due to stabilization of the complex,

$(R_1^2 R_2 N R_2 N H^+)_2\ CdCl_4^{2-}$ (Fig. 3.8) in the organic phase. Na_2-EDTA is unable to re-extract efficiently from the complex. This indicates that though DMOA is a very good carrier for extraction, it can't be efficiently used for the separation until and unless a stronger stripping agent than Na_2-EDTA is found out. However, 0.015 M Na_2-EDTA was chosen as the stripping agent for the further experimentations keeping DMOA as the carrier to investigate whether the change of other parameters can improve the recovery.

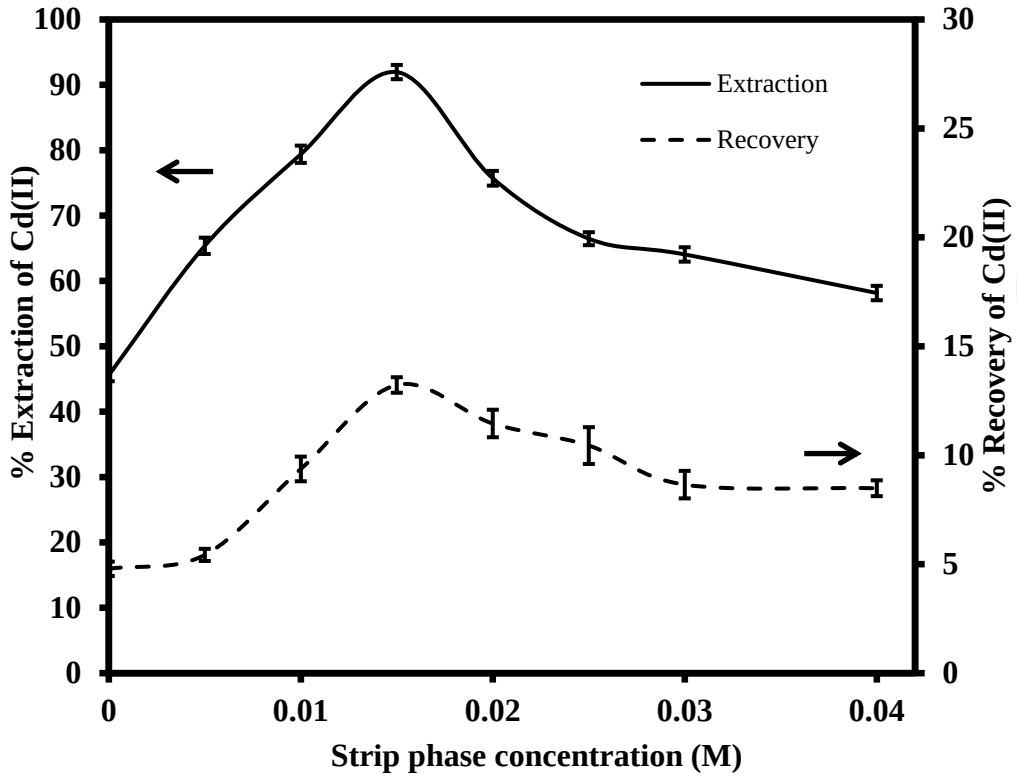


Figure 3.8: Effect of strip phase (Na_2–EDTA) concentration on separation of cadmium (II): *(initial feed sol. conc., = 5 ppm, pH_F = 6.5, V_F = V_S = 65 mL, V_{Org} = 30 mL, carrier (DMOA) conc., = 1% (v/v) and t = 6 h).*

3.1.2.2. Effect of carrier concentration

Experiments were performed with varying carrier concentrations in the range of 0–2% (v/v) and the results were reported in Fig. 3.9. When the carrier is present in the membrane phase, the formation of Cd-DMOA complex (Eq. (3.4)) in the feed-membrane interface takes place

which increases the mass transfer through the feed/membrane interface and eventually yields higher separation. The optimum carrier concentration in organic phase was found as 1% (v/v) for 92% extraction. It is observed that at 1% (v/v) DMOA, solvent gets saturated by the carrier. Any more addition of carrier in the membrane phase does not improve the efficiency of extraction; on the contrary, it reduces the extraction capacity due to enhanced viscosity of the membrane phase. This downfall of extraction is reflected from the lower DC obtained at higher carrier concentration.

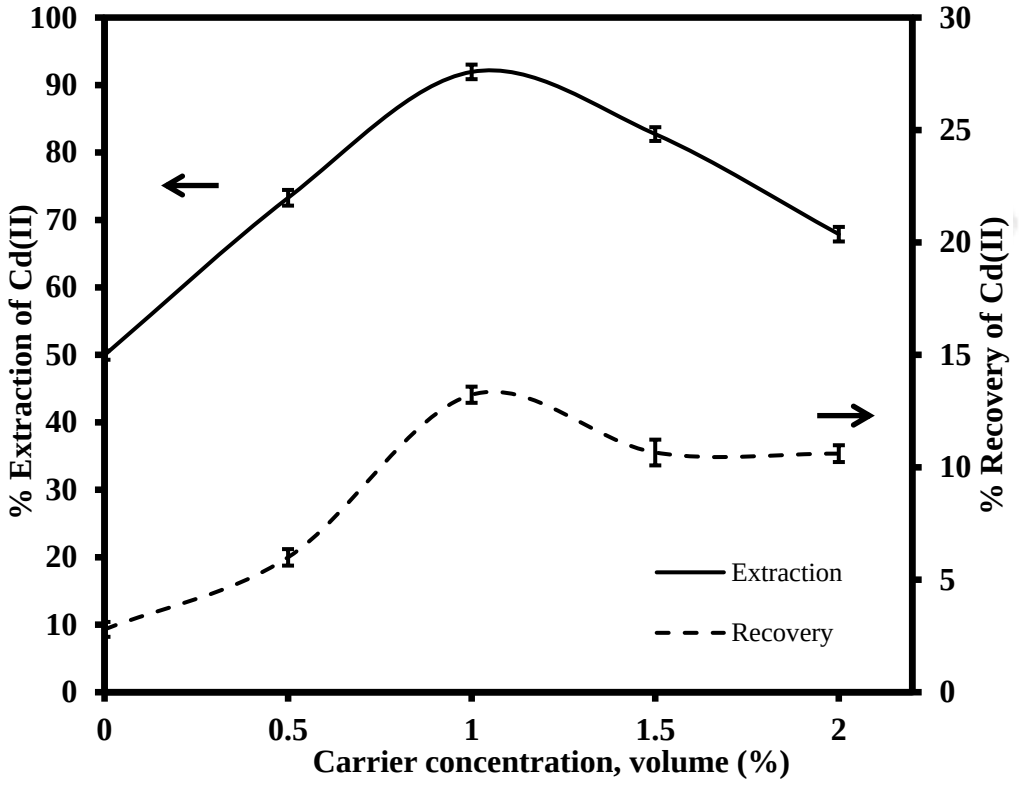


Figure 3.9: Effect of carrier concentration on separation of cadmium (II): *(initial feed sol. conc., = 5ppm, pH_F = 6.5, V_F = V_S = 65 mL, V_{Org} = 30 mL, strip conc., = 0.015 M Na_2–EDTA, pH_S = 4.76 and t = 6 h).*

The optimum carrier concentration is very high as compared to that in two phase equilibrium studies due to two reasons. Firstly, optimum carrier concentration depends upon the volume ratio of membrane phase to feed phase and the other reason is the difference in available

interfacial area through which the solute is transported. 13% recovery of Cd(II) was obtained at the optimum carrier concentration. The reason for such low recovery is already explained in the previous section.

3.1.2.3. Effect of pH

The transport process of cadmium in the presence of a basic (alkaline) carrier (such as DMOA) is driven by a concentration gradient of protons. Thus, feed phase pH plays an important role in the cadmium transport. Experiments were performed with pH variation in the range of 3 to 8 with coconut oil as solvent and 0.015 M Na_2–EDTA as stripping agent. The extraction efficiency (%) of Cd(II) increases with increase in pH of feed solution up to 6.5, as was observed also in two phase study (already discussed in Section 3.1.1.2). Hence the results are not reported here.

The effect of stripping phase (0.015 M Na_2–EDTA solution) pH on the separation of cadmium was measured in the range of 2–9. It was observed that the strip phase recovery is increased with increase in pH in the lower pH region and the recovery declines at higher pH region. It attains a maximum at pH of 4.76 (Fig. 3.10). In very high acidic conditions there are excess amount of chlorine ions which possibly compete with the Cl^- of complex and creates a problem for recovery of Cd(II). On the other hand, Na_2-EDTA is more stable in lower acidic and alkaline condition of strip phase, leading to the difficulty of substitution reaction taking place at the membrane-strip interface for stripping of Cd(II).

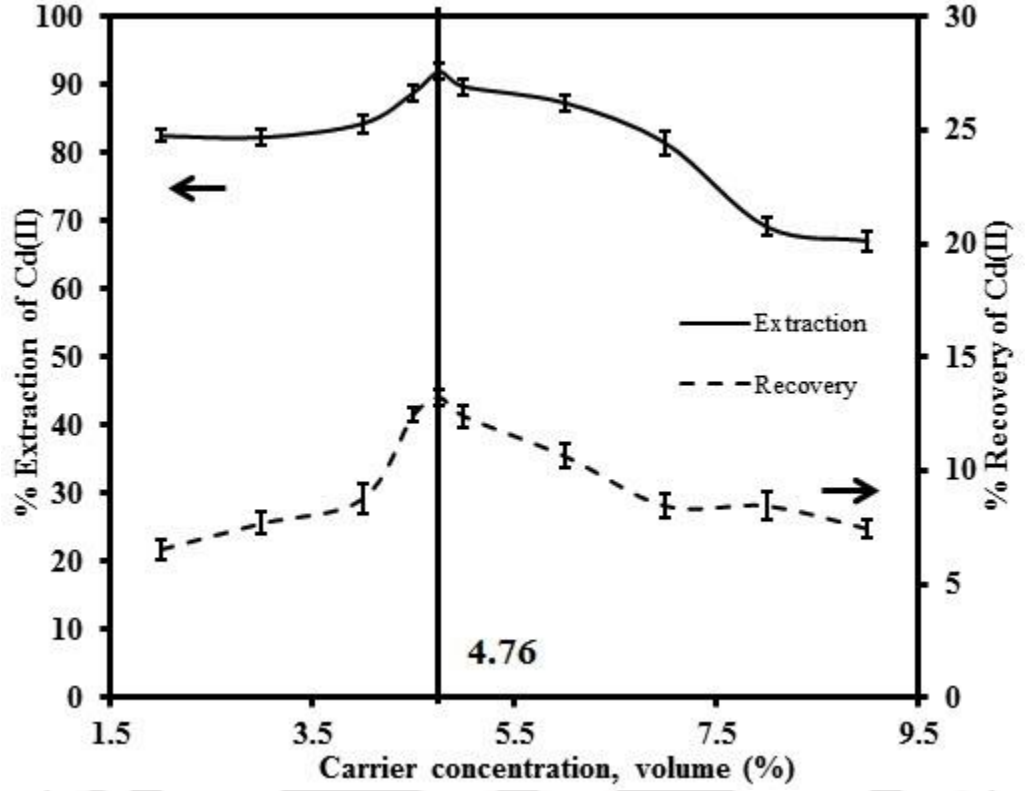


Figure 3.10: Effect of strip phase solution pH on separation of cadmium (II): *(initial feed sol. conc., = 5 ppm, pH_F = 6.5, V_F = Vs = 65 mL, V_{Org} = 30 mL, carrier (DMOA) conc., = 1% (v/v), strip conc., = 0.015 M Na_2–EDTA, and t = 6 h).*

3.1.2.4. Effect of initial feed concentration

The variation of initial feed concentration on the transport of cadmium (II) was studied in the concentration range of 3–8 ppm. The effect of initial feed concentration on extraction and recovery results are shown in Fig. 3.11. Experiments were performed with 1% (v/v) carrier concentration and strip phase concentration of 0.015 M. Both the extraction and recovery were found less for the initial feed concentration of 3 and 8 ppm as compared to that of 5 ppm. The extraction (%) and recovery (%) were recorded on 92% and 13% respectively for initial feed concentration of 5 ppm. The above fact could be attributed to the following reason [86]: The extraction process depends on the feed phase pH as discussed in section before. With changes of initial cadmium (II) concentration in the feed the amount of HCl requirement also changes as can be understood from the reaction mechanism reported in

section discussing the three phase experiment. This in turn changes the pH of the feed and thus the behavior of extraction and recovery. In the above study all the experiments were carried out at the feed phase pH of 6.5 which yielded maximum extraction of cadmium (II) for which the initial feed concentration was always 5 ppm.

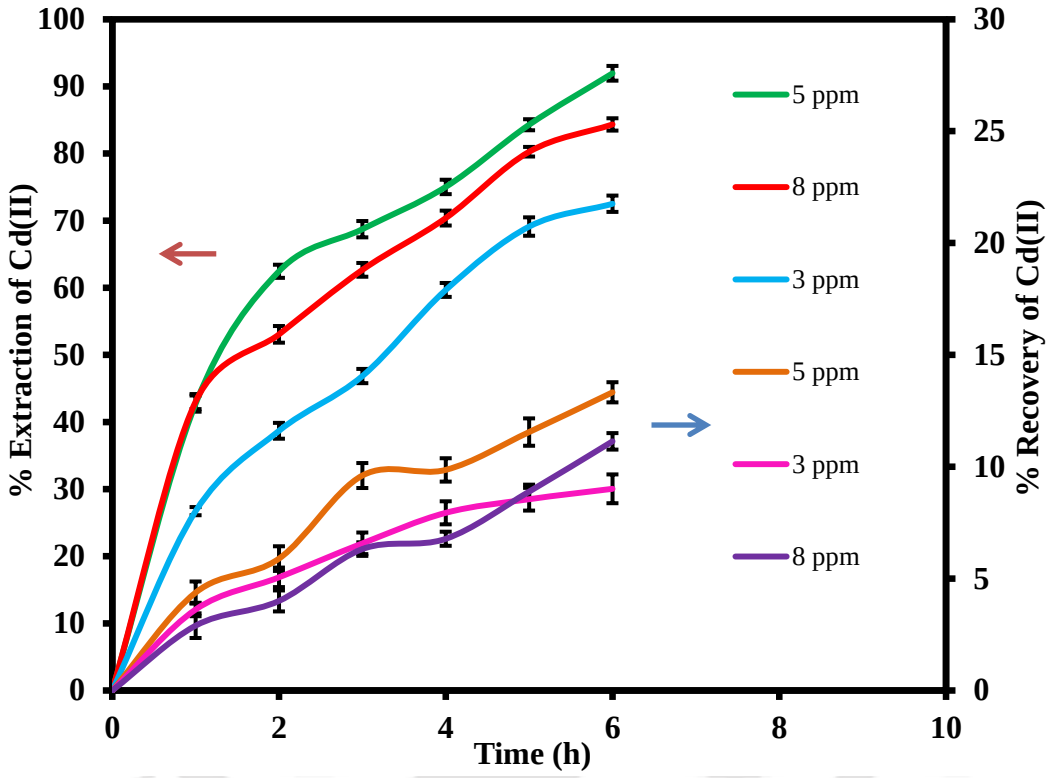


Figure 3.11: Effect of initial feed concentration on separation of cadmium: *(pH_F = 6.5, V_F = V_S = 65 mL, V_{Org} = 30 mL, carrier (DMOA) conc., = 1% (v/v), strip conc., = 0.015 M Na_2–EDTA, pH_S = 4.76 and t = 6 h.*

3.1.2.5. Fed batch system

Experiments were performed in a fed batch system where feed solution was changed after every 6 h keeping the membrane and strip phase as intact. This experiment was carried out in the same BLM set up in order to test whether LM and/or strip phase are able to separate the more and more Cd(II) from feed phase if solute is added in it. Four runs of the experiments were performed through the best operating condition, *viz.* feed phase concentration = 5 ppm,

pH = 6.5, 1% (v/v) DMOA as a carrier in coconut oil, strip phase concentration and pH of 0.015 M Na_2–EDTA and 4.76 respectively. The Cd(II) extraction was obtained 92% after first run of 6 h (Fig. 3.12). With increasing number of runs stripping is marginally increased. Extraction is slightly decreased. The figure indicates that the membrane phase is capable of further extraction of Cd(II) if placed in the feed phase till the availability of DMOA in the membrane phase and till the saturation capacity of the Cd-DMOA complex is reached in the membrane phase.

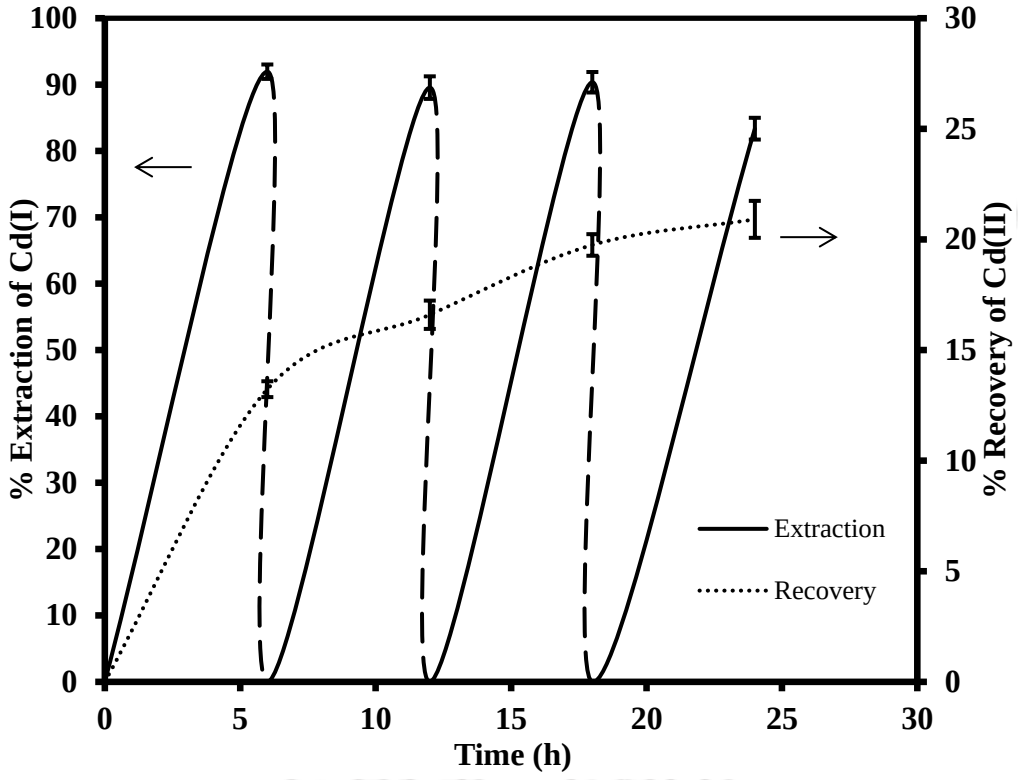


Figure 3.12: Effect of fed batch operation on separation of cadmium: *(initial feed sol. conc., = 5 ppm, pH_F = 6.5, V_F = V_S = 65 mL, V_{Org} = 30 mL, carrier (DMOA) conc., = 1% (v/v), strip conc., = 0.015 M EDTA, and pH_S = 4.76.*

This is because the amount of DMOA in the membrane phase is much higher than the required amount to form complex with Cd(II). However, the marginal decrease in extraction efficiency with every batch fed is possibly due to increased viscosity of the membrane phase

as well as the crowding of the complex, $(R_1^2 R_2 N R_2 N H^+)_2\ CdCl_4^{2-}$ formed in the membrane phase as stated earlier. On the other hand, the % recovery increased from 13% in the first run to slightly above 20% at the end of final run. This exercise confirms that the fed-batch study would be a more useful way of using LM based separation technique for high output domain such as industrial wastewater etc. However, low recovery of solute in the stripping phase is a real concern that needs to be addressed in the future experimental efforts.

3.1.3. Employment of Aliquat 336 as carrier in lieu of DMOA

In order to achieve higher recovery of the solute at the stripping section, few experiments were carried out where Aliquat 336 was used as a carrier in place of DMOA. Other components are unchanged *e.g.* Na_2- EDTA was used as stripping agent and coconut oil was employed as the solvent. The operating parameters are re-optimized for the changed circumstances. Initial observations revealed encouraging results as the percentage extraction was found closer to percentage stripping that essentially means very little accumulation of solute in the membrane phase. A case study with concentration of feed phase = 5 ppm Cd(II), pH of feed phase = 6.5; solvent = coconut oil, carrier = 1% (v/v) Aliquat 336 , concentration of strip phase = 0.015 M Na_2- EDTA, pH of strip phase = 4.7, the percentage extraction and percentage stripping after 6 h of experiment was found to be 61% and 52% respectively. Although efficiency of extraction by Aliquat 336 is less than that of DMOA, efficiency of stripping is much better than with Aliquat 336. This has been due to the fact that Aliquat 336 ($R_1^2 R_2 N R_2 N H^+ Cl^-$) itself is a stable material and just acts as a carrier for transport of $CdCl_4^{2-}$ through anion exchange with Cl^-. Na_2-EDTA is able to re-extract Cd(II) efficiently from the membrane phase. Thus it is argued that though DMOA is best carrier among the tried ones based on extraction, Aliquat 336 is better carrier for recovery of

Cd(II) which is the ultimate objective of this work. Hence, efficacy of Aliquat 336 as carrier was thoroughly investigated in the subsequent studies.

After optimizing operating conditions of LM in order to get maximum transportation of Cd(II), it is also intended to try out a second heavy metal *viz.* Pb(II) and find the efficiency of transport of Pb(II) at the same operating condition that has been optimized for Cd(II). This is to study a potential case of existence of binary pollutant in the target wastewater. A possible solute transport methodology and the results of subsequent experimentations are given below.

3.1.3.1. Solute transport methodology

The target metals (solutes) in this study, *i.e.* lead (II) and cadmium (II), are referred to as a common symbol "M" for easy understanding. The transport methodology of M from feed phase to the stripping side interface has been illustrated below:

The extraction reaction is favorable in acidic pH of feed solution. This is because of following two reasons. Firstly, cadmium salt forms insoluble cadmium hydroxide in presence of OH^- ions and its complex with carrier is not formed [1]. On the other hand, due to lack of Cl^- ions, MCl_4^{2-} is not formed. The formation of MCl_4^{2-} is mandatory for its complexation with carrier. In the feed solution, metal chloride (MCl_2^{2-}) salts are transformed into anion (MCl_4^{2-}) in presence of HCl. Solute-carrier complex of $(R_4N^+)_2\,MCl_4^{2-}$ are formed at the feed-membrane interface in presence of carrier agent, Aliquat 336 (expressed as $R_4N^+Cl^-$). Due to the concentration gradient of solute-carrier complex in the LM, it diffuses from the feed-membrane interface to membrane-strip interface. The schematic diagram for the transportation of both the metals (Cd(II) and Pb(II)) in the co-transport mode is reported in Fig. 3.13.

The reaction mechanism for the transportation of cadmium (II) and lead (II) is as follows:

Complexation of metal (M) by chloride ions in the feed solution:

$$MCl_2 + 2Cl^- \rightleftharpoons MCl_4^{2-} \tag{3.6}$$

In presence of carrier agent, MCl_4^{2-} is exchanged with Cl^- of $(R_4N^+)_2MCl_4^{2-}$ in the membrane phase:

$$2R_4N^+Cl^-(org) + MCl_4^{2-}(aq) \rightleftharpoons (R_4N^+)_2\,MCl_4^{2-}(org) + 2Cl^-(aq) \tag{3.7}$$

The stripping reaction:

$$(R_4N^+)_2\,MCl_4^{2-} + Na_2 - EDTA \rightleftharpoons 2R_4N^+Cl^- + M - EDTA + 2NaCl \tag{3.8}$$

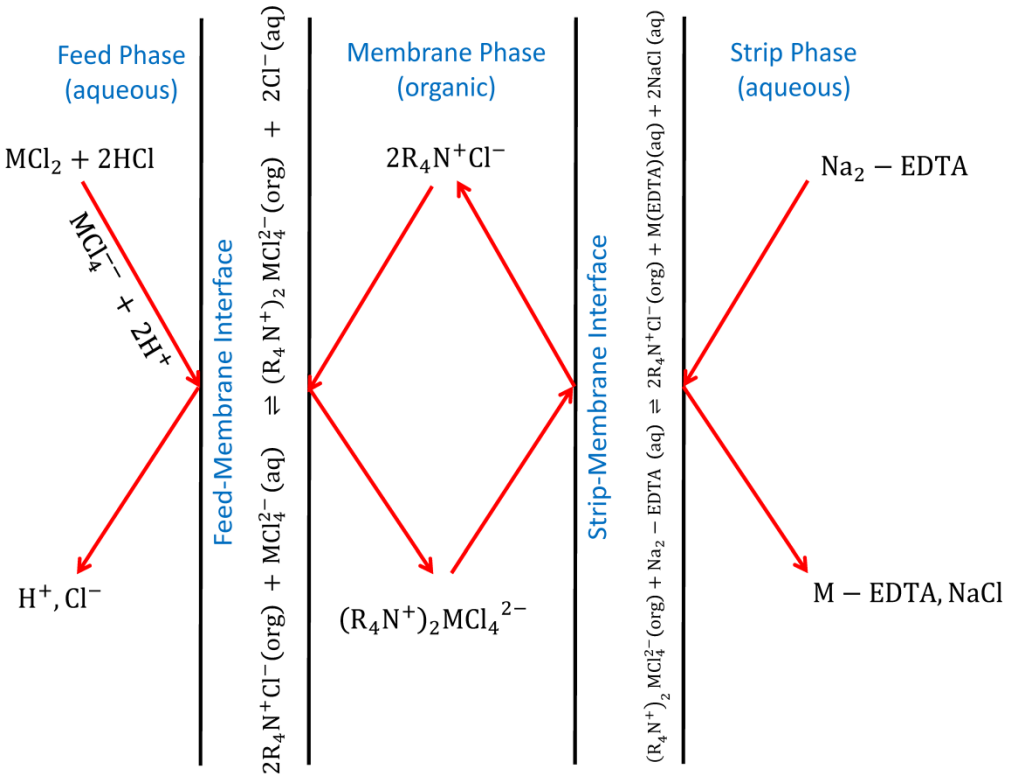


Fig. 3.13: Schematic diagram of transport of heavy metals through LM

3.1.4. Two phase equilibrium study

3.1.4.1. Role of extractant on duration of extraction

The addition of extractant (*i.e.* Aliquat 336) in organic phase facilitates quick extraction. Because presence of extractant results in the formation of complex at the aqueous-organic interface which subsequently diffuses in the organic phase. The diffusivity is enhanced through the complexation. Experimental findings presented in this sub-section provide the justification of the addition of extracant. Experiments were performed both in presence (0.5% v/v Aliquat 336) as well as in absence of extractant in organic phase. It is observed that extraction of cadmium (II) (maximum 92%) in 2 h in presence of extractant. On the other hand, equilibrium (maximum 92%) is reached after 6 h when no extractant was added to the organic phase (Fig. 3.14). Hence, further experiments were carried out in presence of extractant and for 2 h only.

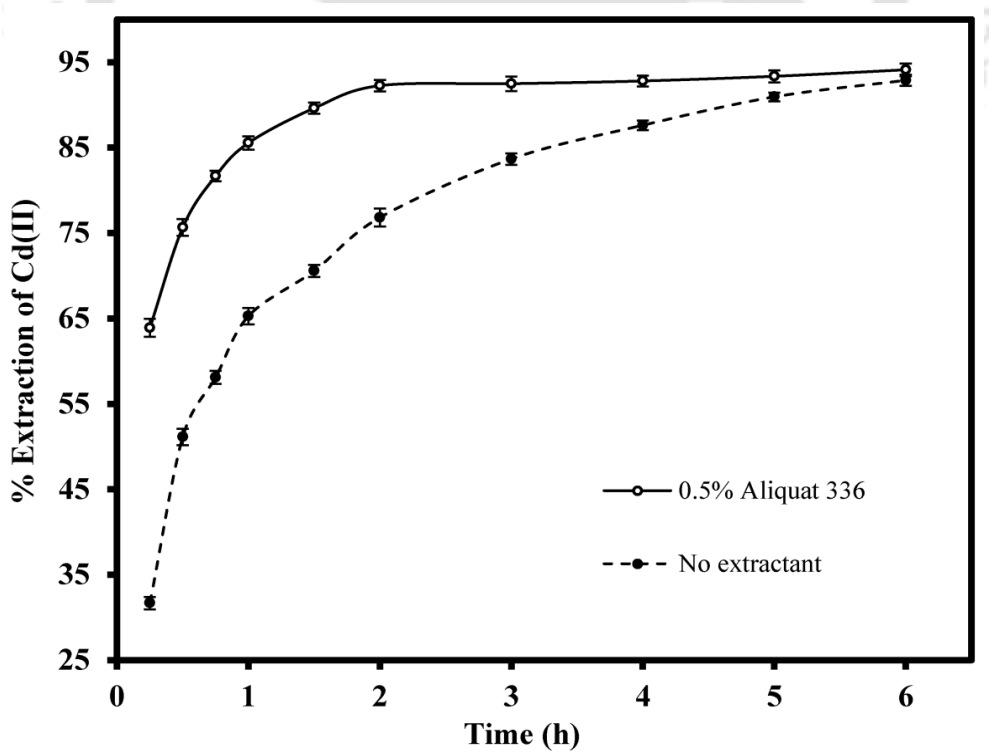


Figure 3.14: Role of extractant on the time to reach the equilibrium: *(initial concentration of aqueous phase = 5 ppm, $V_F = V_{Org}$ = 20 mL, pH_F = 6.5, stirring speed = 200 rpm and T = 25 ^oC).*

3.1.4.2. Effect of concentration of extractant

The experiments were carried out with various cencentrations of extractant in the range of 0 to 2% (v/v). Results are reported in Fig. 3.15. The addition of extractant initially enhances the rate of extraction for obvious reasons however extraction declines beyond a concentration of 0.5% (v/v) due to the crowding effect. The excess extractant creates an extra resistance to solute transfer from aqueous phase to the organic phase at the interface. Hence, 0.5% extractant in organic phase is considered as the saturation concentration for the extraction purpose and in the subsequent studies this concentration of extractant was maintained.

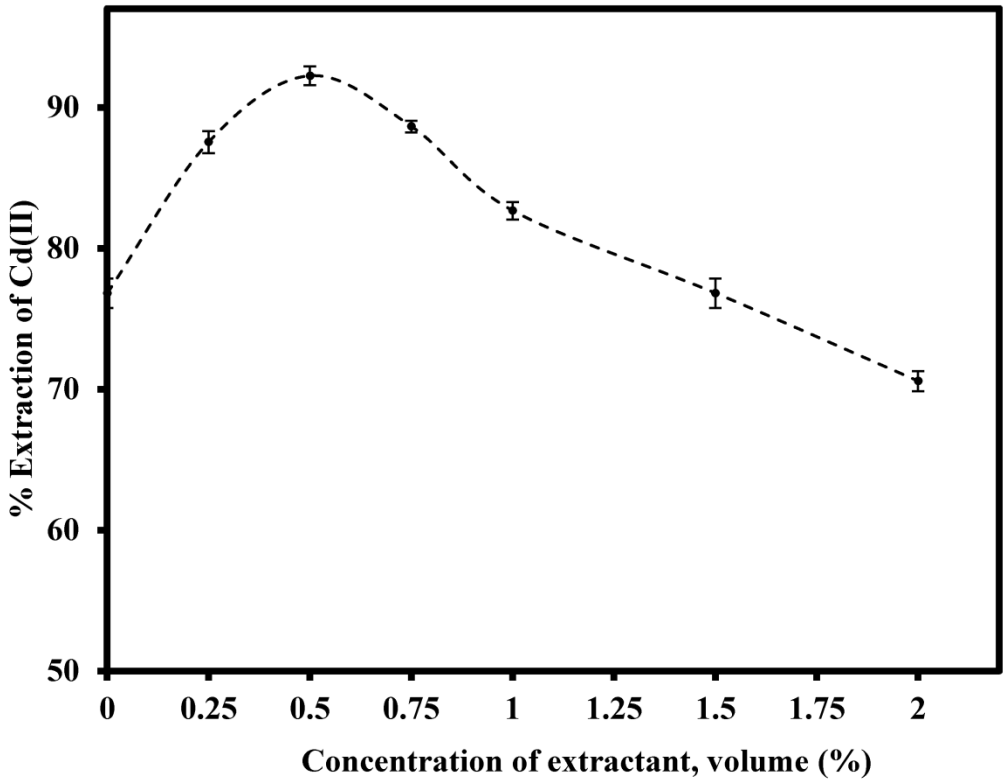


Figure 3.15: Effect of concentration of extractant on the extraction of Cd(II): (*initial concentration of aqueous phase = 5 ppm, V_F = Vo_{rg} = 20 mL, pH_F = 6.5, stirring speed = 200 rpm, t = 2 h and T = 25 ^oC).*

3.1.4.3. Effect of speed of stirring

A gentle stirring was provided to the mixture of aqueous and organic phases to minimize the concentration polarization of the solute and/or solute-extractant complex at the interface. The higher the speed of stirring, higher was the reduction of concentration polarization. However, at high stirring speed emulsion is formed between the membrane phase and aqueous feed phase. Hence, the speed of stirring was optimized for the efficient extraction. In order to determine the optimum stirring speed, two phase experiments were conducted at different stirring conditions ranging from 50 rpm to 250 rpm. The experiments were carried out for two different cases: with and without the extractant in the organic phase. The experimental results were reported in Fig. 3.16.

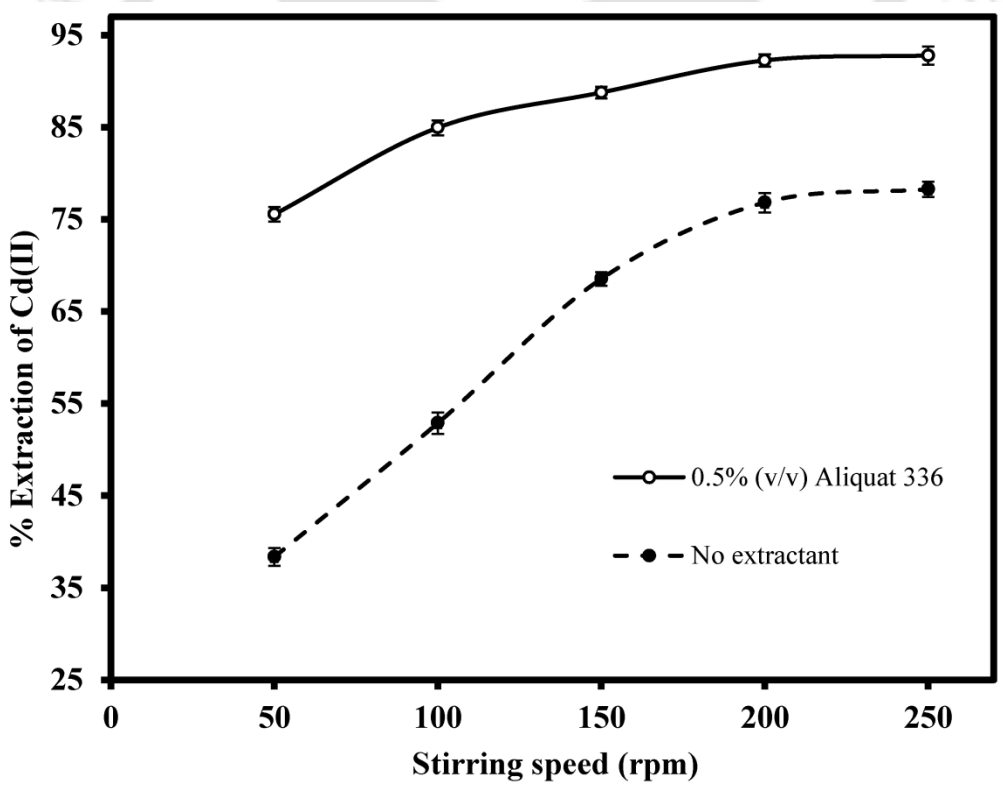


Figure 3.16: Effect of stirring speed for the separation of Cd(II) in the two phase equilibrium distribution: (*V_F = V_{Org} = 20 mL, pH_F = 6.5, concentration of extractant = 0.5% (v/v) Aliquat 336, t = 2 h and T = 25 ^oC).*

It is observed that extraction increased to a great extent with increase in stirring speed for both cases; however it is more prominent when no extractant was added to the organic phase. This kind of behavior was noticed up to 200 rpm beyond which there was practically no change in the percentage of extraction up to 250 rpm. Beyond, this speed of stirring, there was emulsion formation between the phases. Hence, optimum stirring speed was selected to be 200 rpm for further studies.

3.1.4.4. Effect of initial concentration of pollutant in aqueous phase

Initial concentration of pollutant in aqueous phase also plays a vital role in the extraction process. Earlier it was observed from Fig. 3.14 that, at 5 ppm initial concentration of Cd(II), the extraction is about 76.81% and 92.24% with no extractant and 0.5% (v/v) Aliquat 336 respectively. Similar experiments were carried out with other initial concentrations of Cd(II) ranging from 3 ppm to 10 ppm. The results are reported in Fig. 3.17. The interfacial area of solute transport in experimental setup is 19.5 cm^2. It is observed that optimum extraction is achieved with initial concentration of Cd(II) at 5 ppm. Any other initial concentration yields lower extraction. Initial concentration below 5 ppm yields comparatively low driving force for the transportation of solute between the aqueous and organic phases. The flux of cadmium (II) increases with increasing concentration in the feed phase due to higher concentration gradient. However, an optimum is reached at 5 ppm as the initial cadmium concentration over 5 ppm causes crowding effect at the aqueous side interface and causes reduction of the extraction. Hence, subsequent experiments were carried out using initial concentration of Cd(II) at 5 ppm.

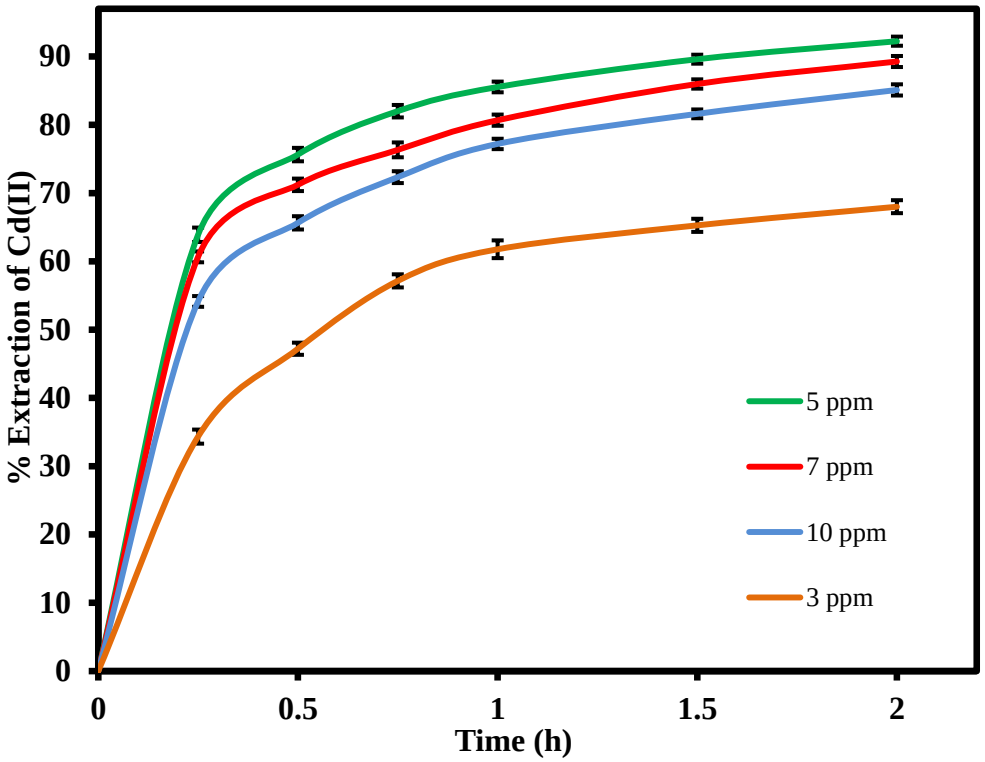


Figure 3.17: Effect of initial concentration of Cd(II) in two phase study: (*V_F = V_{Org} = 20 mL, pH of aqueous phase = 6.5, concentration of extractant = 0.5% (v/v) Aliquat 336, stirring speed = 200 rpm and T = 25 ^oC).*

3.1.4.5. Effect of temperature

The temperature range of 25 ^oC to 50 ^oC was chosen for studying the effect of temperature for the extraction of cadmium (II). The experiments were conducted both in presence of extractant (Aliquat 336) in organic phase. As it is argued before, the fatty acid of coconut oil acts as an extractant in absence of Aliquat 336. In such case, the extraction of cadmium increased with the increase in temperature and reaches an optimum value at 35 ^oC and subsequently decreases significantly with further rise in temperature beyond 35 ^oC (Fig. 3.18). Such behavior is due to combination of various facts with temperature such as different aqueous/organic interfacial reactions in absence of Aliquat as mentioned elsewhere [86]. The properties of the fatty acid change with the change of temperature that affect the % of extraction. However, in presence of Aliquat 366, the extraction was due to the more effective

extracting agent (Aliquat 336) and the change of properties of coconut oil with temperature did not affect the % extraction (92.24%). The summary of two phase equilibrium studies is tabulated in Table 3.2.

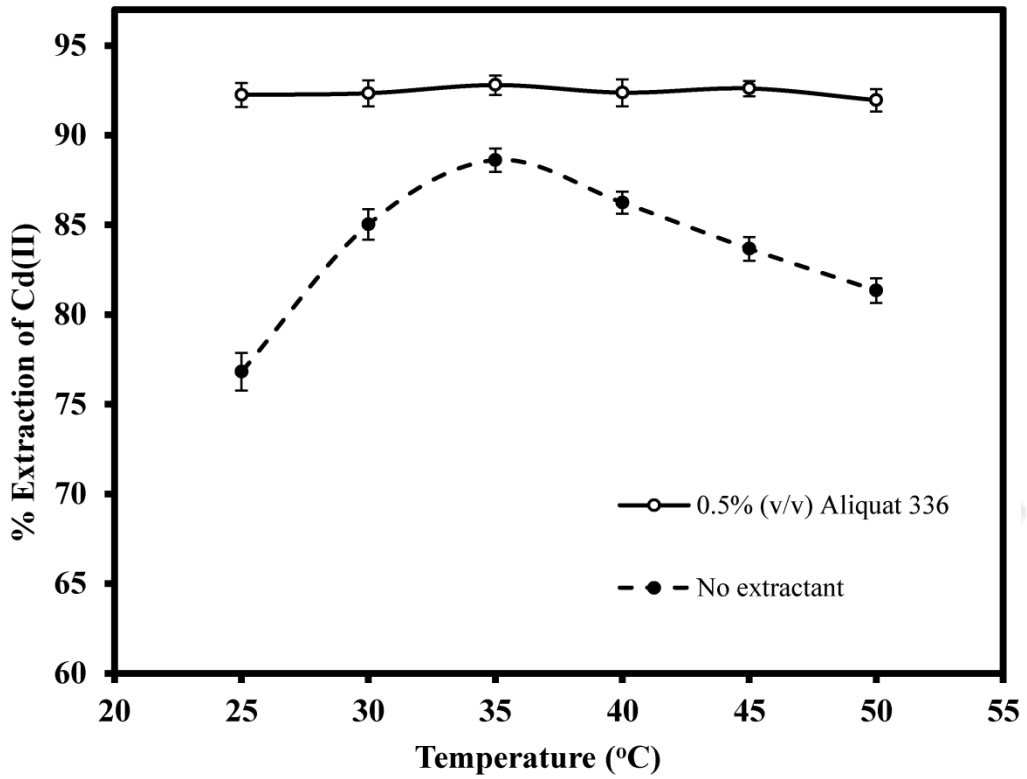


Figure 3.18: Effect of temperature on the separation of Cd(II) in two phase study: (*V_F = V_{Org} = 20 mL, pH of aqueous phase = 6.5, stirring speed = 200 rpm and t = 2 h).*

Table 3.2: Summary of optimum condition for transport of Cd(II) in two phase equilibrium study

S. No.	Parameter	Range studied	Optimum value
1	Solvent	Various vegetable oils	Coconut oil
2	pH of aqueous phase	3–8	6.5
3	Concentration of extractant	0–2% (v/v) Aliquat 336	0.5% (v/v) Aliquat 336
4	Duration of extraction	0–6 h	In absence of extractant: 6 h In presence of 0.5% (v/v) Aliquat 336: 2 h
5	Initial concentration of Cd(II) in aqueous phase	1–10 ppm	5 ppm
6	Temperature	25–50 ^{o}C	In absence of extractant: 35 ^{o}C In presence of 0.5% (v/v) Aliquat 336: significant variation
7	Speed of stirring	50–250 rpm	200 rpm

3.1.5. Transportation of solute through three phase BLM

Three phase transportation studies were performed through the BLM configuration with the operating condition obtained from two phase equilibrium studies (Table 3.2). In addition, concentration of stripping phase was optimized for efficient transportation of solute from LM to strip phase. Contrary to the two phase study where carrier is needed for complexation purpose, three phase BLM involves a de-complexation phenomena too whereby the complex is dissociated at the membrane-strip interface and frees itself for back-diffusion to the feed-membrane interface and thereby re-complexation of solute with stripping agent. Moreover, the ratio of membrane phase to feed phase was low compared to two phase equilibrium

studies. Hence, the requirement of carrier in BLM should be different than that in two phase studies. Finally, transportation efficiencies were compared for two different metals, cadmium (II) and lead (II) for the identical operational parameters.

3.1.5.1. Effect of concentration of EDTA in strip phase

Selection of stripping agent is very important for the efficient recovery of the solute. In this work, Na_2–EDTA is used as a stripping agent taking the reference of a past literature [69, 89]. Na_2–EDTA is a well-known metal chelator and it re-extracts cadmium (II) from the membrane-strip interface and forms Cd-EDTA complex (Eq. (3.8.)). Experiments were conducted with different concentration of stripping solution ranging from 0.005 M to 0.03 M Na_2–EDTA with initial feed concentration of 5 ppm, feed pH 6.5 and carrier concentration of 0.5% (v/v) in coconut oil. The experimental results are reported in Fig. 3.19. It was observed that with increase in the concentration of the stripping phase up to 0.015 M, both the extraction and recovery of the solute increased.

The maximum extraction and recovery were 72% and 64%, respectively. However, beyond 0.015 M concentration, both extraction and recovery start decreasing. Solubility of Na_2–EDTA in the strip phase and back extraction of cadmium ions to the membrane phase were the major reasons behind their reduction. These behaviors were observed also by Altin *et al*. [69]. Hence, 0.015 M Na_2–EDTA was chosen as the optimum concentration of the stripping solution.

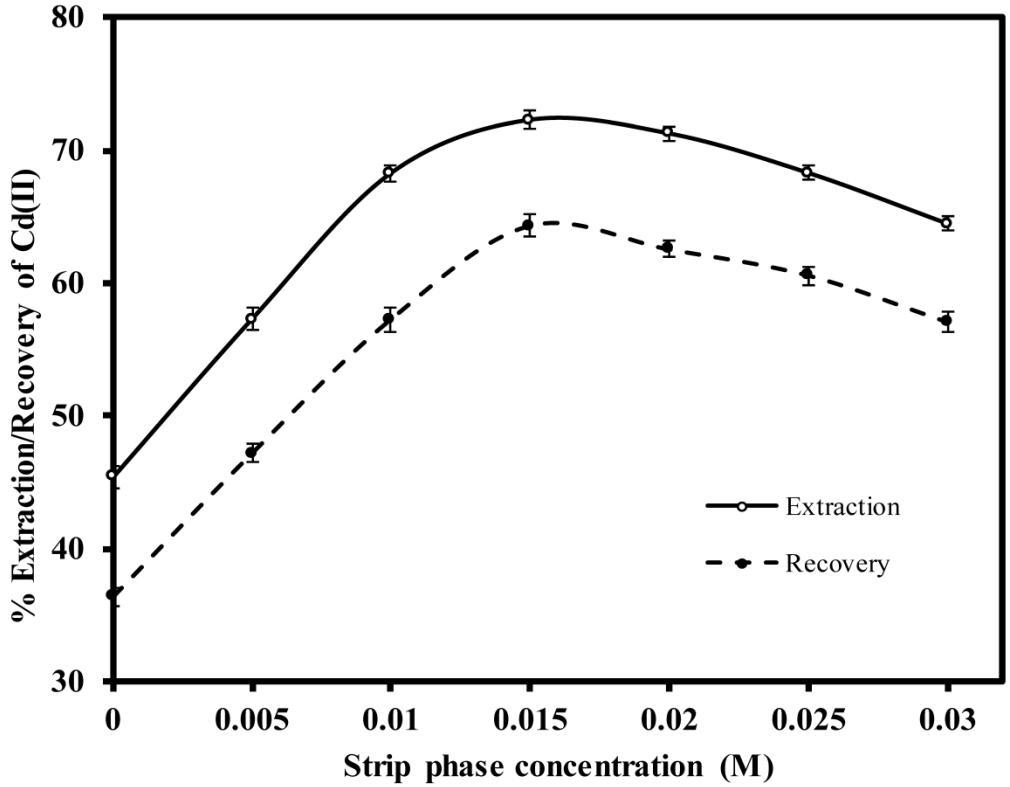


Figure 3.19: Effect of concentration of Na_2–EDTA **in strip phase on the recovery of cadmium (II): (***initial concentration of feed phase = 5 ppm, pH of aqueous phase = 6.5, $V_F = V_S$ = 65 mL, V_{Org} = 30 mL, concentration of exractant = 0.5%(v/v) Aliquat 336, t = 6 h and T = 25 ^oC).*

3.1.5.2. Effect of carrier concentration

Concentration of carrier in the LM was re-optimized by varying the concentration of the carrier in the range 0–1% (v/v). The results are reported in Fig. 3.20. According to Eq. (3.8), in presence of a carrier in the membrane phase, a metal-carrier complex (Cd-Aliquat 336 complex in this case) is formed at the feed-membrane interface which results in the increase of mass transfer rate through the interface and hence higher separation is achieved. The experiments showed that the solvent phase got completely saturated by 0.5% (v/v) Aliquat 336 and yielded the maximum extraction (72%). The carrier Aliquat 336 being very viscous (1500 mPa.s at 30 ^{o}C) increases the viscosity of the LM when added in higher concentration. The diffusion rate of the cadmium (II) complex through the LM becomes lower and the recovery decreases with the increase of carrier concentration in the LM. The optimum carrier

concentration of carrier in organic phase was thus taken to be 0.5% (v/v). An extraction of 72% and recovery of 64% were achieved in 6 h of operation.

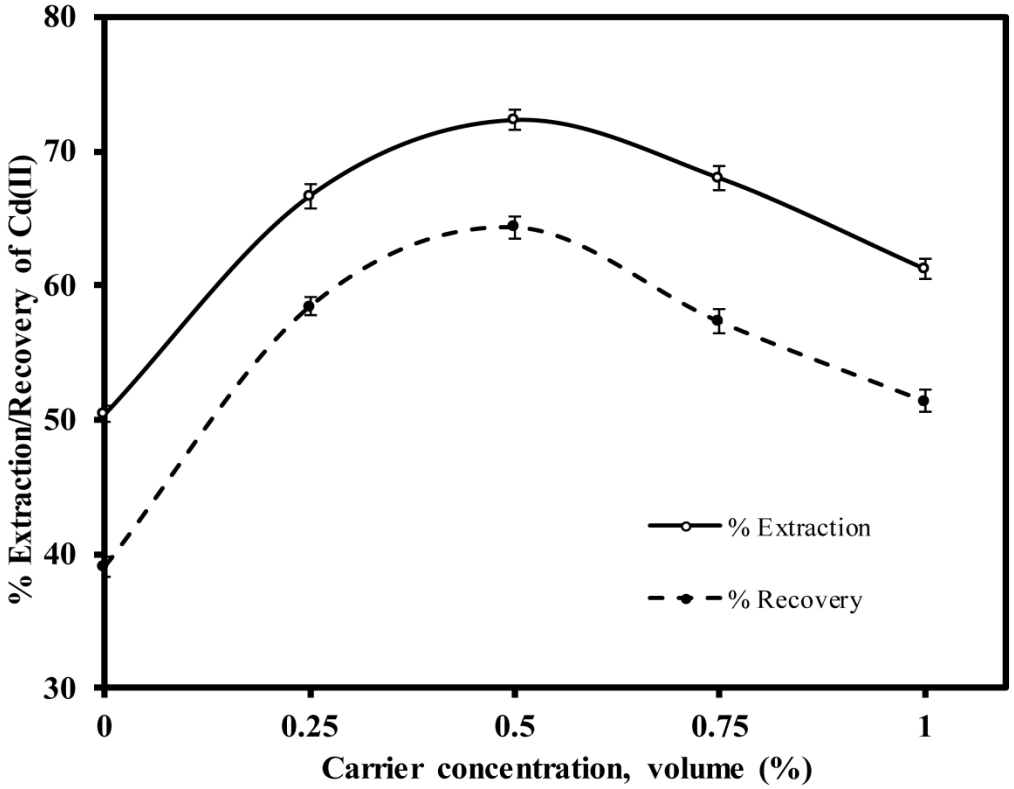


Figure 3.20: Effect of concentration of carrier in organic phase on the transportation of Cd(II): (*initial concentration of feed phase = 5ppm, pH_F = 6.5, V_F = V_S = 65 mL, V_{Org} = 30 mL, concentration of* Na_2–EDTA *in strip phase = 0.015 M, pH of feed phase = 6.5, pH of strip phase = 4.76, duration of three phase operation = 6 h).*

3.1.5.3. Individual transportation of cadmium (II) and lead (II)

It is neccessary to examine whether the operating conditions/parameters, standardized as above, are relevant in case of some other solute, lest a condition of binary pollutants should be found in the wastewater in question. In view of this, lead has been selected as another heavy metal that is widely available in the wastewater emanating from the industries that are targeted for Cd(II) mitigation. The selected LM and the various parameters optimized for cadmium (II) transport were employed for the same purpose for Pb(II). Identical conditions

of feed and stripping phases were maintained. Higher extraction (82%) and recovery (77%) were observed for transportation of lead (II). The accumulation (5%) of metal in the LM was lesser in case of transportation of Pb(II) as compared to that of Cd(II) (8%). Experimental results were reported in Fig. 3.21. The reasons could be explained by the difference in the electronic configurations of lead (II) and cadmium (II). Pb(II) has an atomic number of 82 with electronic configuration as $[Xe]4f^{14}5d^{10}6s^{1}6p^{3}$, whereas, the atomic number of Cd(II) is 48 with electronic configuration as $[Kr]\ 5s^{2}4d^{10}$.

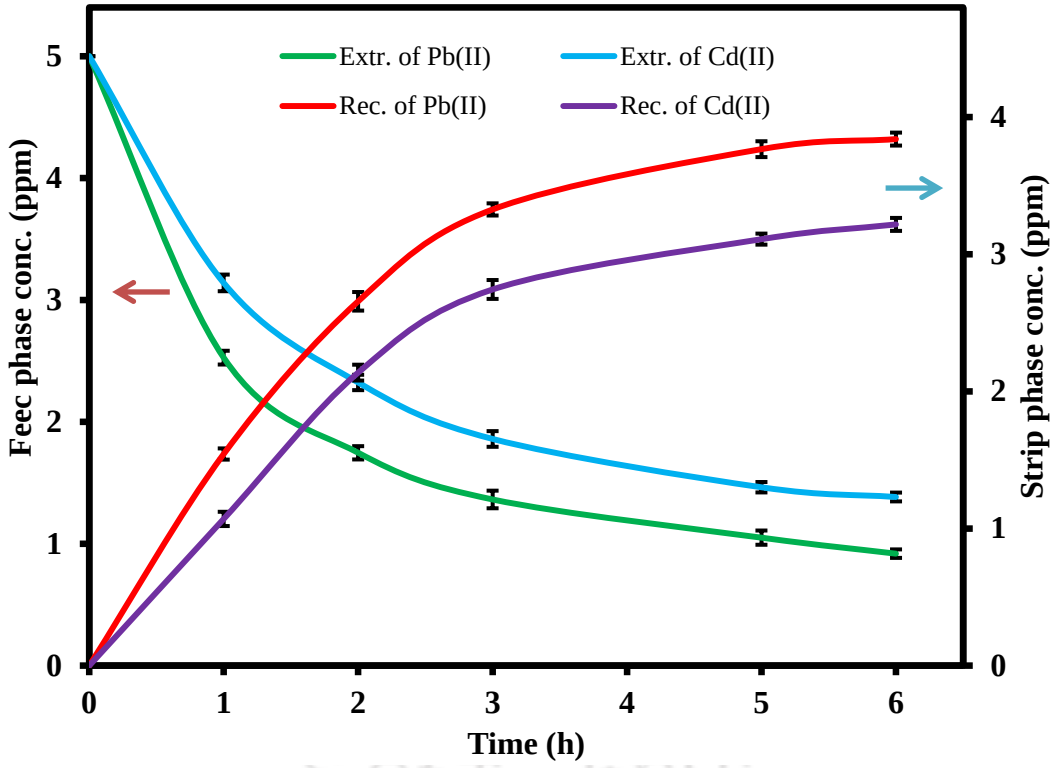


Figure 3.21: Transportation of individual metals cadmium (II) and lead (II)) through the BLM: *(initial concentration of aqueous phase = 5 ppm, pH_F = 6.5, V_F = V_S = 65 mL, V_{Org} = 30 mL, concentration of carrier = 0.5% (v/v) Aliquat 336, strip conc. = 0.015* M *Na_2–EDTA, pH_S = 4.76 and T = 25 ^{o}C).*

The stability of Pb-EDTA complex is high in comparison to the Cd-EDTA complex formed in the stripping solution of Na_2-EDTA which led to higher affinity of the Pb^{2+} ions towards

forming Pb-EDTA complex than of cadmium (II) towards forming Cd-EDTA complex. In fact, the stability constant of Pb-EDTA complex (18.0) is higher than that of Cd-EDTA complex (16.6) [88, 89]. Moreover, higher shielding effect of Pb(II) owing to its higher effective nuclear charge (5.65) compared to Cd(II) (4.35) (Slater's rule) contributed in its higher recovery [90].

Table 3.3: Summary of optimum condition for transport of Cd(II) in three phase BLM study

S. No.	Parameter		Range studied	Optimum value
1	Strip phase (Na_2-EDTA) conc.		0−0.03 M	0.015 M
2	Carrier (Aliquat 336) conc.		0−1 vol%	0.5 vol%
3	Duration of extraction/stripping		0−6 h	6 h
4	**% Extraction**	**% Recovery**	----	At the optimum conditions
	Cd: 72.33 Pb: 81.62	Cd: 64.35 Pb: 76.8		

3.2. Summary of the BLM based separation of Cd(II) and Pb(II)

- Coconut oil was found to be an ideal green solvent for this purpose.
- DMOA was found as the best extractant for extraction of cadmium (II) was 92%, but the recovery was 13% only.
- Carrier Aliquat 336 was found better extractant for both the extraction as well as the recovery of Cd(II) and Pb(II).

BLM based separation of Cd(II) and Pb(II)

- The optimal conditions for Cd(II) recovery through BLM were found as: carrier concentration = 0.5 % (v/v) Aliquat 336, stripping phase concentration = 0.015 M Na_2–EDTA.
- The maximum extraction and recovery of Cd(II) were 72% and 64% respectively whereas the same for Pb(II) were 82% and 77% with same optimum conditions.
- The transportation of lead (II) is relatively preferable due to their favorable electronic configuration and shielding effect than cadmium (II).

CHAPTER-IV

FS-SLM based simultaneous separation of Cd(II) *and* Pb(II)

CHAPTER-IV

FS-SLM based simultaneous separation of Cd(II) *and* Pb(II)

This chapter presents the experimental results of simultaneous extraction and recovery of cadmium (II) and lead (II) from their aqueous solutions through the FS-SLM. The organic and stripping phases used in the BLM study have been employed for FS-SLM too. Initially, the performance of FS-SLM is evaluated only for the transportation of single metal cadmium (II) and the process condition has been optimized for the same. Subsequently these process conditions has been employed for transporting the second metal lead (II), and further subsequently a simultaneous separation of cadmium and lead. A porous polymeric solid membrane viz. PVDF of average pores diameter of 0.2 µm is used as a support in order to hold the organic phase in FS-SLM structure. The effects of various operating conditions viz. concentration of carrier in membrane phase, concentration of stripping agent, pH of feed phase etc. are studied. The three phase transportation studies of Cd(II) are conducted from initial feed concentration of 5 ppm for 10 h. The optimum process conditions for the transportation of Cd(II) are as follows: 0.5% (v/v) Aliquat 336 as carrier agent, 0.015 M Na_2-EDTA as stripping agent, pH of 6.5 in the feed phase. For simultaneous transport of metals, the selectivity of the LM for individual metals is investigated by varying their mass ratios (Cd:Pb) in the feed solution. The preferential transportation of Pb(II) over Cd(II) through SLM can be explained by the difference in their electronic configurations and shielding effects. The transportation of Pb(II) and Cd(II), especially with increasing percentage of Pb(II) in the mixture is an important finding of this experiments. The flux of the

combined feed ratio (mass ratio) 1:4 (Cd:Pb) was found highest for the simultaneous transportation of cadmium (II) and lead (II).

4.1. Results and discussion

4.1.1. Determination of operating range of pH in feed solution

The presence of HCl in the feed phase governs the ionic state $CdCl_4^{2-}$ (Eq. (3.1)) of the solute which in turn leads to favorable complexation of carrier $(R_4N^+)_2\,CdCl_4^{2-}$, at the feed side interface. The rate of transportation of solute is directly related to the degree of complexation. In other words it is dependent on the favorable pH of the feed solution [21]. The methodology of solute transport has already been given in detailed in Chapter 3. We observed that % of extraction is low at higher pH in the feed phase (Section 3.1.1.2).

The present study has been performed with acidic feed solution only, with pH in the range of 3.0−7.0. The maximum extraction (78.77%) and recovery (67.14%) are obtained at a pH of 6.5. The experimental results are reported in Fig. 4.1. The reaction mechanism, as discussed in Section 3.1.1, indicates that cadmium (II) at a higher acidic condition of feed phase (low pH) is expected to be in the form of $CdCl_4^{2-}$ and some components of the coconut oil may form a coordination complex with the $CdCl_4^{2-}$ at the feed-membrane interface. The presence of excess chloride ions (as HCl was used for protonation) in feed phase over and above the amount of $CdCl_2$ (solute) leads to lower extraction and recovery because of competitive environment between Cl^- and $CdCl_4^{2-}$. Moreover $CdCl_4^{2-}$ is also likely to remain undissociated as H_2CdCl_4 at lower pH condition, which further inhibits extraction of Cd(II) [91]. Thus, reductions in extraction and recovery are nearly proportional to the increasing

concentration of protons (lower pH). Similar phenomena were observed by other researchers too [65, 92].

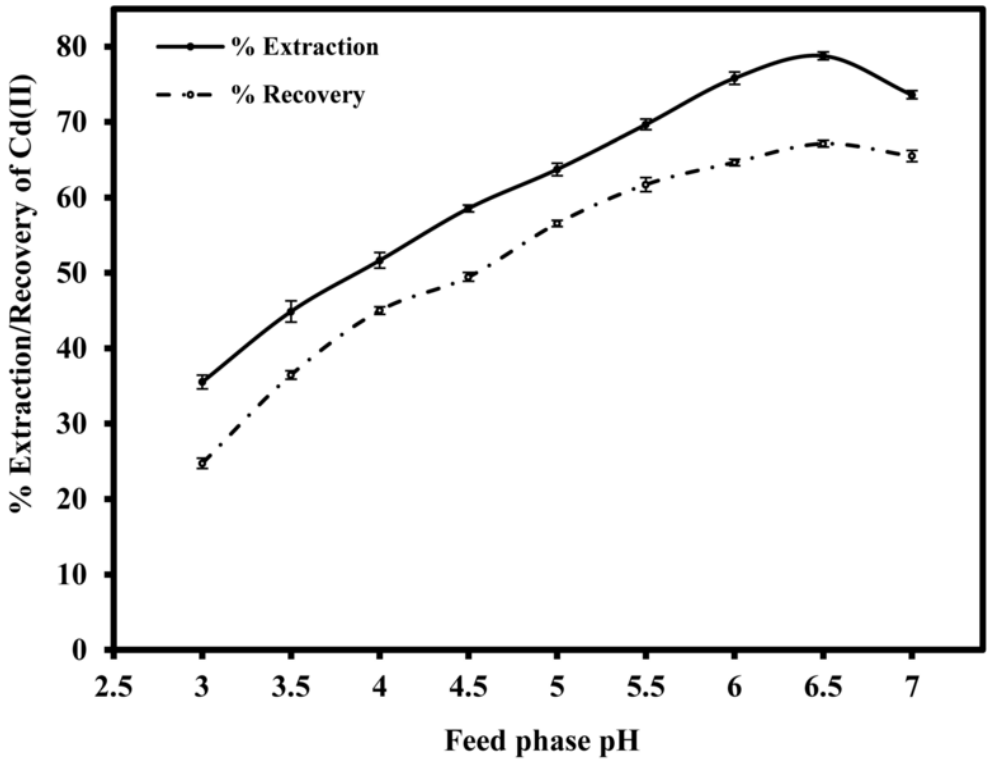


Figure 4.1: Effect of feed phase pH on separation of cadmium (II): *(initial feed sol. conc., = 5 ppm Cd(II), V_F = V_S = 250 mL, carrier conc. = 0.5% (v/v) of Aliquat 336, strip conc. = 0.015 M and run time = 10 h).*

4.1.2. Determination of suitable carrier concentration

The carrier molecules in the solvent phase undergo complexation with the solute and augment its transportation. Concentration of carrier has two opposing effects on the rate of transportation of solute. The rate of transportation increases with number of carriers due to higher rate of complexation, however excess carrier increases the viscosity of the LM that causes hindrance to the diffusion of complex. In this study, experiments were performed with varying carrier concentration in the range of 0-1% (v/v) and the results are reported in Fig. 4.2. The cadmium-carrier complex formed at the feed/membrane interface has higher

chemical affinity in the membrane phase as compared to $CdCl_4^{2-}$ and that facilitates the formation of more amounts of complexes at the interface. It is observed that an increase in carrier concentration up to 0.5% (v/v) yields higher transportation.

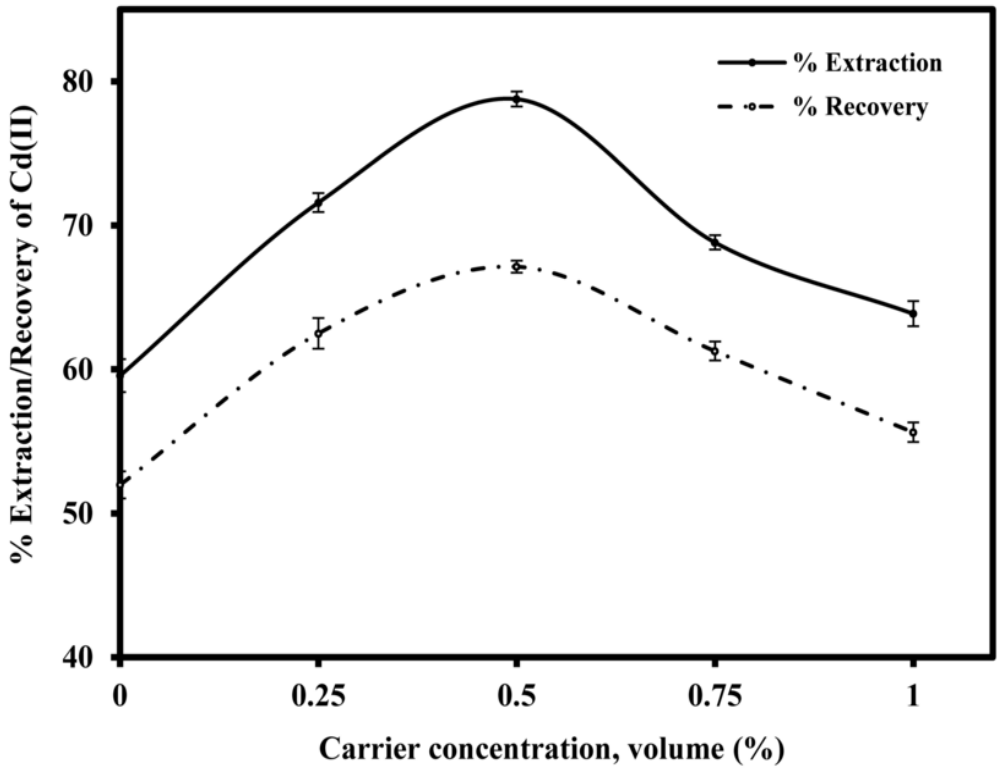


Figure 4.2: Effect of carrier concentration on the extraction of Cd(II): *(initial feed conc., = 5 ppm Cd(II), pH_F = 6.5, V_F = Vs =250 mL, strip conc. = 0.015 M and run time = 10 h).*

At the optimum carrier concentration of 0.5% (v/v), extraction and recovery of cadmium were found to be 78.77% and 67.14% respectively. Further increase of concentration of carrier eventually increases the viscosity (Table 4.1) of membrane phase resulting in the lower rate of diffusion of the complex [93]. Apart from the viscosity, the transportation of Cd(II) is also influenced by surface phenomena. The surface saturation capacity of Cd-carrier complex is very important. Increase in carrier reduces the mobility of Cd-carrier complex due to hindrance created by excess carrier and/or the complex [22].

Table 4.1: Viscosity of membrane phase with different carrier concentration in coconut oil at 25 ^{o}C

Carrier concentration (vol%)	Viscosity (Pa s)
0	0.03029
0.25	0.03259
0.5	0.03678
0.75	0.03916
1.0	0.04213

4.1.3. Determination of appropriate strip phase concentration

A suitable stripping agent and its concentration play a significant role for transportation of cadmium (II) ions. In our previous work [21] and also in the Chapter III, we reported that separation of cadmium (II) in BLM is best possible using Na_2-EDTA as stripping agent. Same stripping agent has also been used in the SLM study too. The stripping agent re-extracts cadmium (II) ions from the Cd-carrier complex at the membrane/strip interface and forms another complex Cd-EDTA in the stripping phase (vide Eq. 3.3), due to famous chelating characteristics of EDTA. The experiments were performed with varying concentrations of Na_2-EDTA in stripping solution in the range of 0.005-0.02 M and the results are reported in Fig. 4.3. The other conditions maintained in this experiment are as follows: initial concentration of feed solution is 5 ppm, pH is 6.5 and 0.5% (v/v) carrier is added in coconut oil to prepare the membrane phase. Both the extraction and recovery increase with the increasing concentration of the stripping solution up to 0.015 M. With further increase in concentration of stripping agent, both extraction and recovery decrease marginally.

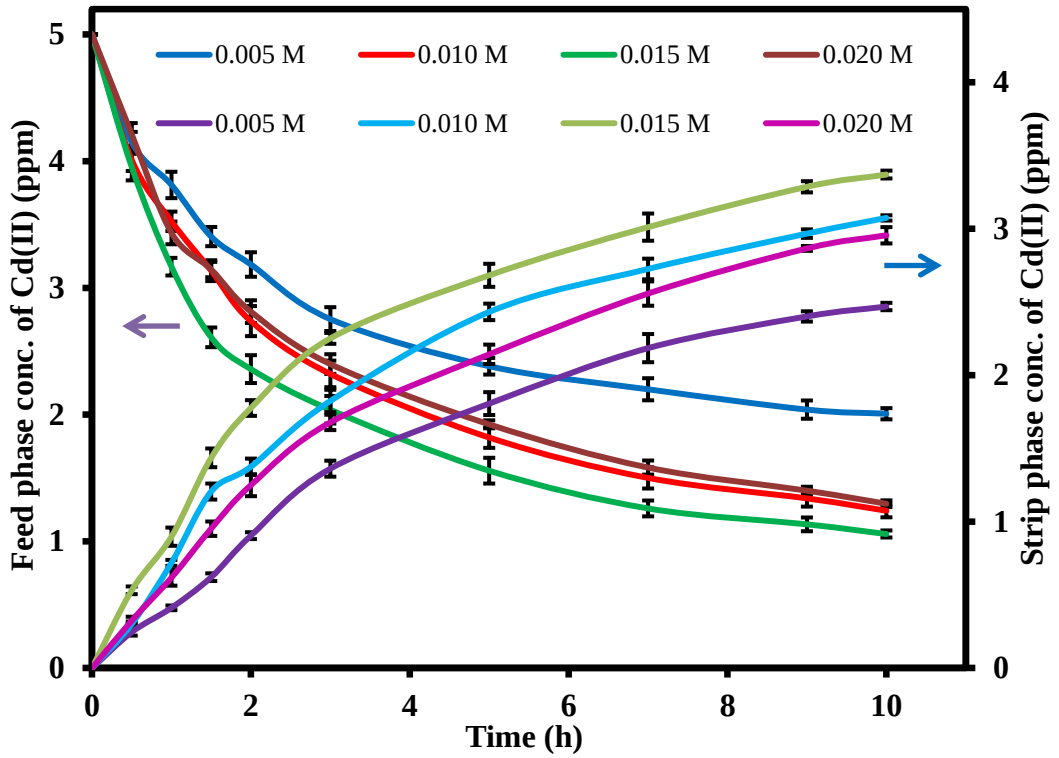


Figure 4.3: Effect of strip phase (Na_2-EDTA) concentration: ***(****initial feed conc. of Cd(II) = 5 ppm Cd(II),* pH_F *= 6.5,* V_F *= Vs = 250 mL, carrier conc. = 0.5% (v/v) and run time = 10 h).*

The adverse effect of the higher concentration is due to the saturation solubility of Na_2-EDTA in the strip phase and also for the reversible nature of stripping reaction that leads to back extraction of Cd(II) ions to the membrane phase. Altin *et al.* [69] also reported similar behavior (adverse effect) of higher concentration of Na_2-EDTA in the stripping agent leading to chelation of Cd(II). We can infer from Fig. 4.3 that the rate of extraction is faster in first 2 h, whereas recovery rate is faster during first 5 h. It can be argued that the loading of Cd-carrier complex in membrane phase is maximum (19.2%) at 2 h and thereafter it declines gradually to a final loading value of 15% at 10 h. The rate of extraction during first half an hour is quite high (21%). On the other hand, the recovery is quite low (4.8%) because diffusion of complex in the membrane phase is the slowest step of the transportation process and the complexes take some time to reach the strip–side interface prior to recovery. Moreover, recovery rate is nearly independent of the concentration of stripping solution

during this time. Hence, 0.015 M Na_2-EDTA was used as stripping solution in subsequent experiments.

4.1.4. Fed batch transport

Transport experiments were conducted in a fed-batch manner in order to examine the possibility of higher enrichment of Cd(II) concentration in strip solution as opposed to a single batch run. Moreover a fed-batch operation establishes the stability of the liquid membrane too. Four such sequential experiments were performed by topping up the feed solution after every 10 h while the membrane and strip phases were left unchanged. The optimal operating conditions, *viz.* pH of feed phase = 6.5, concentration of carrier (Aliquat 336) = 0.5% (v/v) in coconut oil, concentration of strip phase = 0.015 M Na_2-EDTA were maintained in the fed-batch runs too. Nevertheless, the feed phase was topped up by adding required concentration of fresh feed at the beginning of each run in order to replicate the initial concentration (5 ppm) of a fresh run. The extraction of Cd(II) was found to be 78.77% and 70.41% after the first and fourth run respectively. With the increasing no. of runs the percentage of extraction decreased at a faster rate (Fig. 4.4). On the other hand, percentage of recovery decreased more rapidly than that of extraction with increasing no. of runs, *viz.* from 67.14% in the first run to 50.23% in the fourth. This might be due to the loss of certain amount of diluent into the aqueous phases with time due to its solubility in water and/or due to the imbalance of mechanical forces across the membrane phase. From the analysis of cumulative data of all 4 runs, it was observed that the final concentration of Cd(II) in stripping phase was 11.62 ppm and the amount of Cd(II) remained in the feed after the end of final (fourth) run was 1.48 ppm. Thus it is inferred that the Cd(II) was concentrated 7.85 times (enrichment factor of 7.85) in the strip solution with 25.6% reduction of stability of LM.

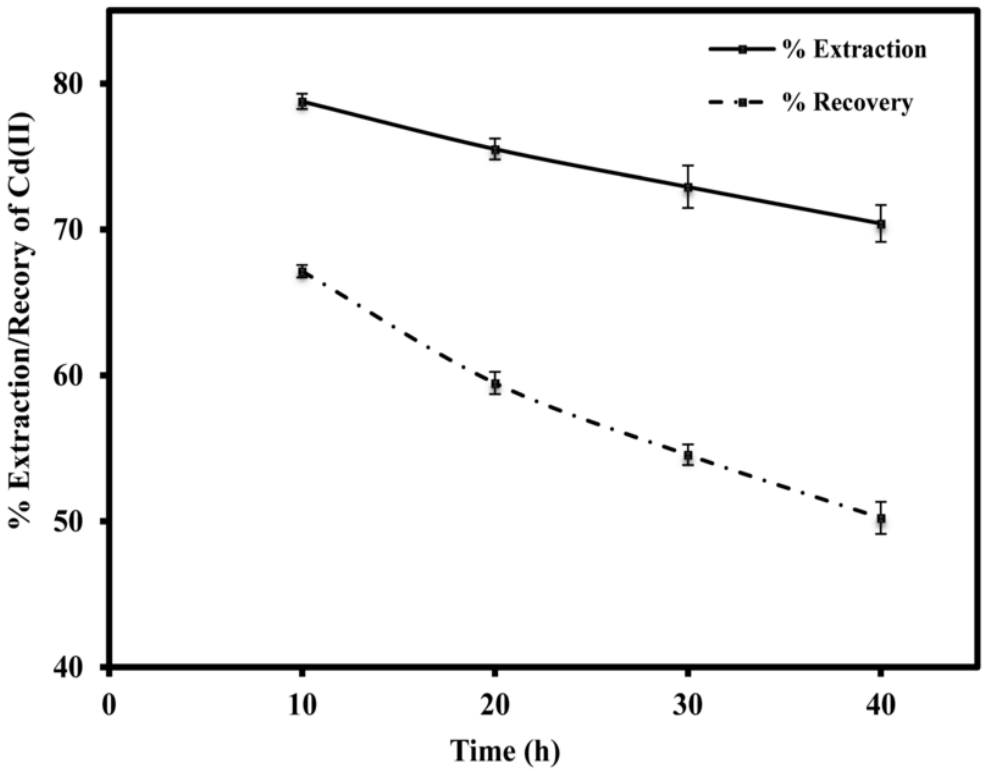


Figure 4.4: Fed batch system in SLM: *(initial feed sol. conc. = 5 ppm Cd(II), V_F = V_S = 250 mL, carrier conc. = 0.5% (v/v) and strip conc., = 0.015M Na_2-EDTA).*

4.1.5. Correlation between feed and strip phase concentrations

The simple stoichiometry between the solute, the carrier and the stripping agent doesn't always hold well in the reaction mechanisms of extraction and recovery (*i.e.,* in the formation/dissolution of complex in the liquid membrane) due to presence of other interfering factors therein. It is very important to observe how much does the "practical" stoichiometry differ from the "calculated" ones. The correlation between concentrations of feed phase and strip phase is an indicator of that practical stoichiometry. The optimal value of concentration of stripping agent in strip phase is 0.015 M Na_2-EDTA (Fig. 4.5). We varied the feed concentration from 5 to 20 ppm with other process conditions unchanged and the concentration of stripping agent was increased proportionally with the concentration of feed. If the optimality of the concentration of stripping agent would still hold, the extraction and recovery should have been unaltered. However, in reality they were found decreasing which

necessarily indicates that mere stoichiometric increase of concentration of stripping agent would not ensure its optimality if concentration of feed changes.

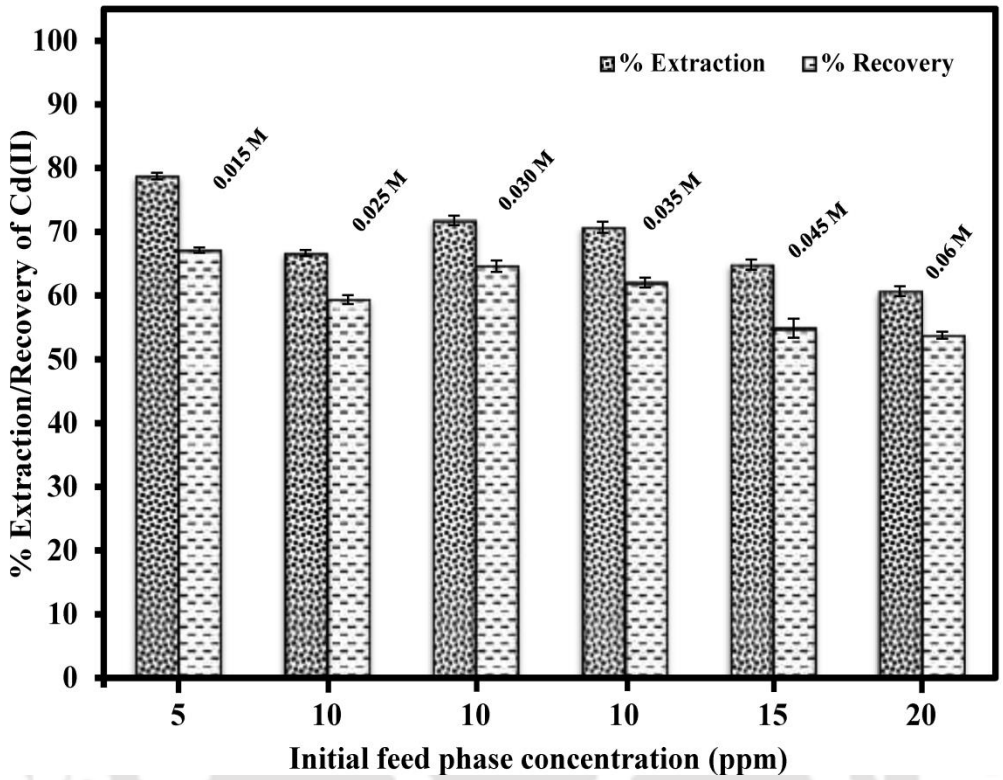


Figure 4.5: Relation between feed and strip phase (Na_2–EDTA) concentrations: *(V_F = V_S = 250 mL, pH_F = 6.5, carrier = 0.5% (v/v) and t = 10 h).*

The above result can be explained in the following way. The liquid membrane and the interfacial area remained same which might be insufficient to handle higher throughput with same efficiency. For an ideal scenario of simple stoichiometry, the optimal concentration of strip phase would have been 0.03 M Na_2-EDTA against a feed concentration of 10 ppm. We investigated the transport performance with slightly more (0.035 M Na_2-EDTA) and slightly less (0.025 M Na_2-EDTA) concentrations of stripping agent too. In both the cases, extraction and recovery were found lesser (Fig. 4.5) than the case when the strip concentration was 0.030 M Na_2-EDTA. But the excess stripping agent garners higher yield (70.72% extraction

and 62.02% recovery) than the lesser stripping agent (66.67% extraction and 59.35% recovery).

4.1.6. Combinatorial separation of Cd(II) and Pb(II)

The combinatorial separation (extraction and recovery) of two heavy metals, Cd(II) and Pb(II), has also been studied in this work. The model wastewater was synthesized with Pb(II) and Cd(II) as solutes in varied proportions; nonetheless the same aggregate mass of 5 ppm was maintained. The experiments were performed with the same LM as well as the operating parameters which were optimized during the study of transportation of Cd(II). The results are tabulated in Table 4.2. Extraction of Pb(II) was 5% more than that of Cd(II), whereas the recovery of Pb(II) was 11% more than that of Cd(II) while they were transported individually (Fig. 4.6). Hence, the equilibrium loading of Pb(II) or its complex in the membrane phase is less than Cd(II). The preferential transportation of Pb(II) over Cd(II) can be explained by the difference in their electronic configurations. Atomic number and electronic configurations of Pb(II) are 82 and [Xe] $4f^{14}5d^{10}6s^{1}6p^{3}$, respectively, and those of cadmium (Cd) are 48 and [Kr] $5s^{2}4d^{10}$, respectively.

The shielding effect of Pb(II) is more and also the effective nuclear charge of Pb(II) is 5.65 against 4.35 of Cd(II) (from Slater's rule [90]). Therefore, the affinity of Pb^{2+} to the acetate ions originated from aqueous solution of Na_2-EDTA in the stripping solution is more compared to that of Cd^{2+}. This leads to the higher stability of the Pb-EDTA complex than that of Cd-EDTA which is again confirmed by stability constants of the respective metal complexes (stability constants of Pb-EDTA complex is 18.0 compared to 16.6 of Cd-EDTA complex) in the same pH condition of strip solution [88, 89]. On the other hand, interference effect of the second metal is active when it is transported together. As a result both the

extraction and the recovery were found slightly less for the mixed feed in all cases as observed in Table 4.2. The reason for the above result is the lower driving force (concentration difference) available for the transportation of individual metals in the mixed feed (since total mixed feed concentration remained constant) and this driving force reduces with the presence of higher proportion of the second metal. However, both extraction and recovery were found slightly selective for lead (II) in all cases. Moreover, extraction of both metals was highest (77.52% for cadmium (II) and 81.28% for lead(II)) when particular metal is abundant in the mixture, *i.e.* Cd(II):Pb(II) mass ratio of 4:1 or 1:4 (Table 4.2) and so is the recovery. But recovery of Cd(II) (67.67%) is less compared to that of Pb(II) (69.24%).

Table 4.2: Percentages of extraction and recovery for various feed ratios (Cd:Pb)

Cd(II)	Pb(II)	Cd(II):Pb(II)	Cd(II)		Pb(II)	
(ppm)	(ppm)	(mass ratio)	% Extraction	% Recovery	% Extraction	% Recovery
5	-	-	78.77	67.14	-	-
-	5	-	-	-	84.23	77.73
2.5	2.5	1:1	68.62	53.15	74.38	62.26
1.667	3.33	1:2	65.03	52.54	75.55	62.94
1.25	3.75	1:3	60.80	48.72	78.30	65.18
1	4	1:4	53.92	46.14	81.28	69.24
3.33	1.67	2:1	72.10	61.58	71.60	61.91
3.75	1.25	3:1	75.28	65.36	65.35	56.60
4	1	4:1	77.52	67.67	55.10	45.28

The above observation can be explained by the fact that Pb(II) complex is less accumulated in the membrane phase as compared to Cd(II) complex and that was found in their individual transportations (Fig. 4.6) too. From this particular study it has been realized that transportation of lead (II) is slightly preferable over cadmium (II), and this preference increases with abundance of lead (II) over cadmium (II) in the mixed feed.

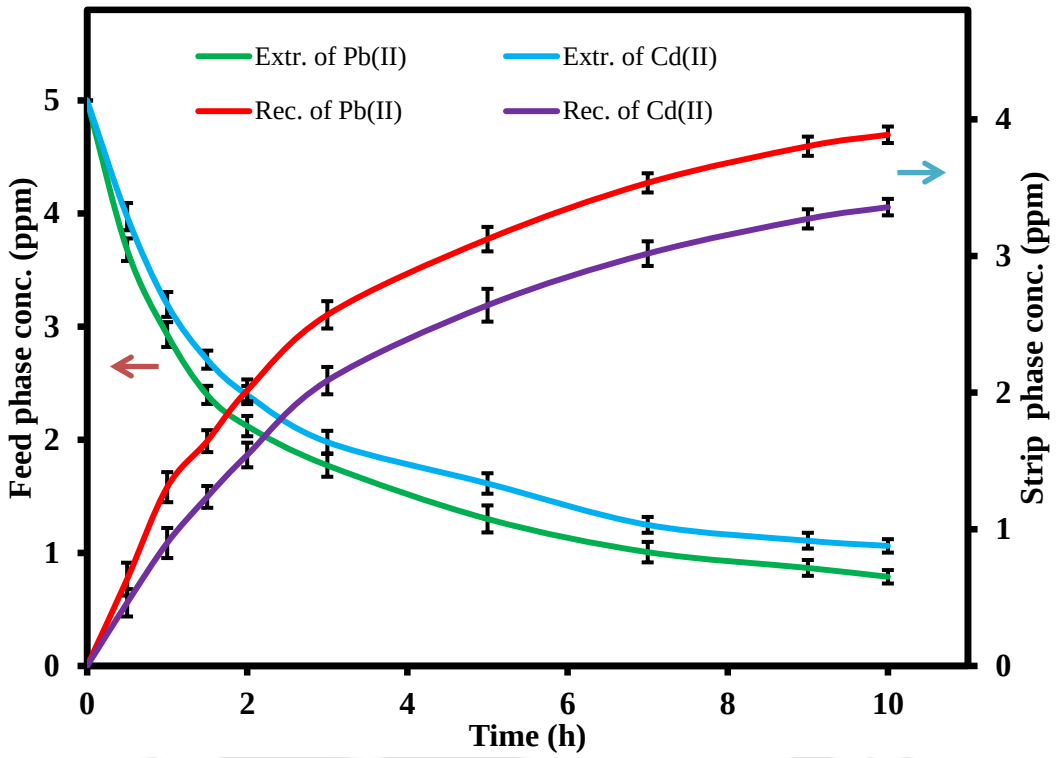
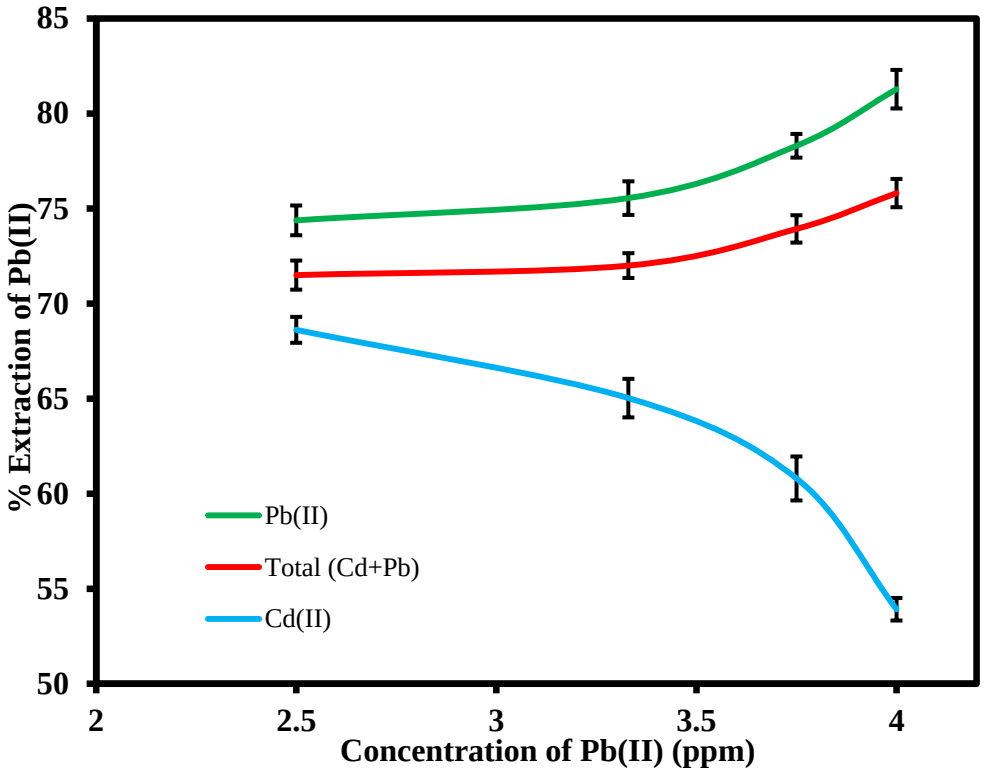


Figure 4.6: Transportation of individual metals (cadmium (II) and lead (II)) through the FS-SLM: (*V_F = V_S = 250 mL, initial feed phase conc. = either 5 ppm Pb(II) or 5 ppm Cd(II), pH_F = 6.5, solvent = coconut oil, carrier = 0.5% (v/v) Aliquat 336, strip conc., = 0.015 M Na_2-EDTA and membrane support = PVDF (0.2µm)).*

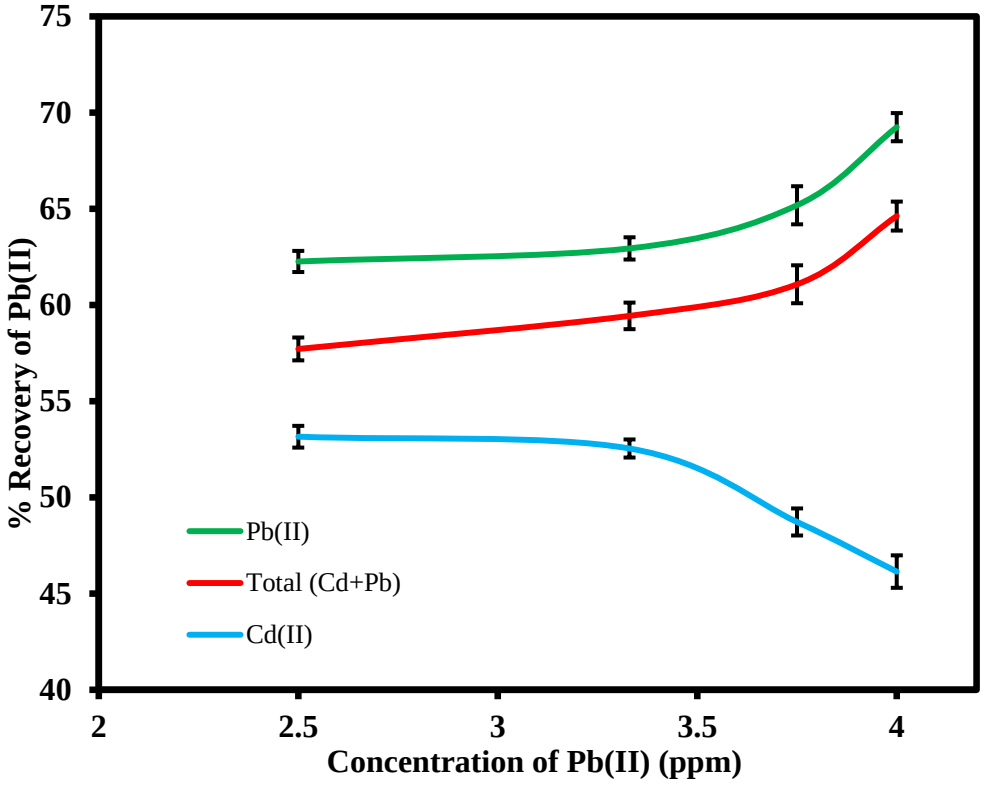
4.1.7. Effect of competition between the metals in their transportation

From the results of combinatorial separation studies of Pb(II) and Cd(II) it is certain that there exists interference effects of the second metal on the transportation of the first one. So, we thoroughly investigated the effect of interference with more data points (more mass ratios

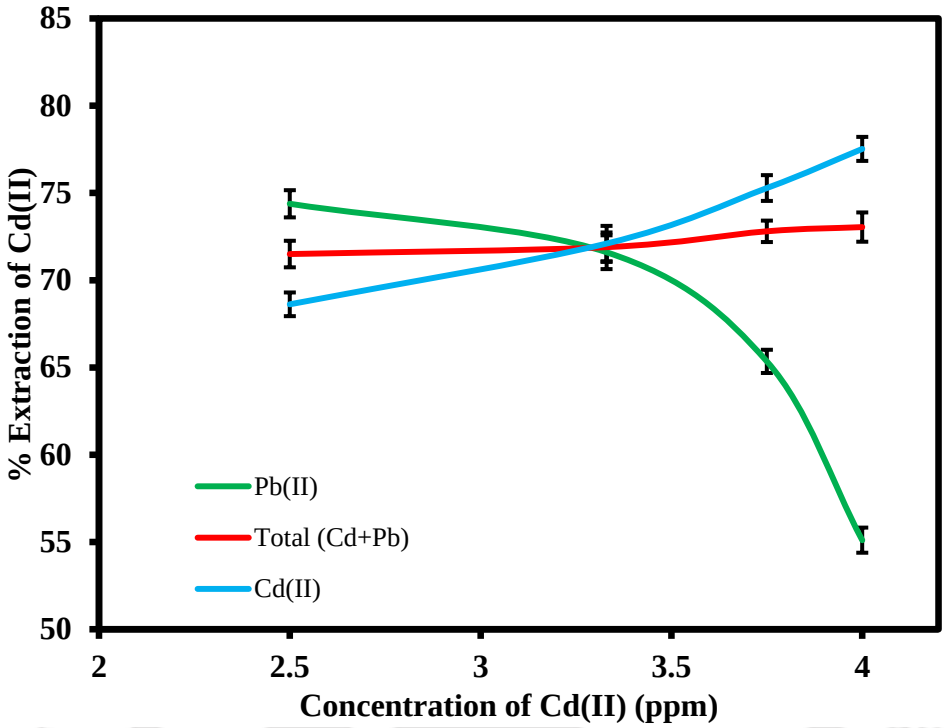
of multiple metals) and the quantitative analyses are depicted in Table 4.2 and Fig. 4.7(a–d). Both the extraction and the recovery of Cd(II) decrease with increasing Pb(II) (interfering effect of the second metal) amount in the aggregate of 5 ppm feed solution (Fig. 4.7(a) and (b)). However, the aggregate (Pb and Cd) extraction and recovery increase with increasing Pb(II) concentration as Pb(II) transportation prevails over the Cd(II). Both the percentage extraction and recovery are in between that of pure Cd(II) and pure Pb(II) of same concentration of 5 ppm, which confirms the negative interference effect for all ratios of metals. Similar trends are observed with increasing Cd(II) concentration in the combined feed of 5 ppm (Fig. 4.7(a) and (b)). The above results confirm the preferential transportation of Pb(II) over Cd(II) and accumulation of Cd(II)-carrier complex in the membrane phase. With increasing Pb(II) concentration in the mixed feed the percentage of total (Pb(II) and Cd(II)) extraction increases to 75.81% at Cd(II) to Pb(II) ratio of 1:4 and that of total recovery increases to 64.62% (Fig. 4.7(a) and (b)). On the other hand, with increasing Cd(II) concentration in mixed feed (at Cd(II) to Pb(II) ratio of 4:1) maximum total (Pb(II) and Cd(II)) extraction and recovery were found as 73.04% and 63.19%, respectively (Fig. 4.7(c) and (d)).



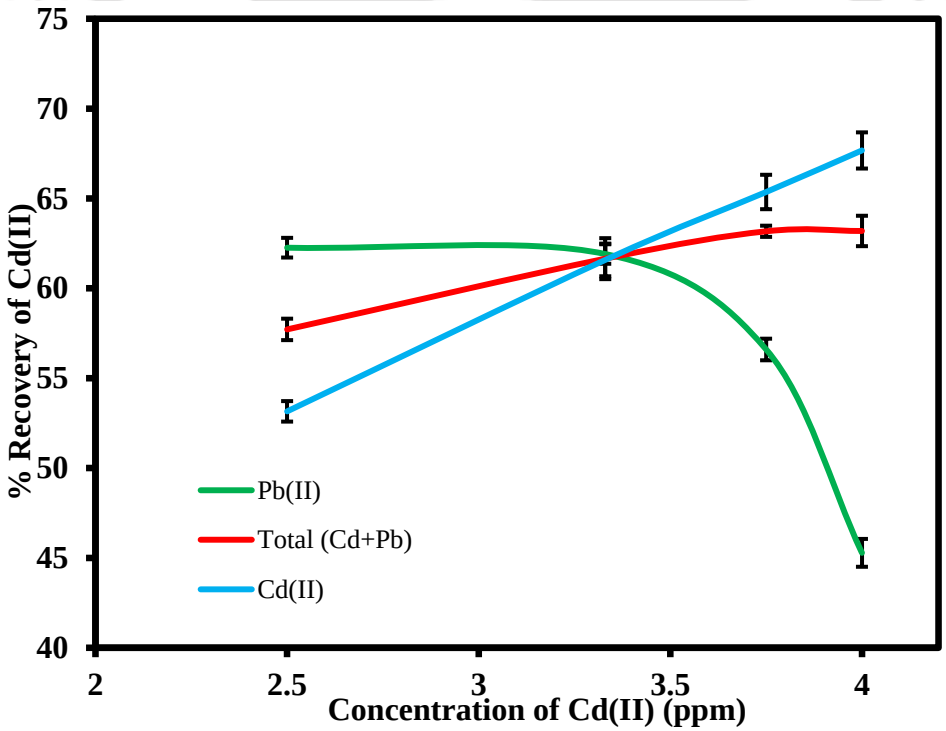
(a)



(b)



(c)



(d)

Figure 4.7(a−d): Effect of competition between the metals in their transportation (Individuals as well as total extraction and recovery in various mass ratios of the bi-metals): *(V_F = V_S = 250 mL, pH_F = 6.5, solvent = coconut oil, carrier = 0.5% (v/v) Aliquat 336, strip conc., = 0.015 M Na_2-EDTA and membrane support = PVDF (0.2µm)).*

4.1.8. Mass transfer modeling

The effect of the competition between metals on the overall transport was studied on the basis of permeability and change of flux of the solute with the mass ratio of metals in the feed solution of total concentration of 5 ppm. The permeability and the flux was calculated with the simplified model equation (Eq. (4.1)) proposed by Danesi *et al*. [94], in which it is assumed that the concentration of organic complex at the feed-membrane interface can be assumed to be negligible, and thus, the transport depends only on concentration of solute in the feed phase at various time of transportation. Thus,

$$ln\left(\frac{C_t}{C_0}\right) = -\frac{A}{V}.P.t \qquad (4.1)$$

where, C_t and C_0 are the metal concentrations in the feed phase at an elapsed time *t* and time zero, respectively. *A* is the effective interfacial area for mass transfer, *V* is the volume of feed solution and *P* is the solute permeability. The initial flux (*J*) is calculated using the following equation (Eq. (4.2)) [95].

$$J = P \times C_0 \qquad (4.2)$$

The permeability as well as flux values of combined metal transportation for various mass ratios of metals in the mixture feed have been shown in Table 4.3. The total permeability as well as flux values for various ratios of metals indicates that the presence of second metal reduces the transportation as compared to the pure metal. Both the overall permeability and the flux is minimum for the case of 1:1 ratio of the Cd(II) and Pb(II) *i.e.* when transportation of one metal is maximum affected by the presence of the maximum amount of the other. With decreasing amount of the second metal, both the permeability and flux increases to attain the value of individual pure metal.

Table 4.3: Total permeability and flux of various ratios of metals

Cd(II):Pb(II) (mass ratio)	Permeability ($Px10^{-4}$) ($cm.s^{-1}$)	Flux ($Jx10^{-8}$) ($g.cm^{-2}.s^{-1}$)	Total extraction (%)	Total recovery (%)
Pure Cd(II)	9.00	4.50	78.77	67.14
Pure Pb(II)	10.20	5.10	84.23	77.73
1:1	8.17	4.08	71.50	57.71
1:2	8.20	4.10	72.00	59.43
1:3	8.35	4.18	73.93	61.07
1:4	8.70	4.35	75.81	64.62
2:1	8.25	4.12	71.89	61.65
3:1	8.38	4.19	72.80	63.17
4:1	8.56	4.28	73.04	63.24

Table 4.4: Summary of optimum condition for transport of Cd(II) in three phase FS-SLM study

S. No.	Parameter		Range studied	Optimum value
1	Feed phase pH		3-7	6.5
2	Carrier (Aliquat 336) conc.		0-1 vol%	0.5 vol%
3	Strip phase (Na_2-EDTA) conc.		0.005-0.02 M	0.015 M
4	Duration of extraction/stripping		0-10 h	10 h
5	**% Extraction** Cd: 78.77% Pb: 84.23%	**% Recovery** Cd: 67.14% Pb: 77.73%	----	At the optimum conditions

4.2. Summary of the FS-SLM based simultaneous separation of Cd(II) and Pb(II)

- Use of Aliquat 336 as carrier, coconut oil as solvent and Na_2-EDTA as stripping agent made a very efficient FS-SLM system for recovery of Cd(II) and Pb(II).
- The optimum conditions for three phase studies are as follows: pH of feed solution = 6.5, concentration of carrier in the membrane phase = 0.5% (v/v) Aliquat 336, concentration of the stripping phase = 0.015 M Na_2-EDTA and initial concentration of metals = 5 ppm.
- The fed-batch study reveals that the Cd(II) can be concentrated in the strip solution 7.85 times of the concentration of Cd(II) in the exhaust feed.
- A study on combinatorial transportation of lead (II) and cadmium (II) with varied proportion in a mixed feed was also studied.
- The change in efficiency of individual transportation due to interaction effect has been investigated.
- The preferential transportation of Pb(II) over Cd(II), especially with increasing percentage of Pb(II) in the mixture, is the important finding of this research work.
- The flux of the combined feed is minimum at 1:1 ratio of Cd(II) and Pb(II).

CHAPTER-V

FS-SLM based simultaneous separation and precipitation of Pb(II) *and* Cd(II)

CHAPTER-V

FS-SLM based simultaneous separation and precipitation of Pb(II) and Cd(II)

This chapter focuses on the simultaneous separation of two heavy metals, lead (II) and cadmium (II), from mixed feed through FS-SLM followed by precipitation of metal salts in strip phase. This technique yields an ever-unsaturated condition in the strip phase that maintains higher gradient of chemical potential across the SLM. Initially, optimization of the influential parameters on the transportation of single metal, viz. Pb(II), was carried out. These optimized parameters were employed in the simultaneous transportation of both the metals, viz. Pb(II) and Cd(II), present in various molar ratios in the mixed feed. The carrier-solvent combination of "D2EHPA (4% v/v) in environmentally benign coconut oil" was used as the organic phase. Na_2CO_3 was used as the stripping agent. Carbonate salts of lead (II) and cadmium (II) were formed in the stripping side interface (which are insoluble in water) leading to precipitation inside the stripping solution. The transportation of solute is positively affected due to the precipitation. Lead (II) removal was found to be preferential due to its favorable electronic configuration and shielding effect. The conversion of the liquid waste to the solid one was added advantage for the final removal of hazardous heavy metals.

5.1. Theoretical background

Although Na_2 – EDTA was found to be an excellent stripping agent for Cd(II) and Pb(II) (yielding as high as 77% *i.e.* the heavy metals in wastewater was concentrated by

approximately four times in the recovery phase) it is not regarded as the best one as far as the industrial treatment processes are concerned. Solid waste generation from the vast volume of liquid waste is a far better alternative. Hence, Na_2CO_3 was tried as stripping agent in lieu of Na_2-EDTAwith an intention to form carbonate salts of heavy metals that can be precipitated in the stripping phase for easy removal and disposal. However, problem of back diffusion of Na_2CO_3 through LM has been observed when a combination of "coconut oil - Aliquat 336 - Na_2CO_3" was used for SLM operation. A white precipitate of ammonium carbonate salt $(NH_4)_2CO_3$ (produced in the reaction between Aliquat 336 and Na_2CO_3) formed in the LM itself. The use of acidic carrier D2EHPA solved the problem and resulted in the recovery of metal ions as the precipitate of respective carbonates in the stripping phase, without forming any undesired salt in the LM.

Now, as it was observed from the results of previous chapters that Pb(II) is preferentially transported across the FS-SLM over Cd(II), the subsequent experimentations were planned in such a way that the operating conditions were optimized for lead transport only. The effect of addition of second element cadmium was studied thereafter.

5.1.1. Solute transport methodology

The feed and strip phase comprise aqueous solutions of $PbCl_2$ and Na_2CO_3, respectively. The organic phase was composed of D2EHPA (as the carrier agent) in coconut oil (as the solvent). The target metals under the examples *i.e.* Pb(II) and Cd(II) are referred to as a common symbol M for easy understanding. The transport methodology of M from feed phase to the stripping side interface has been illustrated below:

The reaction mechanism indicated that MCl_2 at a moderately acidic condition of feed phase (pH = 5) is in the form of M^{++} at the feed phase. HCl is used for maintaining the desired level of acidity (pH 5) in the aqueous feed phase. Dimeric D2EHPA (acidic carrier) exchanges H^+ at the feed side interface and forms metal-carrier complex which metal thus gets extracted and diffuses to the strip-membrane interface due to concentration gradient. The stripping agent (sodium carbonate) strips the metal from the said metal-carrier complex at the strip-membrane interface in exchange of sodium to form the $PbCO_3$ or $CdCO_3$ that precipitate in the stripping chamber as the water solubility of both $PbCO_3$ and $CdCO_3$ is very less. The sodium-carrier complex diffuses back to the feed-membrane interface due to concentration gradient that eventually exchanges $2Na^+$ with M^{++} at the feed side interface to form another metal-carrier complex [83]. This transport mechanism has been demonstrated in Fig. 5.1.

D2EHPA *i.e.* $(C_8H_{17}O)_2POOH$ is referred to as RH in the remaining text where $R \equiv (C_8H_{17}O)_2POO$. The sodium salt of D2EHPA is denoted by RNa. The reaction mechanism for transportation of M (metal) is summarized as follows:

Feed phase: Complexation of M by chloride ions

$$MCl_2 \rightleftharpoons M^{++} + 2Cl^+ \quad (5.1)$$

Feed-membrane interface: M^{++} is exchanged with $H^+$of RH and/or RNa in the membrane phase:

$$M^{++}(aq) + 2Cl^-(aq) + 2(RH)\,(org) + 2(RNa)\,(org) \rightleftharpoons MR_2.(RH)_2(org) + 2NaCl\,(aq) \quad (5.2)$$

Membrane-strip interface: The stripping reaction forms metal carbonate, RH and RNa

$$MR_2(RH)_2\,(org) + Na_2CO_3(aq) \rightleftharpoons MCO_3(aq)\downarrow + 2RH\,(org) + 2RNa\,(org) \quad (5.3)$$

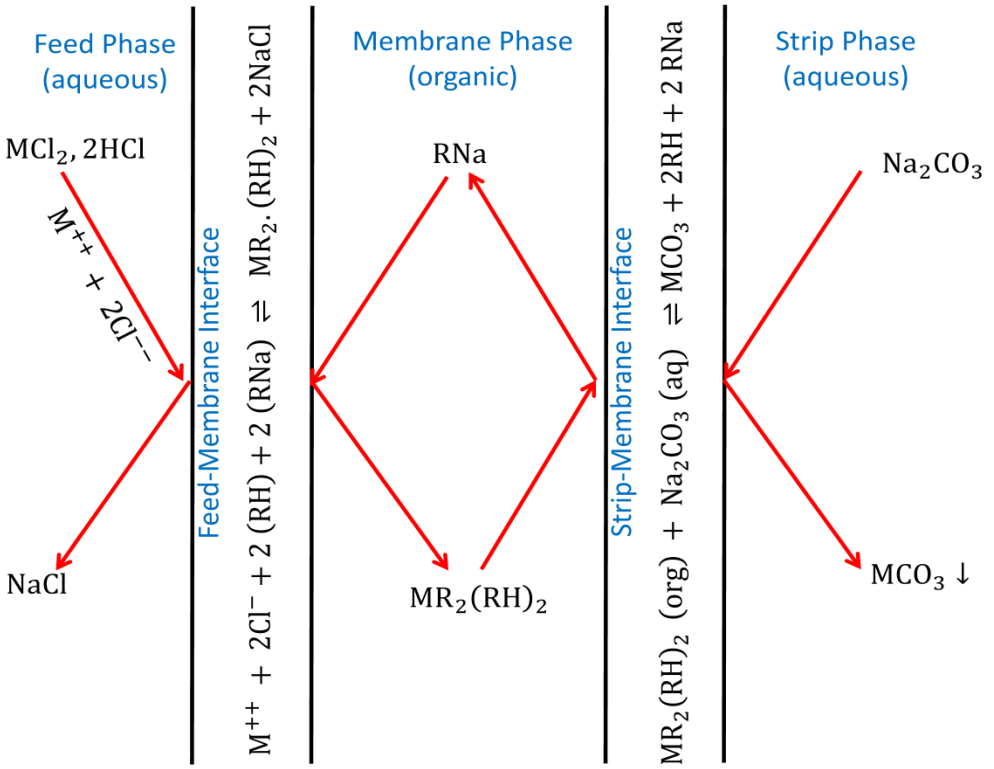


Figure 5.1: Schematic diagram of the transport mechanism of Pb(II) and Cd(II)

5.1.2. Mass transfer modeling

There exists possibility of competition between the metal ions of the same group to be extracted by the carrier at the feed side interface. The overall transportation of metals was determined with the results of permeability and flux of individual metals. It was assumed that the concentration of organic complex at the feed-membrane interface is negligible. The permeability and the flux were calculated for each metal with the model equation (Eq. (4.1)) proposed by Danesi *et al*. [94]. Hence, the transport depends only on concentration of solute in the feed phase at various instants of transportation. The initial flux (J) is obtained from the equation (Eq. (4.2)) [3].

5.2. Results and discussion

5.2.1. Determination of appropriate operating range of pH in feed solution

The amount of dissociation of $PbCl_2$ and $CdCl_2$ to respective cations is dependent on the pH of feed phase [21]. The cations eventually participate in the metal-carrier complexation. On the other hand, the transport of solute is proportional to the degree of complexation. Hence, pH of the feed solution is an important parameter for the transportation of metal and the experimental study was performed with acidic feed solution in the range of pH 3.0−7.0. The maximum extraction (92.53%) and recovery (87.89%) were obtained at a pH of 5.0. The experimental results were reported in Fig. 5.2. The reaction mechanism, as discussed in Section 5.1.1, indicates that Pb(II) at a higher acidic condition of feed phase (low pH) was expected to be in the form of Pb^{++} at the feed-membrane interface. The presence of the excess chloride ions (as HCl was used for protonation) in feed phase leads to less extraction and recovery. Similar results were reported by other researchers too [91, 65]. Both the extraction and recovery start decreasing beyond the pH of 5.0 when sufficient HCl is unavailable for the protonation.

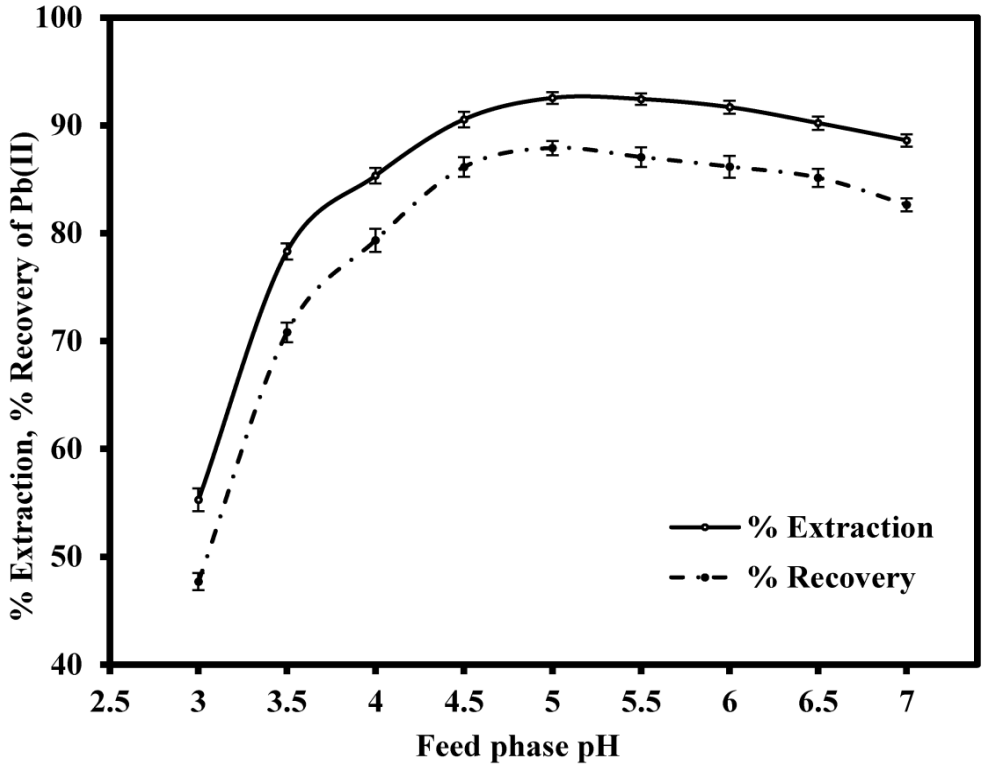


Figure 5.2: Effect of pH of feed phase: ***(****initial feed sol. conc. = 5 ppm Pb(II),* $V_F = V_S$ *= 250 mL, carrier (D2EHPA) conc. = 4% (v/v), strip conc. = 0.2 M* Na_2CO_3*).*

5.2.2. Determination of suitable carrier concentration

The concentration of carrier in LM has two opposite effects. The complexation between solute and the carrier is less at lower concentration of carrier, while excess concentration of carrier increases the viscosity of LM. In both these cases transportation of solute is lower. Hence, there is a need to find a concentration that yields optimum transport of solute through the LM. The optimum concentration of carrier (DMOA) for treating 5 ppm Cd(II) in the feed phase was found to be 1% (v/v) in the BLM experimentations (Section 3.1.2.) whereas for the treatment of same concentration of Cd(II) using Aliquat 336 as carrier the optimum concentration of carrier was found to be 0.5 % (v/v) in the BLM and SLM experimentations (Section 3.1.5.2. & Section 4.1.2.). In this study, experiments were conducted for varied carrier concentration in the range of 0-6.0% (v/v) and the results are reported in Fig. 5.3. At

the optimum carrier concentration of 4.0% (v/v), extraction and recovery of Pb(II) were found to be 92.53% and 87.89%, respectively. Beyond the optimum carrier concentration, mobility of Pb-carrier complex was reduced due to hindrance effect created by excess carrier and/or the complex leading to the reduction in both extraction and recovery [22, 60, 68 and 93].

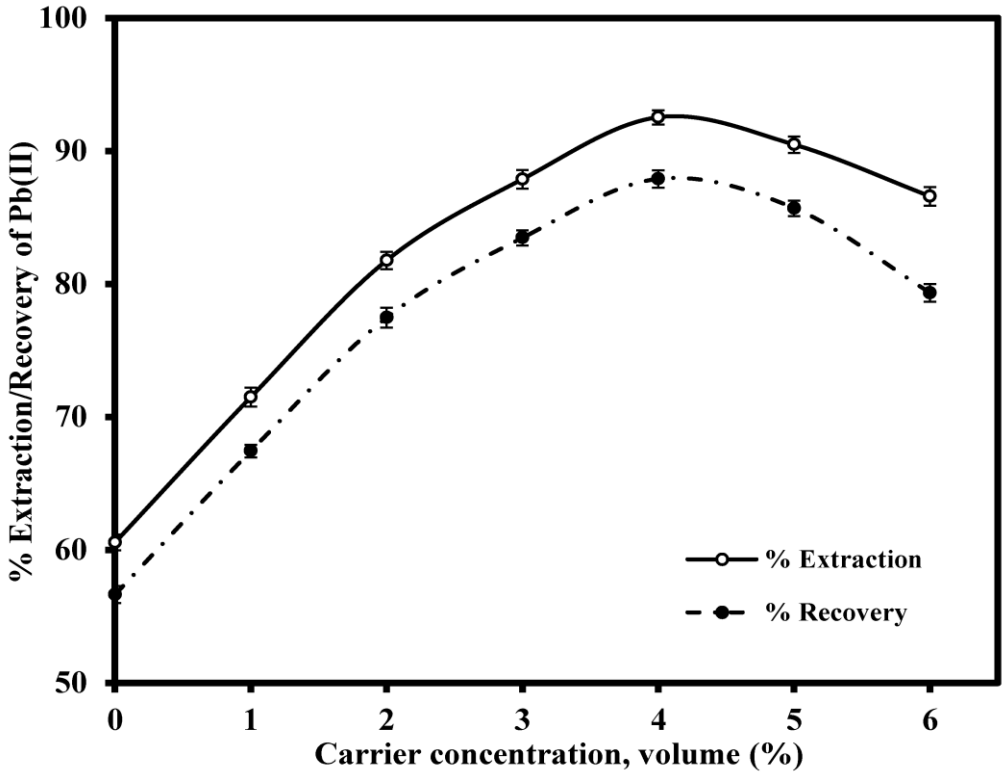


Figure 5.3: Effect of carrier concentration on Pb(II) transportation: *(pH of feed phase = 5, initial feed sol. conc. = 5 ppm Pb(II), $V_F = V_S$ = 250 mL, strip conc. = 0.2 M Na_2CO_3).*

5.2.3. Role of concentration of Na_2CO_3

Na_2CO_3 is soluble in water however lead carbonate is insoluble in water beyond a particular concentration (low solubility product). Hence, lead carbonate salt (solubility product is 7.4×10^{-14} moles/L only) precipitates in an aqueous solution beyond the concentration of 7.4×10^{-14} moles/L. Hence it is advantageous to use Na_2CO_3 as a stripping agent because it re-

extracts lead ions from the Pb-carrier complex at the membrane/strip interface and forms lead carbonate which is prone to precipitation when the desired concentration is met. The concentration of stripping agent is the determining factor for precipitation. Batch studies were performed with varying concentrations of Na_2CO_3 in stripping solution in the range of 0-0.3 M while initial concentration of feed phase was kept at 5 ppm. The results are reported in Fig. 5.4. Both the extraction and recovery increased with the increase in concentration of the Na_2CO_3 in the stripping solution, due to shift of chemical equilibrium of Eq. (5.3) towards right (Le Chatelier's principle). This increase holds up to 0.2 M where the extraction and recovery were 92.53% and 87.90%, respectively.

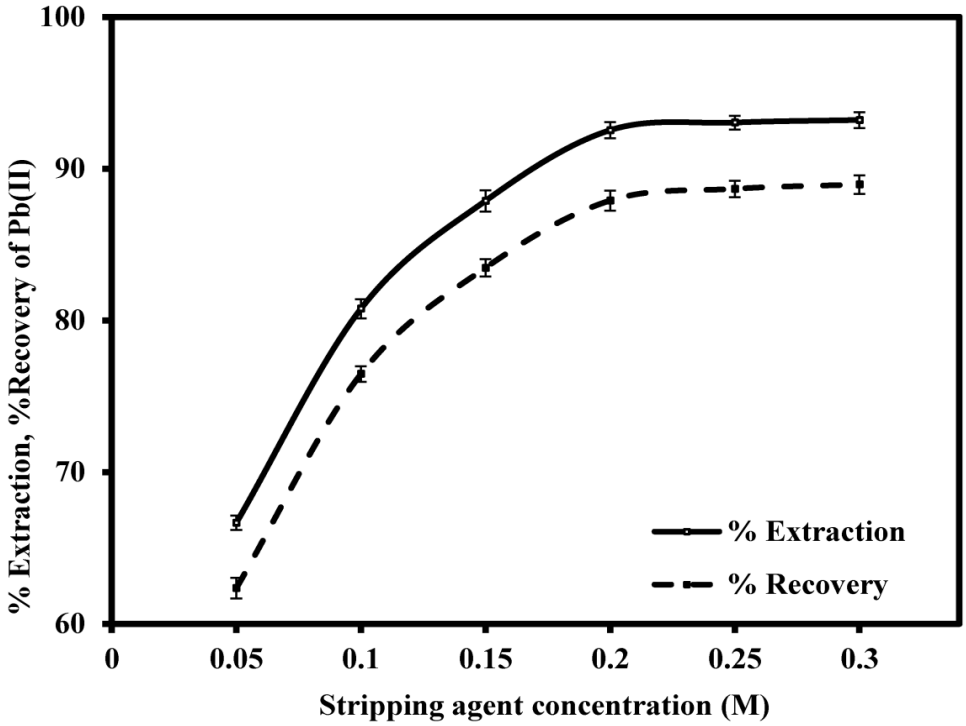


Figure 5.4: Effect of stripping phase concentration: *(pH of feed phase = 5.0, initial feed sol. conc. = 5 ppm Pb(II), $V_F = V_S$ = 250 mL, carrier conc. = 4% (v/v) of D2EHPA).*

However, with further increase in concentration of stripping agent, neither extraction nor recovery improved. It can be concluded that 0.2 M concentration of Na_2CO_3 is the saturation

concentration for the particular purpose *i.e.* for stripping the metals from the metal-carrier complex. The excess amount of Na_2CO_3 above and over this concentration lies inactive in the solution. Hence, 0.2 M was considered as the saturation concentration of Na_2CO_3 in the stripping phase. Further studies were conducted at 0.2 M Na_2CO_3 stripping solution.

5.2.4. Effect of nature of Pb(II) salts in the feed solution

The two most predominant forms of inorganic salt of lead (II) that exist in the wastewater from various industries are $PbCl_2$ and $Pb(NO_3)_2$, though in a dissociated form in their respective cations and anions. Experiments were carried out using these two salts in the feed phase separately. The change in concentration of metals in the both feed and the strip phases with time is shown in Fig. 5.5. The transportation appears to be complete after 10 h. The extraction and recovery of lead were 92.53% and 87.89% respectively from its chloride salt whereas they were 96.73% and 92.40% respectively from nitrate salt.

The extraction of Pb(II) from its nitrate salt is slightly higher than its chloride counterpart. This is due to bond strength between Pb^{2+} and NO_3^- ions which are weaker than that between Pb^{2+} and the Cl^- ions [22, 96].The solubility product of the lead nitrate ($5.88\ M^3$) is higher than that of lead chloride ($1.6\times10^{-5}\ M^3$) which results in the more ionization of the nitrate salt in the aqueous feed phase. Hence, the formation of the complexation between carrier and the metal ion is easier for the case of $Pb(NO_3)_2$.

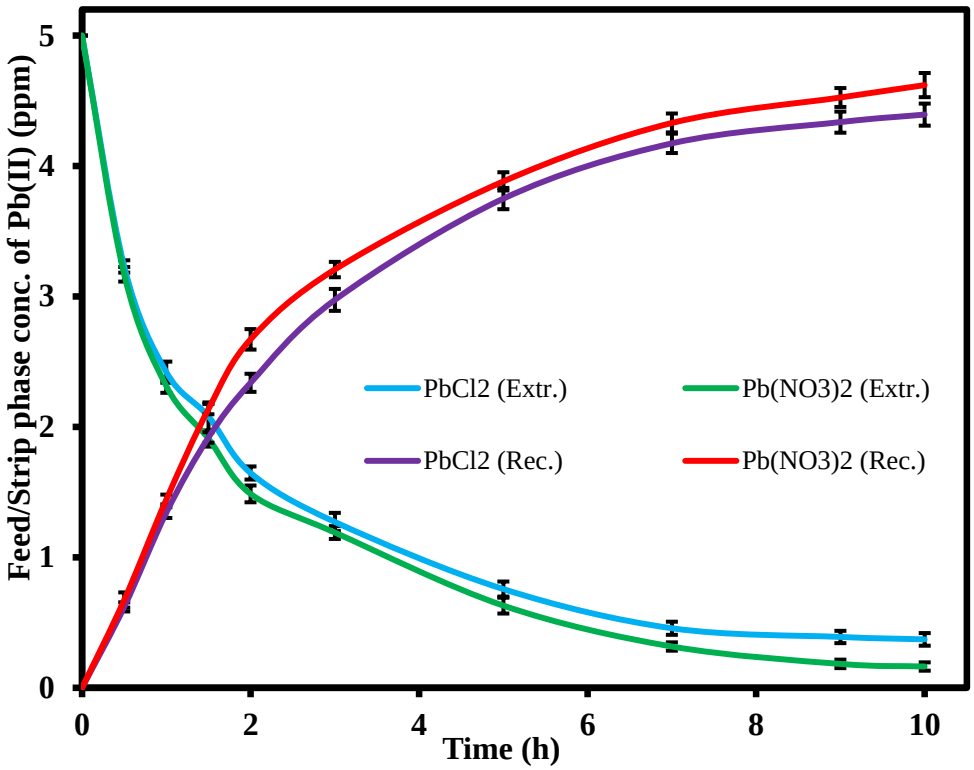


Figure 5.5: The effect of the nature of the salts: (*initial feed sol. conc. = 5 ppm Pb(II), V_F = V_S = 250 mL, feed phase pH = 5, carrier conc. = 4% (v/v) D2EHPA and strip conc. = 0.2).*

5.2.5. Influence of initial feed concentration

The amount of lead (II) and cadmium (II) in the industrial wastewater varies from 1.0-5.0 ppm [9, 82]. Hence, the experiment was conducted for the concentration of lead (II) in feed phase in the range 3-10 ppm. The permeability and the flux of lead (II) for various concentrations are shown in Table 5.1 and Fig. 5.6. The flux increased with the concentration very rapidly up to 5 ppm and increased slowly thereafter. At lower concentration of Pb(II) in feed, the concentration differential is higher which leads to rapid increase of flux, however at higher initial concentrations, the interfacial area (804.2 mm^2) is the constraint against higher flux.

Table 5.1: Total permeability and flux in case of various initial concentration of Pb(II) in feed solution

Pb(II) (ppm)	Permeability ($P\times10^{-4}$) ($cm.s^{-1}$)	Flux ($J\times10^{-8}$) ($g.cm^{-2}.s^{-1}$)	Extraction (%)	Recovery (%)
3	9.20	2.76	76.00	71.07
5	15.20	7.60	92.53	87.89
7	12.99	9.09	87.85	82.42
10	10.66	10.66	82.80	77.16

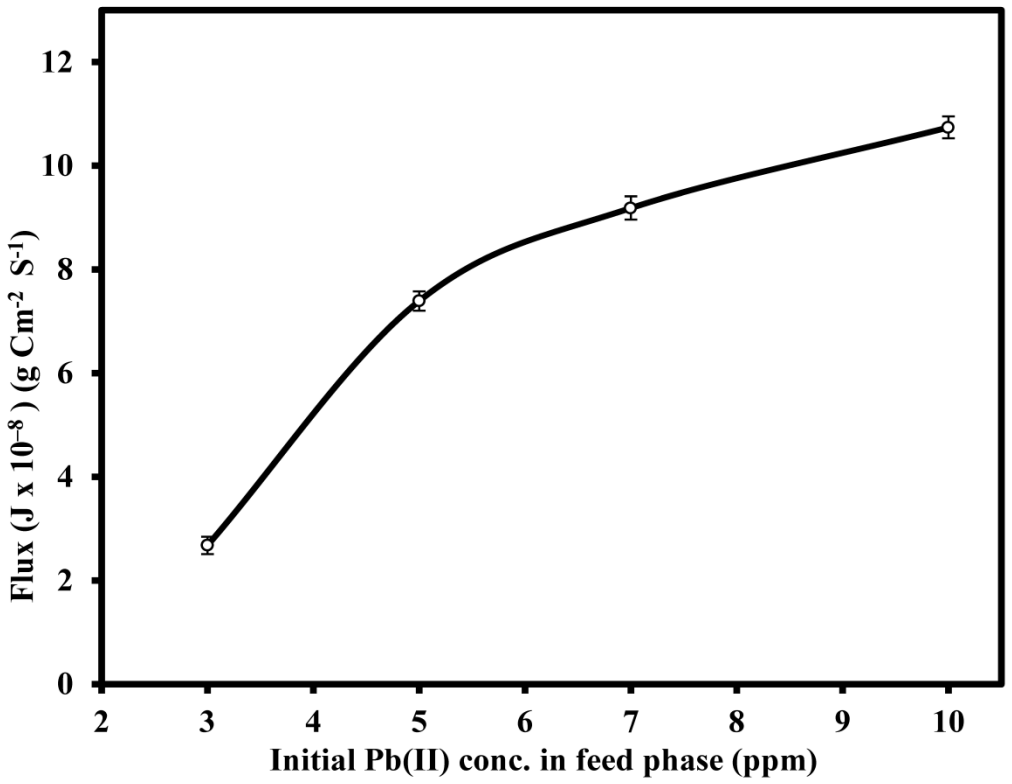


Figure 5.6: Initial feed concentration (varied from 3-10 ppm of Pb(II)): *(V_F = V_S = 250 mL, feed phase pH =5, carrier conc. = 4% (v/v) D2EHPA and strip conc. = 0.2 M Na_2CO_3).*

5.2.6. Fed batch study

Experiments were conducted in a fed-batch manner with the aim of examining the possibility of higher enrichment of Pb(II) in strip solution. Moreover, a fed-batch operation establishes the stability of the LM too. Four sequential batch experiments (Fig. 5.7) were conducted by topping up the feed solution after every 10 h without disturbing the other two phases. The optimal operating conditions, *viz*. pH of feed phase = 5, concentration of carrier (D2EHPA) = 4% (v/v), concentration of strip phase = 0.2 M Na_2CO_3 (0.2 M aqueous solution of Na_2CO_3 exhibits pH = 11.47) as resulted from the Sections 5.2.1−5.2.5, were maintained in the fed-batch runs. Topping up of feed was carried out by adding required concentration of fresh feed at the commencement of subsequent batch runs in order to replicate the initial concentration (5 ppm) of a fresh run. With the increasing no. of runs the percentage of extraction decreased at a faster rate. It was found to be 92.53% and 71.49% after the first and fifth runs respectively. On the other hand, percentage of recovery decreased more rapidly than that of extraction with increasing no. of runs, *viz.* from 87.90% after the first run to 61.43% after the fifth. The rapid decrease in the rate of recovery in consequent runs demonstrates either the instability of the SLM or the saturation of the stripping phase.

Although, the LM is sufficiently viscous the stability might be reduced due to the loss of certain amount of diluent into the aqueous phases with time due to its slight solubility in water and/or due to disproportionate mechanical forces applicable across the membrane phase. It was calculated from the analysis of cumulative data of all 5 runs that the final concentration of Pb(II) in stripping phase was 19.03 ppm and the amount of Pb(II) remained in the feed after the end of final (5th) run was 1.425 ppm. Hence, the enrichment factor can be achieved as high as 13.3 after 5 runs against 11.76 in case of single run transportation.

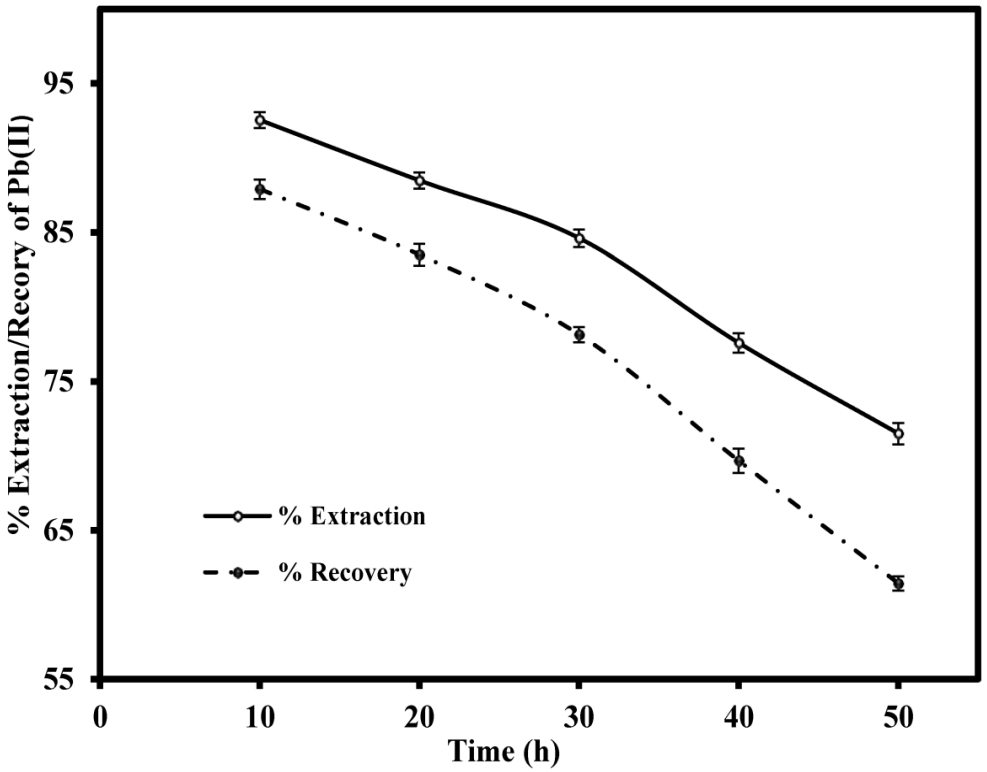


Figure 5.7: Fed batch system: ***(****initial feed sol. conc. = 5 ppm Pb(II),* $V_F = V_S = 250$ *mL, feed phase pH = 5, carrier conc. = 4% (v/v) D2EHPA and strip conc. = 0.2 M* Na_2CO_3*).*

5.2.7. Determination of stability of SLM

Stability of the SLM was established by repeated runs of experiment with the same SLM but with fresh feed and fresh stripping phases. The FS-SLM was found to be stable for 100 h with decrease in percentage of transportation from 92.53% to 85.10% (Fig. 5.8). The extraction decreased by only 7.43% up to the first 100 h and then it started decreasing with higher rate up to 130 h. Beyond 130 h the extraction decreased rapidly and reached 40% within a mere 40 more hours. Hence, it is concluded that the stability of the SLM is 100 h. The viscosities of coconut oil and carrier are 30.29 mPa.s and 47.32 mPa.s respectively while the viscosity of their combination (*i.e*. the organic solution) was found to be 32.02 mPa.s. The stability of the SLM would actually be higher than that of the experimentally found results. A lower value in experimental results can be explained in the following manner: The stability studies were

carried out in subsequent batch processes of duration 10 h each. After every 10 h the feed and the strip phases were changed manually with care.

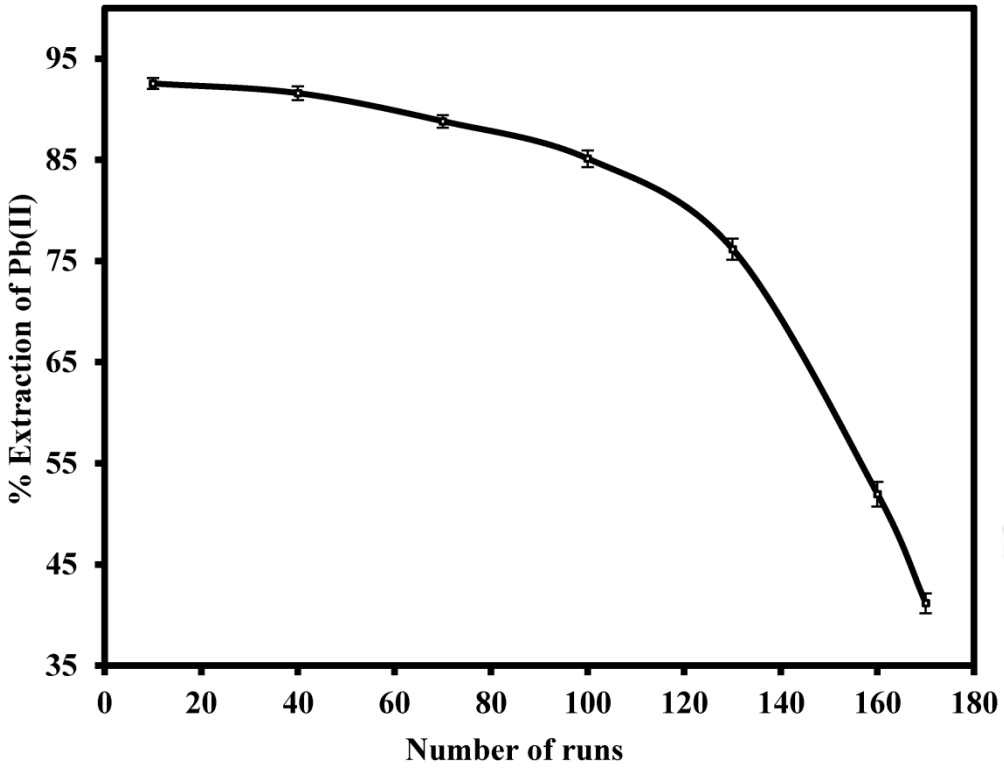
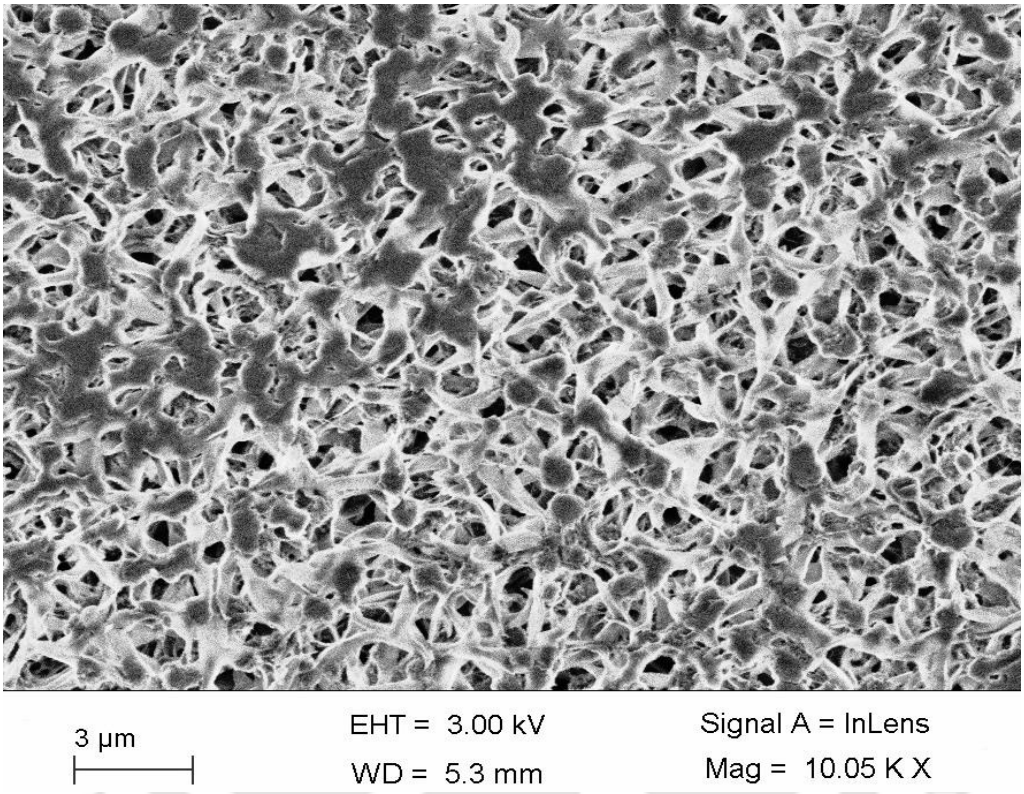


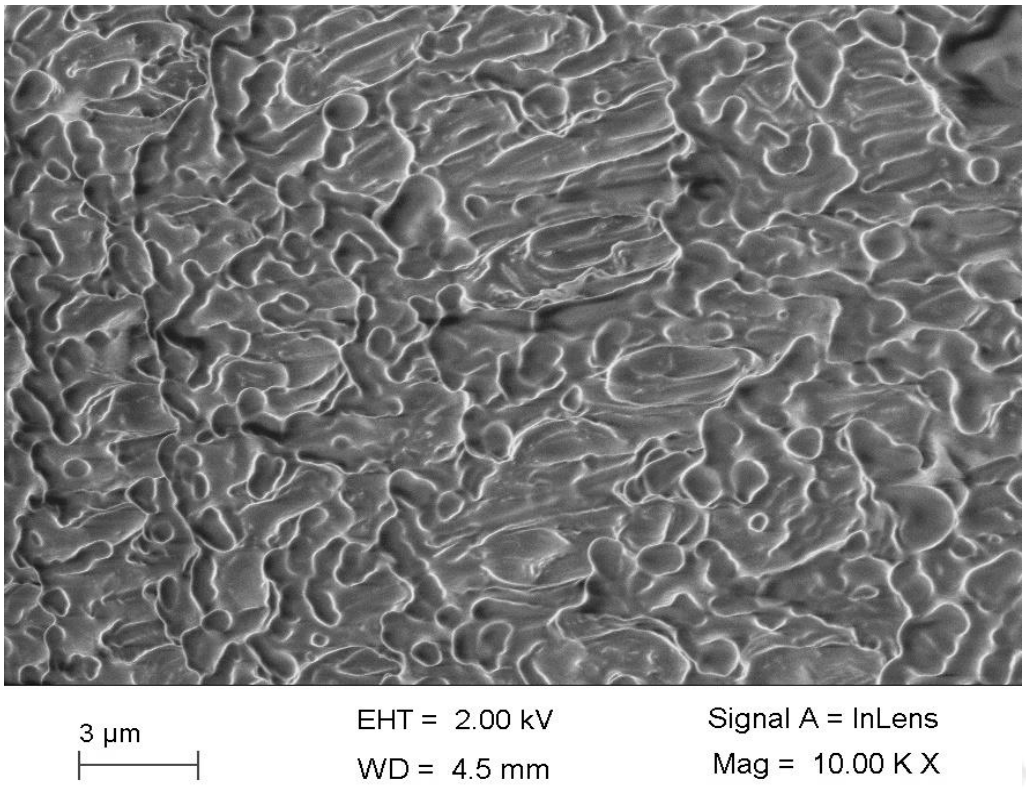
Figure 5.8: Stability behavior of SLM, % extraction versus number of runs: *(initial feed sol. conc. = 5 ppm Pb(II), $V_F = V_S$ = 250 mL, feed phase pH = 5, carrier conc. = 4% (v/v) D2EHPA, strip conc. = 0.2 M Na_2CO_3 and each run time = 10 h).*

Nevertheless, the organic phase must have been disturbed during the filling up of the feed and strip compartments and some amount of organic solution were surely washed out from the pores. This fact was confirmed by the FESEM analyses of the support membrane before and after the experimental runs (Fig. 5.9(a-d)). The physical properties and characteristics of PVDF support was discussed in Section 2.5.2. The pores of the support membrane were found empty before the impregnation of organic solution therein (Fig. 5.9(a)). The pores were filled up by the organic solution through the impregnation of the support (Fig. 5.9(b) and

5.9(c)) by the organic solution. Some amount of organic solution came out of the pores after 15 consecutive batch experiments (each run is 10 h duration) which resulted in the channeling of feed and stripping phases (Fig. 5.9(d)).



(a)



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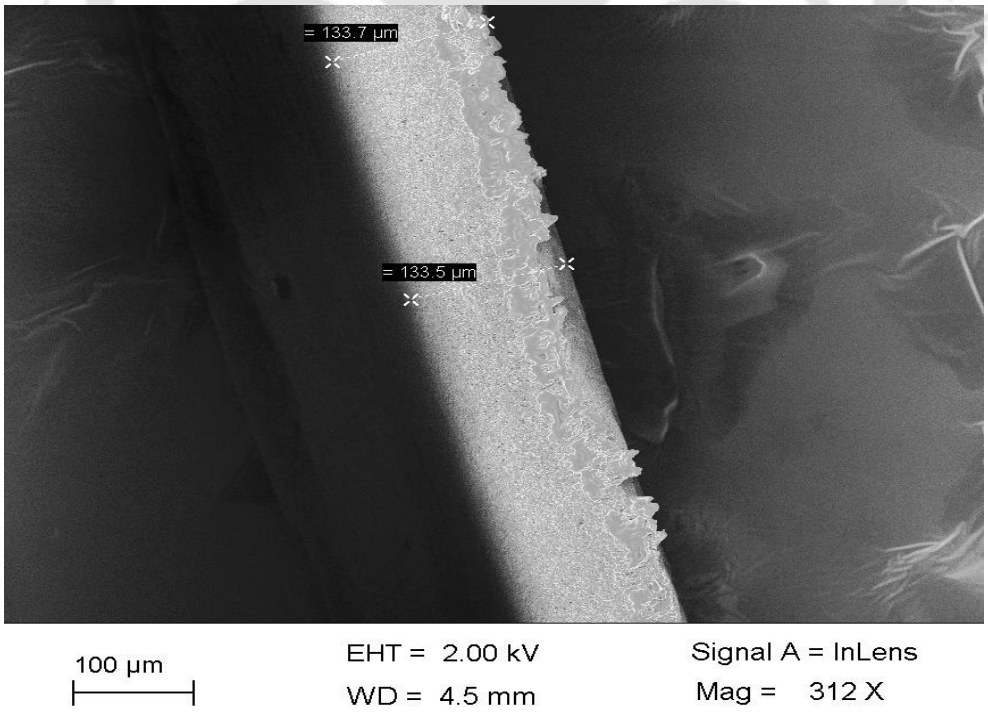

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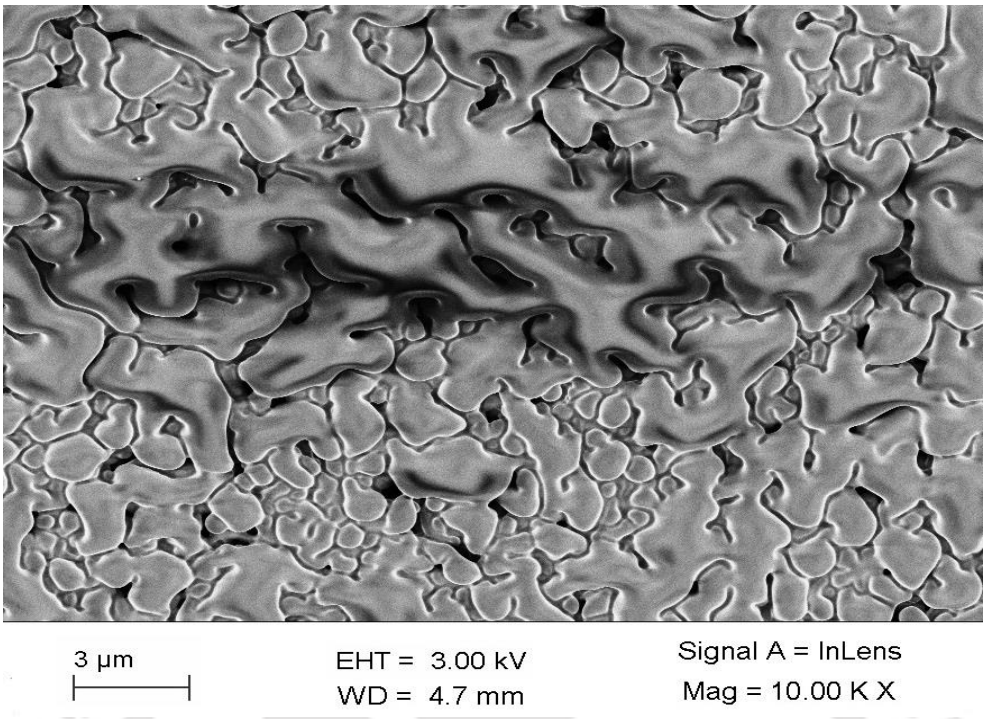


(d)

Figure 5.9(a-d): FESEM images of the surfaces (top view) and cross-section morphologies of an membrane support (PVDF): *(a) before ML impregnation on support (b) after ML impregnated (unused) support (c) after ML impregnated (unused) cross sectional view of the support and (d) after 150 h continues run on the same membrane support.*

5.2.8. Treatment of mixed feed

It has been intended to use the operating condition, that has been optimized for the extraction and recovery of Pb(II), for the transport Cd(II) as well. This is to evaluate whether and how much this operating condition is effective for transport of mixed feed. Experimental results reveal that extraction and recovery of Cd(II) were 82.48% and 76.4% respectively when Cd(II) was the sole pollutant. The results of the individual transportation of lead (II) and cadmium (II) have been shown in Fig. 5.10. Extraction of Pb(II) was 10.2% more than that of Cd(II), whereas the recovery of Pb(II) was 11.4% more than that of Cd(II). The preferential electronic structure of Pb(II) over Cd(II) explains the higher affinity of Pb(II) to the stripping agent leading to its better stripping. Atomic number and electronic configurations of Pb(II)

are 82 and [Xe] $4f^{14}5d^{10}6s^{1}6p^{3}$, respectively, while they are 48 and [Kr] $5s^{2}4d^{10}$, respectively for Cd(II). The shielding effect or the effective nuclear charge of Pb(II) is 5.65 against 4.35 of Cd(II) from Slater's rule [90]. Hence, Pb^{2+} is easily stripped off by stripping agent Na_2CO_3 in the stripping phase as compared to Cd^{2+}. On the other hand, the lower value of the solubility product for lead carbonate (0.074×10^{-12}) compared to that of cadmium carbonate (1.0×10^{-12}) is another reason of higher rate of precipitation of lead in the stripping phase compared to that of cadmium. Next, the mixed feed of Pb(II) and Cd(II) in various proportions were transported in the same optimized conditions and results were reported in the Table 5.2. Both the extraction and the recovery were found slightly less for the mixed feed in all cases which confirms the interference effect for transportation of two metals in mixed feed. Moreover, the available driving force (concentration difference) for the transportation of individual metals in the mixed feed is less compared to the same in "sole pollutant" feed (since total mixed feed concentration remained constant) and this driving force reduces with the presence of higher proportion of the second metal. However, both extraction and recovery were found slightly selective for lead in all cases. Moreover, extraction of both metals was highest (80.64% for cadmium (II) and 90.16% for lead (II)) when particular metal is abundant in the mixture, (*i.e.* Cd(II):Pb(II) mass ratio of 4:1 or 1:4). Same is true for the recovery as well. But recovery was less for Cd(II) (74.16%) compared to Pb(II) (85.14%). The above observation could be explained by the fact that Pb(II) complex was less accumulated in the membrane phase as compared to Cd(II) complex and that was found in their individual transportations (Fig. 5.5) too. Hence it is concluded that transportation of lead is slightly preferable over cadmium and that preference enhances with richness of lead over cadmium in the mixed feed. The cumulative transportation of Pb(II) and Cd(II) from combined feed was found higher for the decreasing ratio of Cd(II) to Pb(II).

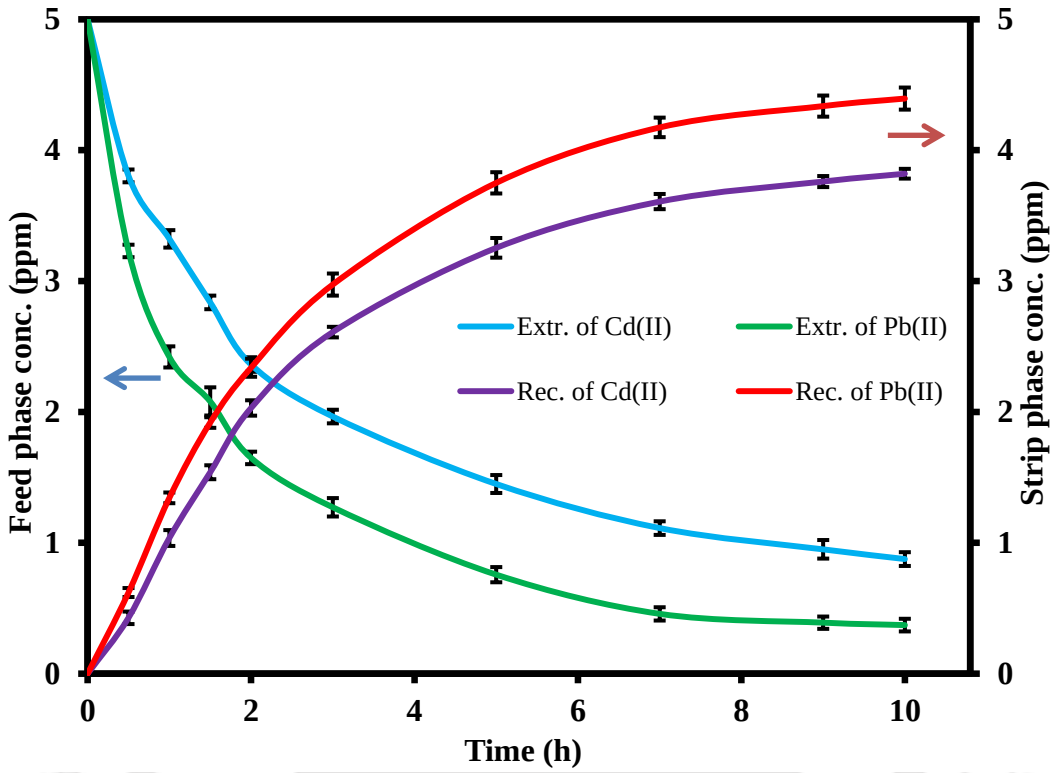


Figure 5.10: Individual metal transportation of Pb(II) and Cd(II): *(V_F = V_S = 250 mL, initial feed phase conc. = either 5 ppm Pb(II) or 5 ppm Cd(II), feed phase pH = 5, carrier conc. = 4% (v/v) D2EHPA, strip conc. = 0.2 M Na_2CO_3 and t = 10 h).*

Table 5.2: Percentages of extraction and recovery of mixed feed for various feed ratios (Cd(II):Pb(II)) and its total permeability and flux

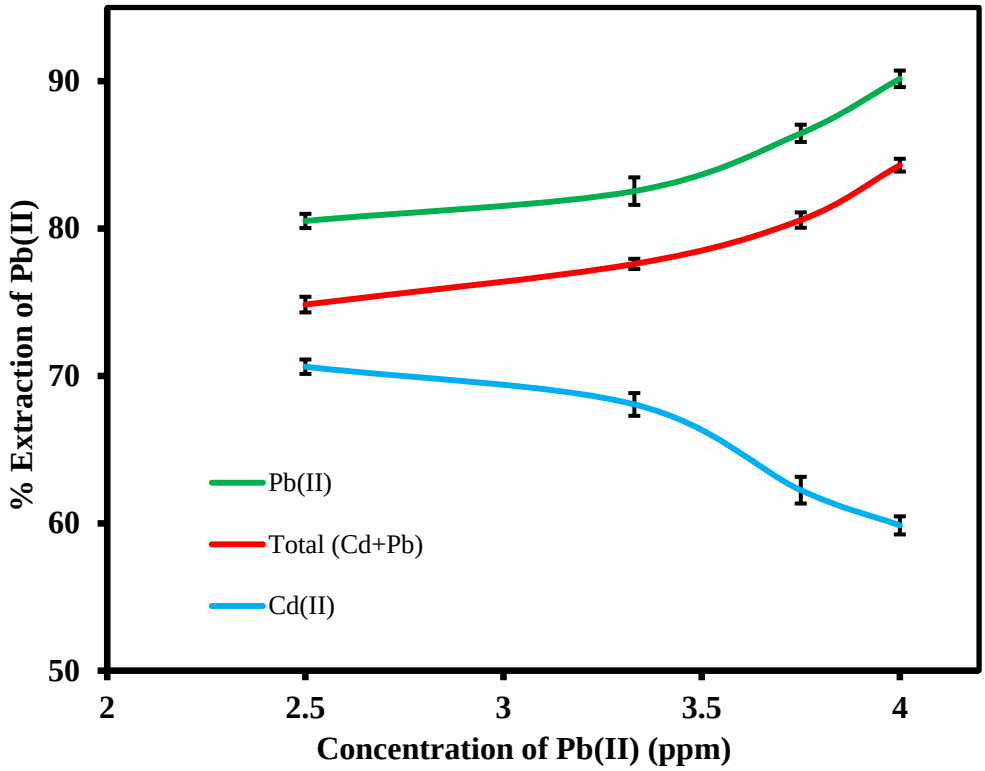
Cd(II):Pb(II)	Cd(II)		Pb(II)		Total extraction	Total recovery	Permeability ($P\times10^{-4}$)	Flux ($J\times10^{-8}$)
(mass ratio)	Extraction (weight %)	Recovery (weight %)	Extraction (weight %)	Recovery (weight %)	(weight %)	(weight %)	($cm.s^{-1}$)	($g.cm^{-2}.s^{-1}$)
Pure Cd(II)	82.48	76.40	-	-	82.48	76.40	12.16	6.08
Pure Pb(II)	-	-	92.53	87.89	92.53	87.89	15.20	7.60
1:1	70.63	66.64	80.51	76.41	74.84	70.76	9.88	4.94
1:2	68.07	62.21	82.54	77.38	77.60	72.20	10.92	5.46
1:3	62.25	56.80	86.46	81.44	80.58	74.46	12.02	6.01
1:4	59.86	52.57	90.16	85.14	84.30	77.40	13.54	6.77
2:1	75.24	70.76	76.99	72.64	76.09	71.52	10.29	5.15
3:1	78.30	72.68	74.06	67.82	77.17	71.77	10.79	5.39
4:1	80.64	74.16	67.41	62.33	78.05	71.92	11.53	5.76

5.2.9. Competitive transportation between lead (II) and cadmium (II)

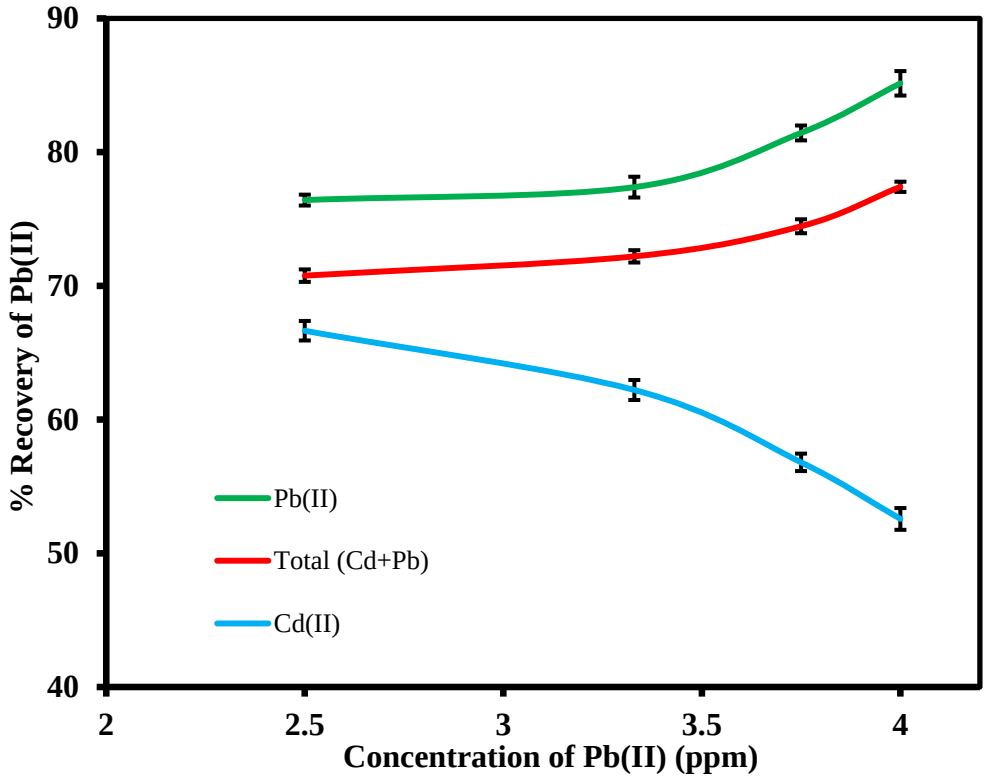
We inspected the interference effect of second metal on the transportation of the first one in detail with more data points. The experiments were carried out with synthesized feed containing Pb(II) and Cd(II) in diverse proportions; nonetheless the same cumulative mass of 5 ppm was maintained. The quantitative analyses were depicted in Table 5.2 and Fig. 5.11(a-d). Both the extraction and the recovery of Cd(II) reduced with increasing Pb(II) (interfering effect of the second metal) amount in the aggregate of 5 ppm feed solution (Fig. 5.11(a) and (b)). However, the cumulative (Pb(II) and Cd(II)) extraction and recovery increase with increasing Pb(II) concentration as Pb(II) transportation was preferential over the Cd(II). The transportation efficiencies were in between that of pure Cd(II) and pure Pb(II) of same concentration of 5 ppm, which confirms the negative interference effect for all ratios of metals. Similar trends were observed with increasing Cd(II) concentration in the combined feed of 5 ppm (Fig. 5.11(c) and (d)). Above results confirm the privileged transportation of Pb(II) over Cd(II) and accumulation of Cd(II)-carrier complex in the membrane phase. With increasing Pb(II) concentration in the mixed feed the percentage of total (Pb(II) and Cd(II)) extraction increased to 84.3% at Cd(II):Pb(II)::1:4 and that of total recovery increased to 77.4% (Fig. 5.11(a) and (b)). On the other hand, with increasing Cd(II) concentration in mixed feed (at Cd(II) to Pb(II) ratio of 4:1) maximum total (Pb(II) and Cd(II)) extraction and recovery were found as 78.05% and 71.92% respectively (Fig. 5.11(c) and (d)). The detailed finding confirms the preferential extraction and recovery of lead for the presence of said heavy metals in any proportions in the wastewater.

The permeability as well as flux values of combined metal transportation for various mass ratios of them in the mixed feed were shown in Table 5.2. The total permeability as well as total flux values for various ratios of metals indicated that the presence of second metal

reduces the transportation as compared to the pure metal. Both the overall permeability and the flux were minimum for the case of 1:1 ratio of the Cd(II) and Pb(II) *i.e.* when transportation of one metal is maximum affected by the presence of the maximum amount of the other. With decreasing amount of the second metal, both the permeability and flux increased to achieve the value of distinct pure metal.



(a)



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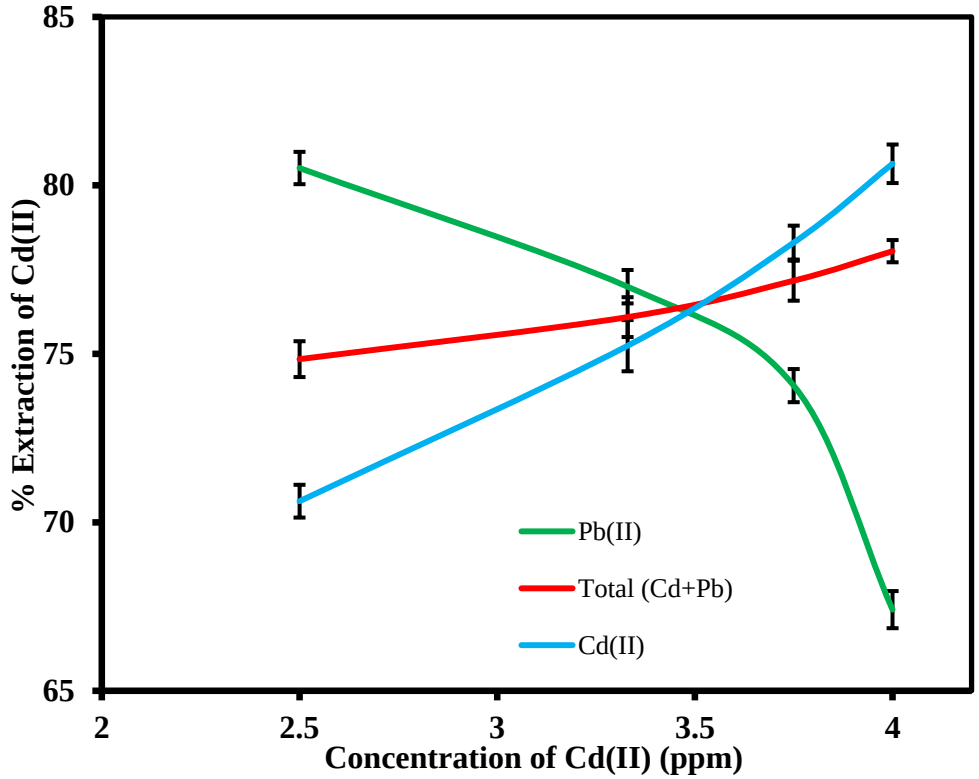


(c)

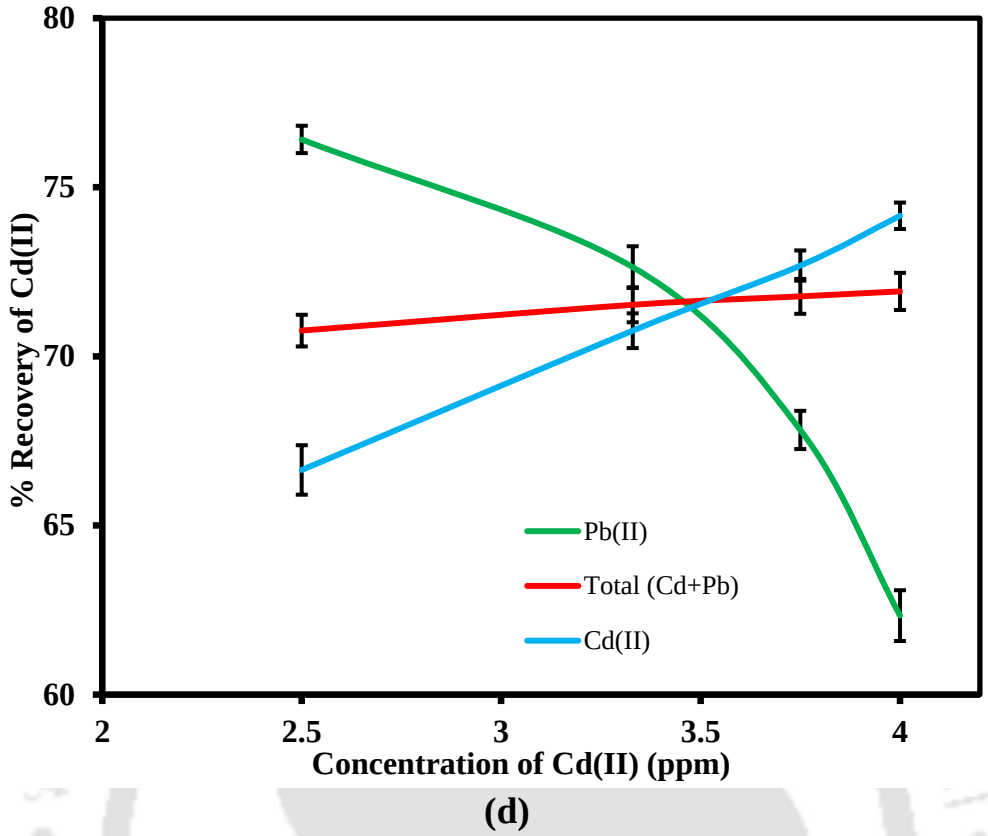


Figure 5.11(a-d): Effect of competition between the metals in their transportation (individuals as well as total extraction and recovery in various mass ratios of bi-metals): *(V_F = V_S = 250 mL, pH_F = 5.0, solvent (coconut oil) in carrier conc. = 4% (v/v) D2EHPA, strip conc. = 0.2 M Na_2CO_3, membrane support = PVDF (0.2 µm of pore size) and run time = 10 h).*

Table 5.3: Summary of optimum condition for simultaneous transport and precipitation of Cd(II) and Pb(II) in three phase FS-SLM study

S. No.	Parameter		Range studied	Optimum value
1	Feed phase pH		3-7	5
2	Carrier (D2EHPA) conc.		0-6 vol%	4 vol%
3	Strip phase (Na_2CO_3) conc.		0.05-0.3 M	0.2 M
4	Initial feed conc. (ppm)		3-10	5
5	Duration of extraction/stripping		0-10 h	10 h
6	**% Extraction**	**% Recovery**	----	At the optimum conditions
	Cd: 82.48% Pb: 92.53%	Cd: 76.40% Pb: 87.89%		

5.3. Summary of the FS-SLM based simultaneous separation and precipitation of Pb(II) and Cd(II)

- FS-SLM based separation technique has been found to be an efficient means for separation of cadmium (II) and lead (II) from wastewater.
- The hazardous heavy metals, *viz.* Pb(II) and Cd(II) were precipitated as insoluble carbonate salt in the stripping phase by using Na_2CO_3 as stripping agent.
  - Aliquat 336 is not suitable when Na_2CO_3 is used as stripping agent as it reacts with Na_2CO_3 and white precipitate of salt is formed. On the other hand, an acidic carrier *viz.* D2EHPA may be used in place of Aliquat 336 as D2EHPA doesn't react with Na_2CO_3.
  - The optimal operating conditions for FS-SLM studies have been found *viz.* pH of feed phase = 5, concentration of carrier (D2EHPA) = 4% (v/v), concentration of strip phase = 0.2 M Na_2CO_3.

- Simultaneous removal of metals (Pb(II) and Cd(II)) from the wastewater was studied.
- The preferential transportation of Pb(II) over Cd(II), especially with increasing percentage of Pb(II) in the mixture, is another important finding of this work.
- The flux of the combined feed is minimum at Cd(II):Pb(II)::1:1. The Pb(II) from its nitrate salt is easier to be transported compared to that from its chloride salt.
- The use of coconut oil in the organic phase makes the process environmentally and physiologically benign. The SLM was found to be stable up to100 h.

CHAPTER-VI

FS-SLM based simultaneous separation and electro-deposition of Pb(II) *and* Cd(II)

CHAPTER-VI

FS-SLM based simultaneous separation and electro-deposition of Pb(II) and Cd(II)

This chapter provides an improved process for separation of heavy metals from liquid wastes and/or industrial effluents. The experimental work presents the electro-deposition of hazardous heavy metals by the process of electroplating following their selective separation using SLM technique. An electric potential gradient (voltage) is applied through the electrodes in the stripping Section for deposition of metals recovered in the stripping phase. The amalgamation of above two processes i.e. separation of metals and their electrodeposition serves the dual purposes i.e. transformation of liquid waste to solid state for advantageous waste management and the recovery of metals in their purest (atomic) form for further utilization as value added product. Both lead (II) and cadmium (II) wastewater are studied separately prior to their simultaneous deposition. The graphite rod and the copper plate are used as anode and cathode, respectively for the purpose. Initial experiments are carried out to find out the best set of optimum parameters for simultaneous transportation and electroplating of lead (II) only. Lead (II) metal deposition on the copper plate as cathode is found higher (88% of initial lead (II) present in the feed phase) compared to that on stainless steel plate (73%). Other operating parameters like pH of stripping phase, electric potential across the stripping solution, area of the cathode plate for depositions of heavy metals are also investigated. At the optimum condition, i.e. pH of 4, electric potential of 2.5 V and area of cathode plate of 16.20 cm^2, for the deposition of cadmium (II) is found that 72% as compared to 88% of lead (II). Experiments were also carried out for simultaneous deposition of both the metals (Pb(II) and Cd(II)). Total deposition of lead (II)

and cadmium (II) are found for the higher ratio of lead (II) to cadmium (II) in mixed feed and that is consistent with the preferential transportation of lead (II) over the cadmium (II) in their individual studies. Energy-dispersive X-ray (EDX) analysis of the cathode plate confirmed the deposition of pure metals on the copper surface.

6.1. Introduction

Electrode coatings are now extensively employed for the improvement of the performance of modern electrochemical techniques [97]. It is recognized that the electrodeposition can be employed for the preparation of the stable metal coatings with suitable phase structures and on extensive surface morphology. Moreover, substantial modification to the physical properties and catalytic activities of the said coating can be possible through doping and fabrication of nanostructured deposits [98]. The standard potential for lead in aqueous solution is -0.13 V. The high value of hydrogen over potential of lead leads to easily deposition of it from strongly acidic solutions with cathodic efficiency approaching 100% [99]. The electrochemical equivalent for the reaction, $Pb^{2+} + 2e \rightarrow Pb$, is 3.865 g Ah^{-1}. Investigations for the deposition of lead-cadmium alloys were carried out with the aim of their possible application for bearings [97, 98]. Lead-indium alloy is a good bearing alloy due to its high fatigue strength and corrosion resistance against oxidation. However, indium is very costly metal. On the other hand, lead-cadmium alloy with cadmium content of up to 30% is a good alternative. Owing to the closeness of the standard potential of the lead and cadmium, the co-deposition from their solutions is adequately possible [99-103]. A huge field of application of electroplated lead is there in the production of lead accumulators. All the parts that come into contact with sulphuric acid are plated with 200 μm lead. The base material is usually copper, but there is also reference of using the aluminum leading to lesser weight of the electroplated component [101, 103]. Moreover, the use of electrodeposited lead

layer for the applications in the field of superconductivity is referred in the literature [104-106].

6.2. Theoretical background

The process involves simultaneous transportation of lead (II) and cadmium (II) from the feed phase and electroplating of the said heavy metals on electrode placed in the stripping chamber of SLM, thus facilitating enhanced and faster recovery of said heavy metals. The stripping chamber of SLM is integrated with in-situ electroplating means with an applied electric potential gradient (voltage) on the electrodes, thereby facilitating transportation of heavy metals from feed phase to the electrode through electroplating means. Advantageously the integrated process involves SLM based extraction and stripping of heavy metals and their simultaneous electrodeposition, from the wastewater/ industrial effluents. Hence it serves for dual purposes *i.e.* advantageous waste management from industrial effluent and the recovery of metals in their purest (atomic) form for further utilization as value added product.

6.2.1. Transportation methodology

The mechanism of extraction of lead (II) and cadmium (II) ions by the acidic carrier/extractant is provided in Section 5.1.1 of Chapter V. The mechanism of complexation and the transportation of the complex through the LM are identical as reported there. The complex coming to the stripping side interface reacts with nitric acid (HNO_3) and lead (II) and/or cadmium (II) are liberated as Pb^{++} and Cd^{++} respectively. Cations are electroplated at cathode. The electrochemical reactions at anode and cathode plate are shown below (Eq's. 6.2 & 6.3):

Strip phase:

$$MCO_3 + 2HNO_3 \rightarrow M^{++} + 2NO_3^- + H_2O + CO_2 \uparrow (g) \quad (6.1)$$

Electrodes:

Anode: $2H_2O \rightarrow 4H^+ + O_2 \uparrow (g) + 4e^-$ (6.2)

Cathode: $M^{++} + 2e^- \rightarrow M\ (electroplating)$ (6.3)

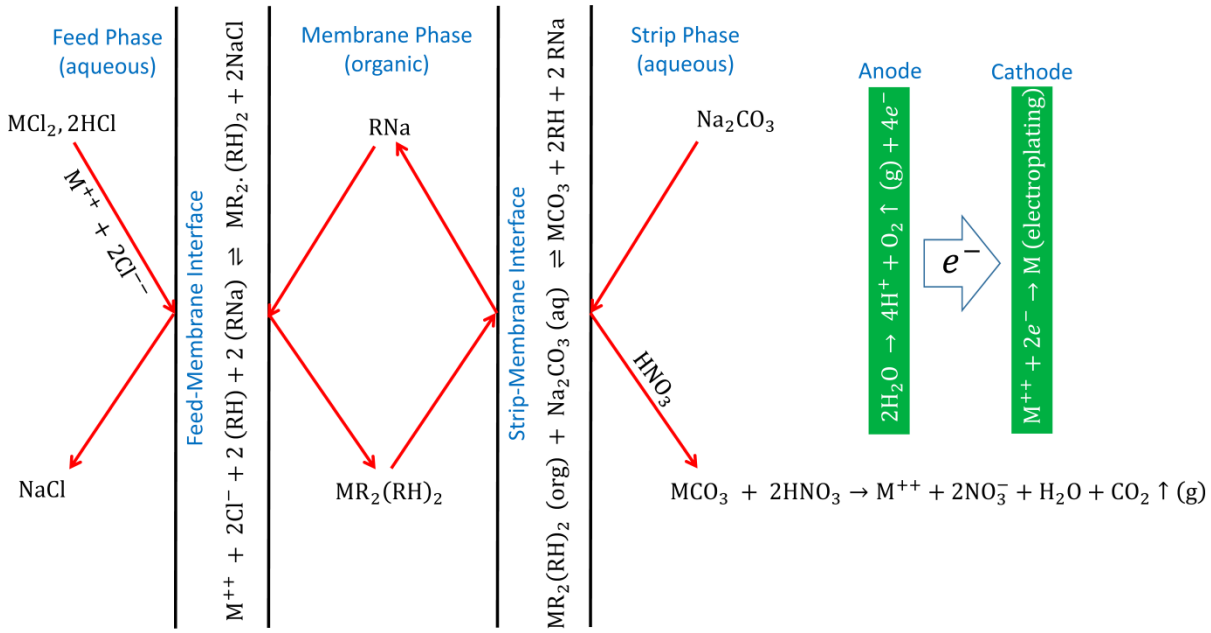


Figure 6.1: Schematic diagram of counter-transport mode of Pb(II) and Cd(II) and electrodeposition

6.3. Results and discussion

From the previous chapters 4 and 5 indicates that for identical operating condition, Pb(II) is preferentially transported across an FS-SLM over Cd(II) in a binary mixture of salts in feed phase. In this study, the additional operating conditions for electroplating has been optimized while experimenting with Pb(II). Simultaneous transport of Pb(II) and Cd(II) and their subsequent electroplating have been studied in the said optimized condition.

6.3.1. Determination of appropriate pH of stripping solution

The pH of aqueous phases of SLM plays an important role in separation of solute. Appropriate pH of the feed phase has been determined at first. The reaction mechanism, as demonstrated in Fig. 5.1. & explained in Section 5.1.1, indicates that the best operating pH of feed phase to lie in the acidic range (below pH 7). The experiments were carried out within the range of pH 3-7. It was found that if Na_2CO_3 is used as stripping agent then lead (II) precipitates in the stripping phase as lead carbonate salt which is not desired in the process of the present invention as lead (II) needs to be transported from feed phase to the electrode through electroplating means. However, on maintaining the following condition (from 5.2.1 to 5.2.5): initial concentration of lead chloride in feed solution = 5 ppm, volume of feed phase = 250 mL, volume of stripping phase = 250 mL, concentration of carrier D2EHPA = 4% (v/v), concentration of stripping phase = 0.2 M Na_2CO_3, the maximum extraction (92.53%) and recovery (87.89%) of lead (II) were obtained at a pH of 5.0 [83].

Similarly the pH of stripping phase also plays a vital role for the metal ions to be deposited on the cathode plate. The effect of the pH of stripping phase was investigated in the wide pH range of 2.0−12.0. The results have been shown in Fig. 6.2. The maximum deposition (88%) of metal ions (lead) on the electrode was observed at pH of 4.0. It was thus significantly found that only nitric acid yields the dissociation of lead carbonate salt at the lower pH of stripping phase and the lead (II) transportation to the cathode is facilitated. At higher pH, higher than (4.0), dissociation is less and as a result lead deposition on the cathode is less. On the other hand, at pH lower than pH 4, there is the crowding effect of protons surrounding the lead (II) cations which effectively inhibits the transportation of lead (II) to the cathode plate. Hence, pH of stripping phase was maintained at 4.0 for the further experiments.

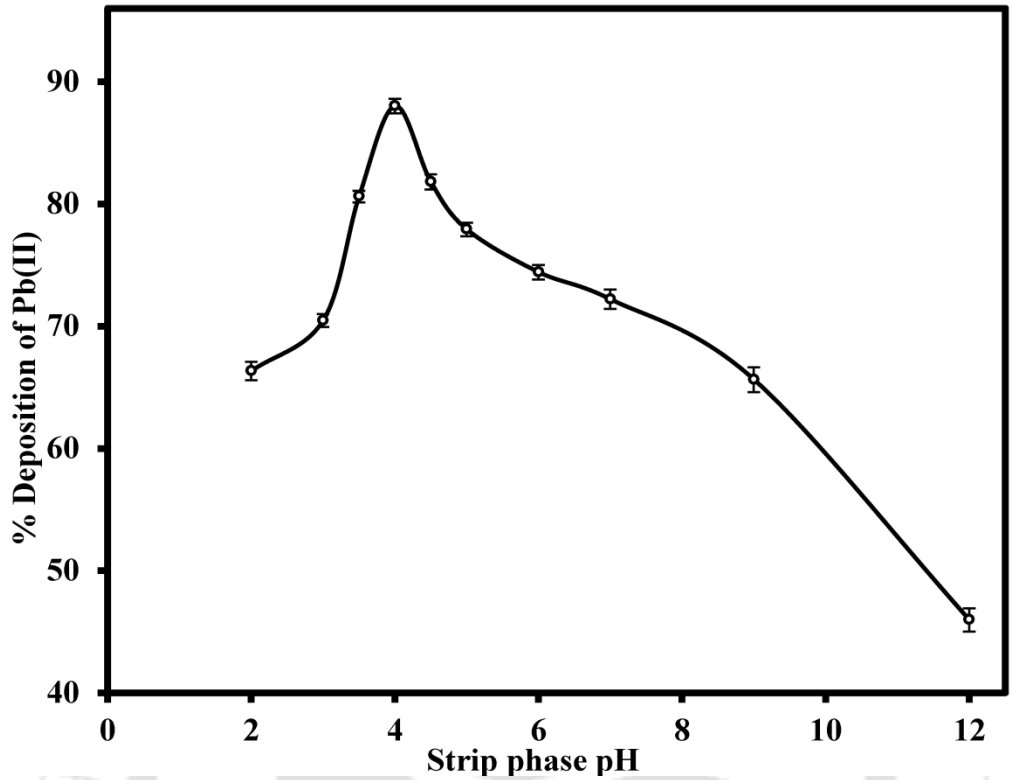


Figure 6.2: Role of pH of strip solution for the deposition of lead ions on cathode (copper plate): *copper plate surface area = 16.2 cm^2, $V_F = V_S$ = 250 mL, strip conc. = 0.2 M Na_2CO_3, voltage = 2.5 V and run time = 10 h.*

6.3.2. Selection of suitable cathode

Lead ion was re-extracted/stripped by the stripping agent Na_2CO_3 to form the lead carbonate once it reached to the stripping side interface. Lead (II) cation was replaced by Na^+ in the stripping reaction. Lead carbonate transforms to the lead nitrate immediately in presence of HNO_3 in the stripping phase. Lead nitrate dissociates into Pb^{2+} cations and NO_3^- in aqueous stripping phase in presence of excess HNO_3. The electroplating of lead (II) takes place on the cathode on application of electric potential across the electrodes. Due to high rate of electrodeposition of lead, the concentration of lead in the stripping phase remains very low. Hence the concentration gradient of lead (II) across the SLM is grossly enhanced, which in turn facilitates more transportation of metal across the SLM. Graphite plate was used as the anode and two other metal plates, *viz.* copper and stainless steel were tested as cathodes.

Percentages of deposition were measured against time for both the cathode plates and the results are plotted in Fig. 6.3. Although the electro-deposition is very fast process, LM based transportation is rather a slow and rate determining step. A copper plate serves better than the stainless steel in term of the % depositions due to the higher electrical conductivity of copper as compared to that of stainless steel (Table 6.1). By using copper plate as cathode, 76% of lead that was initially present in the feed phase got deposited within first 3 h of experiment and the extent of deposition reached its ultimate value at 88% after 10 h of operation. On the other hand, deposition of lead on the stainless steel cathode is 58.06% and 72% of the initial amount after 3 h and 10 h respectively. Hence, graphite and copper plates were chosen as anode and cathode, respectively.

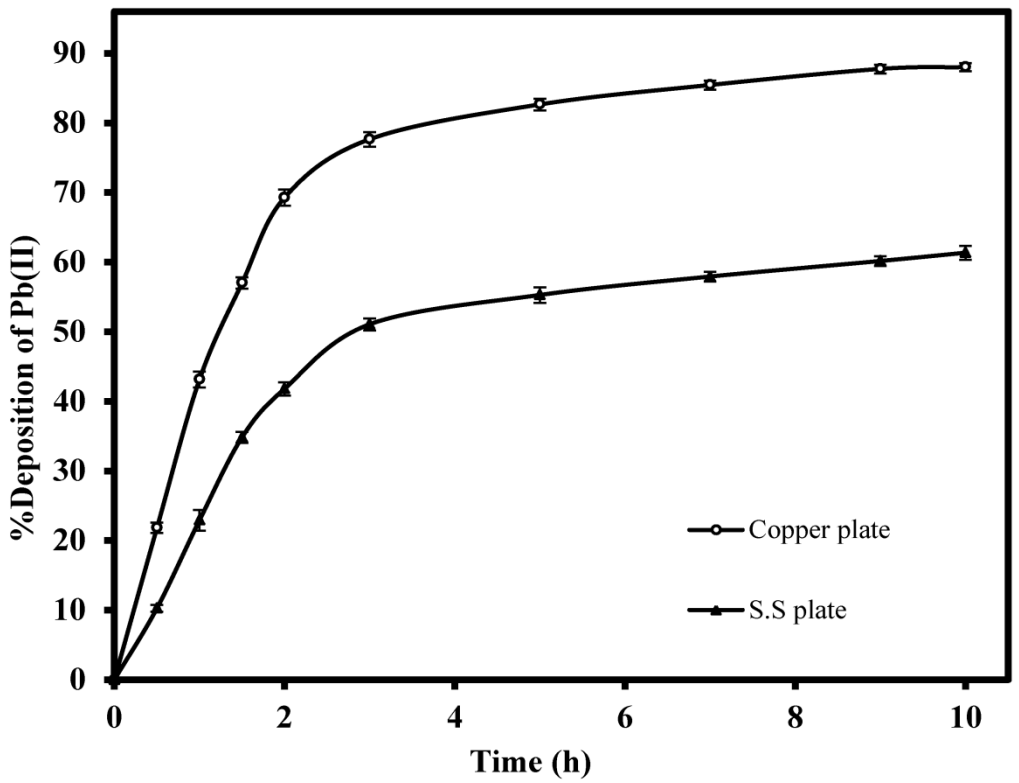


Figure 6.3: Deposition of lead for different material for cathode: *cathode surface area = 16.2 cm^2, $V_F = V_S = 250$ mL, strip conc. = 0.2 M Na_2CO_3, stripping phase pH = 4, voltage = 2.5 V and run time = 10 h.*

Table 6.1: Conductivity of copper and stainless steel

Name of the metal	Electrical conductivity (S/m)
Copper	5.96×10^{7}
Stainless Steel (S.S)	1.45×10^{6}

6.3.3. Role of electric field for Pb(II) transportation

The importance of the application of electric field in the stripping solution for the deposition of metals on the cathode was compared with the case when no electrical potential was applied across the stripping phase. The concentrations of lead (II) in both the feed and stripping phases are plotted against time for both the cases (Fig. 6.4). Metal deposition increases with time. Reduction of lead (II) in feed phase is higher when electric field is applied across the electrodes. After 10 h of run, the concentration of lead (II) in the feed phase is 0.06 ppm when electric field is applied while it is 0.38 ppm in absence of any electric field. On the other hand, the concentration of lead (II) goes up to 4.3 ppm in stripping phase when no electric field is present across the electrodes.

However, the same stripping phase shows a meagre ~0.4 ppm concentration of lead (II) on application of electric field. The transferred lead (II) to the stripping phase was deposited immediately on the cathode plate with the application of the electric potential and concentration in the stripping phase was found very less (~0.4 ppm) throughout the running time (Fig. 6.4). Energy-dispersive X-ray (EDX) analysis of the cathode confirmed the deposition of pure lead (II) metal on the copper surface (Fig. 6.5). The presence of copper in the copper plate before the deposition of lead (II) (Fig. 6.5a) and the presence of lead (II) after the deposition of lead (II) (Fig. 6.5b) on the same copper plate confirmed the lead deposition during the operation.

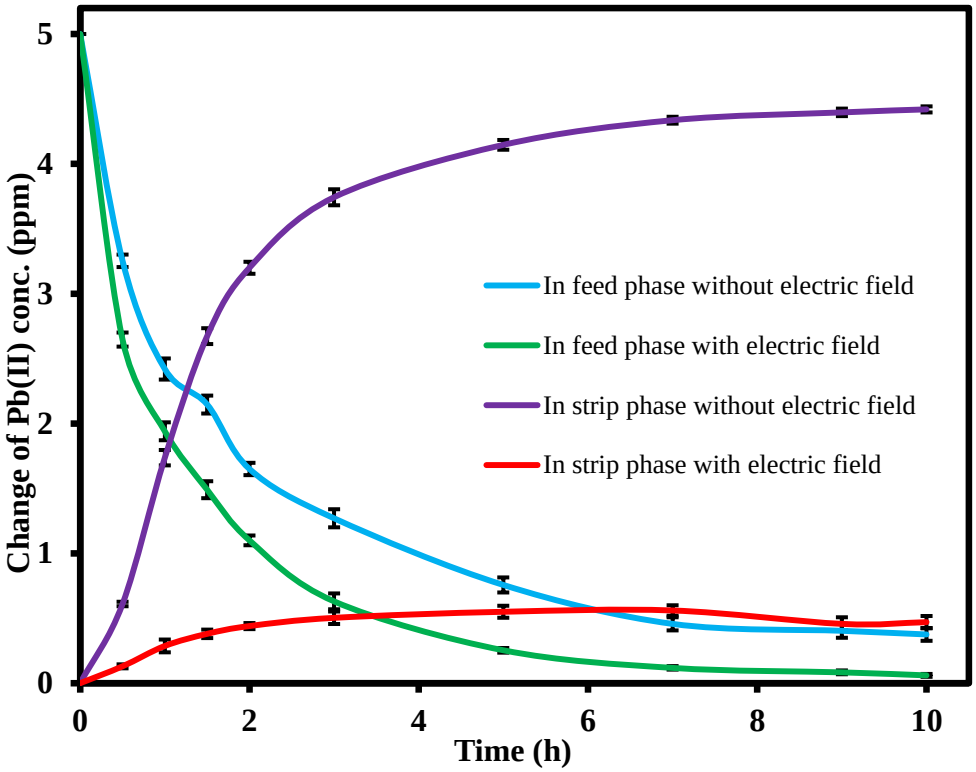
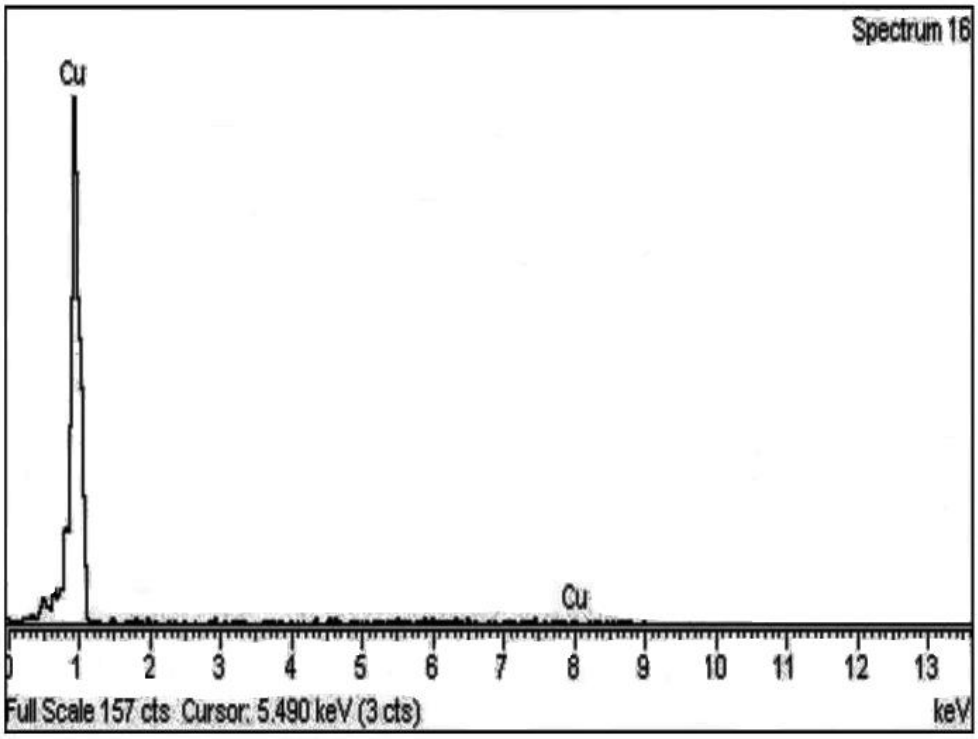
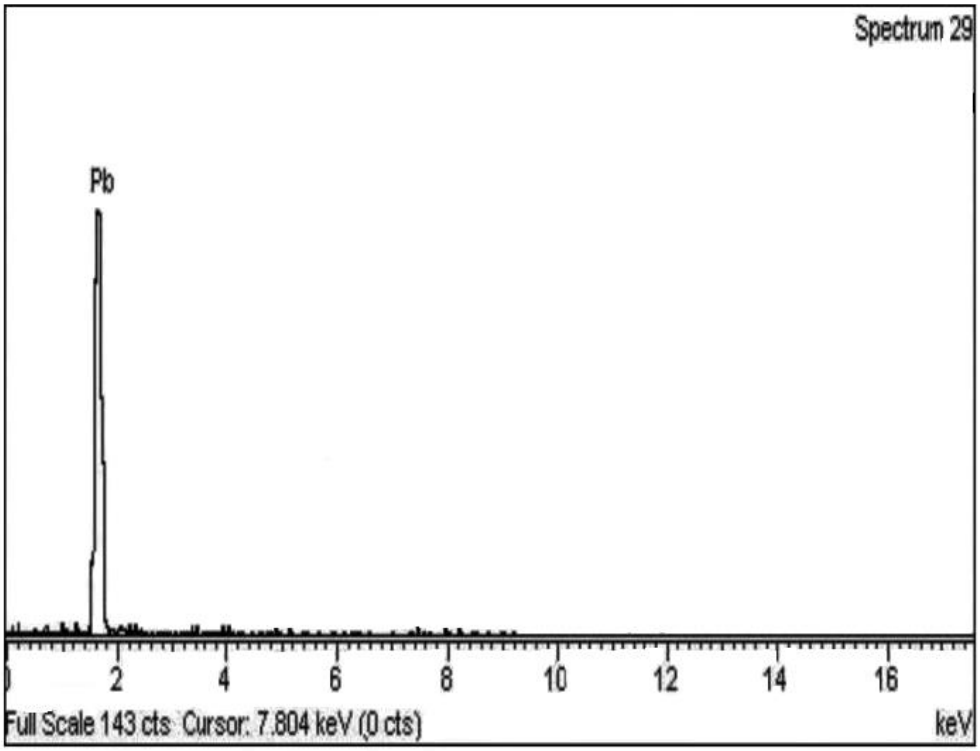


Figure 6.4: Concentration of lead (II) in feed and stripping phases with time: *copper plate surface area = 16.2 cm^2, V_F = V_S = 250 mL, carrier conc. = 4% (v/v) D2EHPA, solvent = coconut oil, strip conc. = 0.2 M Na_2CO_3 and voltage = 2.5 V.*



(a)



(b)

Figure 6.5: EDX analysis of copper plate: (a) before lead (II) deposition (b) after 5 runs lead (II) deposition.

6.3.4. Optimization of electric potential for Pb(II) deposition

Percentage deposition of lead (II) was measured for various electric potentials applied to the electric circuit in the stripping solution (Fig. 6.6). Percentage of lead (II) deposition increases with increase in the applied voltage up to 2.5 volt. It indicates a saturation value of 88% at around 2.5 V and the percentage of lead (II) deposition doesn't increase any further with increase of voltage. Hence, 2.5 V is found to be the selective voltage required for performing electroplating of lead (II) on the cathode plate. It is also important to mention that though both lead (II) and sodium cations were present in the stripping solutions, only lead (II) was deposited on the cathode plate not the sodium because the standard reduction potential of sodium (-2.71 V) is lower than that of lead (-0.13 V).

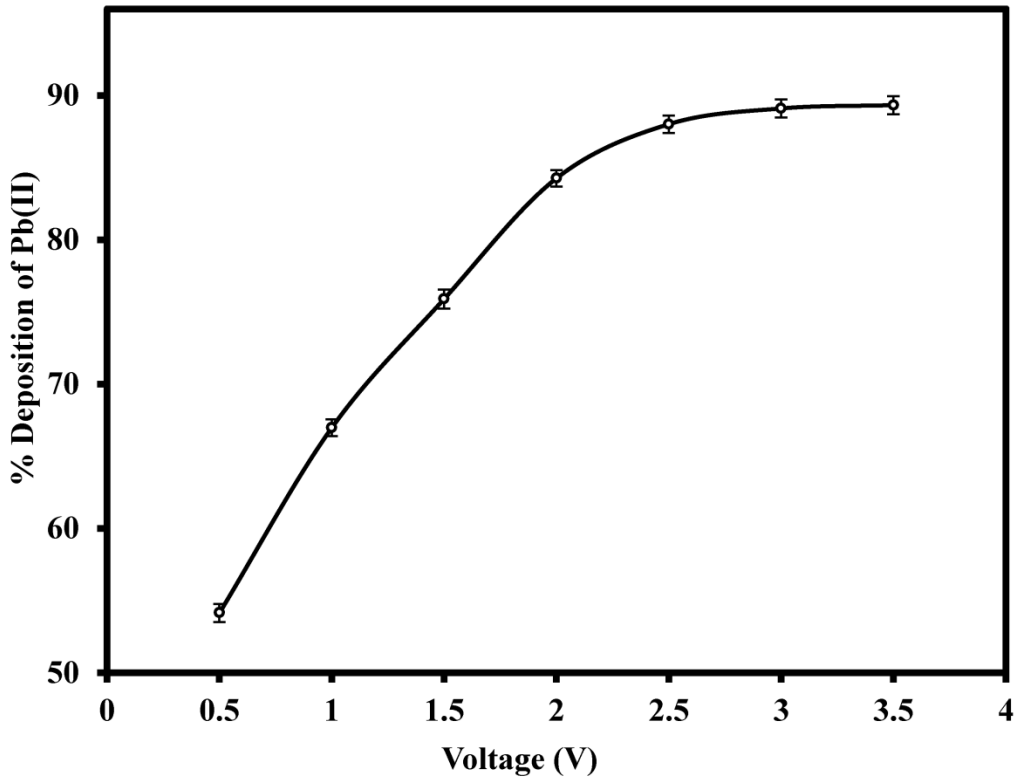


Figure 6.6: Role of voltage for lead (II) deposition: *copper surface area = 16.2 cm^2, V_F = V_S= 250 mL, strip conc. = 0.2 M Na_2CO_3, pH_S = 4, voltage = 2.5 V and each run time = 10 h.*

Similarly, the standard reduction potential of the lead (II) is slightly higher than that of cadmium (II) (-0.40 V) which leads to the deposition of lead (II) on the cathode plate on preferential basis (Table 6. 2).

Table 6.2: Standard electrode potentials of lead, cadmium and sodium in aqueous solution at 25°C

Cathode (Reduction) Half-Reaction	Standard Potential E° (volts)
Pb^{2+} (aq) + $2e^-$ → Pb (s)	-0.13
Cd^{2+} (aq) + $2e^-$ → Cd (s)	-0.40
Na^+ (aq) + e^- → Na (s)	-2.71

6.3.5. Optimization of cathode surface area

The effect of surface area of a cathode plate was studied by consecutive runs of SLM followed by electroplating on the same plate. Surface area of a cathode plate varies with its size. Plates of various sizes were used for experiments. Table 6.3 shows the percent of initial lead (II) content of the feed phase that is deposited on the cathode plate after successive runs of electroplating. The percentage deposition decreases when all the available surface area gets covered by the lead (II) metal. The optimum deposition (87.87%) is not affected up to 4th run when a cathode with surface area 16.2 cm^2 is used. But, % deposition reduces to 66.74% in the 5th run. Hence, it can be concluded that all the available surface area of cathode was covered with deposition of lead (II) in 5 runs. The above argument is confirmed by using two more cathode plates of areas 4.05 cm^2 (Plate II) and 36.45 cm^2 (Plate III). It is observed that Plate II gets saturated after 2nd run when the percentage deposition drops to 30.40% in the 3rd run. On the other hand, Plate III gets saturated at the 8th run and the deposition drops to 13.80% in the last run. Hence, the lead deposition is very effective only for the single layer of the lead (II) metal on the copper plate. The double or more layers formation is not effective as electrical conductivity of lead (II) is very less compared to that of copper.

Table 6.3: Total deposition of lead (II) vs. area of cathode surface in the following conditions: (*volume of feed phase = 250 mL, volume of stripping phase= 250 mL, concentration of stripping phase = 0.2 M Na_2CO_3, pH of stripping phase= 4, voltage = 2.5 V and each run time = 10 h*).

Plate no.	Surface area of copper plate (cm^2)	% Deposition does not change up to run no.	% deposition in the last run	Total amount of deposition (mg)
Plate I	16.20	4	66.74	20.91
Plate II	4.05	2	30.40	10.31
Plate III	36.45	7	13.08	31.45

6.3.6. Comparison between lead (II) and cadmium (II)

The process of SLM plus electroplating has been repeated for mitigation of Cd(II). The same operating conditions which have been optimized for the separation and electrodeposition of Pb(II) were applied in the case of Cd(II) too. The results are depicted in Fig. 6.7. The trends of the % deposition of metal are similar for both the metals as the nature of the metals are similar too. However, the deposition is preferable for the lead (II) over the cadmium (II) due to favorable atomic structure of the lead (II) [3, 21]. Most of the metals were deposited within the first 3 h of run time as the concentration differential is very high at the beginning of the transportation run.

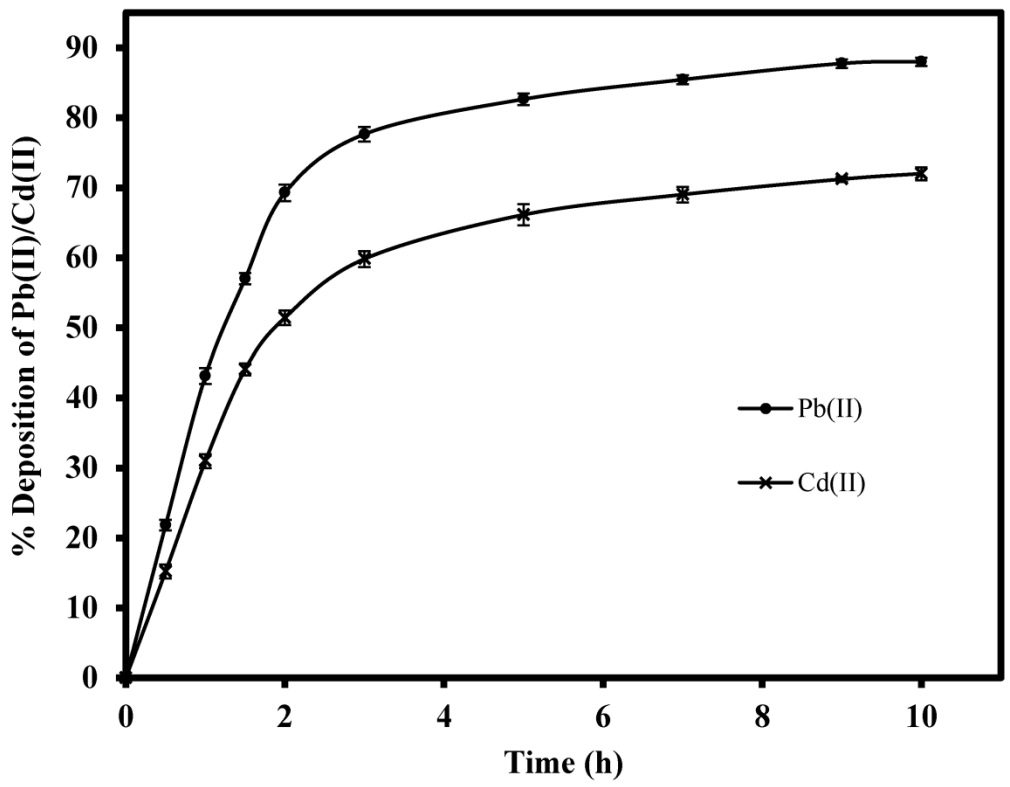


Figure 6.7: Deposition of individual metals: (*copper plate surface area = 16.2 cm^2, $V_F = V_S$ = 250 mL, initial feed phase conc. = either 5 ppm Pb(II) or 5 ppm Cd(II), carrier conc. = 4% (v/v) D2EHPA, solvent = coconut oil, strip conc. = 0.2 M Na_2CO_3 and voltage = 2.5 V).*

Nevertheless, the concentration gradient diminishes with time and the rates of deposition gets grossly reduced. After 10 h of operation, the equilibrium is reached for both the metals at deposition of 88.0% and 72.0% for Pb(II) and Cd(II), respectively.

6.3.7. Simultaneous separation of metals

Wastewater with Pb(II) and Cd(II) at various proportions has been taken as feed solutions of binary nature. Simultaneous transportation and deposition of both the metals were carried out. The detailed results are reported in Table 6.4. The maximum recovery and deposition are obtained at the Cd:Pb::1:4 (mass ratio) that confirms the preferential transportation as well as deposition of lead (II) over the cadmium (II). The atomic number and the electronic configuration of Pb(II) are 82 and [Xe] $4f^{14}5d^{10}6s^{1}6p^{3}$, respectively, and those of Cd(II) are 48 and [Kr]$5s^{2}4d^{10}$, respectively. The shielding effect of Pb(II) is more and also the effective nuclear charge of Pb(II) is 5.65 against 4.35 of Cd(II) (from Slater's rule [90].

Table 6.4: Electro-deposition of Pb(II) and Cd(II) from their mixed feed in various ratios

Cd(II) (ppm)	Pb(II) (ppm)	Cd(II):Pb(II) Mass ratio	% Extraction of Cd(II)	% Extraction of Pb(II)	Total extraction (Cd+Pb) (%)	Total recovery (Cd+Pb) (%)	% Total deposition of metals on cathode (weight)
5	-	-	87.34	-	87.34	84.74	72.00
-	5	-	-	98.80	98.80	97.00	88.00
2.5	2.5	1:1	73.13	84.32	71.14	69.14	64.00
1	4	1:4	61.70	94.63	88.04	86.04	72.00
4	1	4:1	84.40	69.96	81.51	79.11	64.00

So, the affinity of Pb^{2+} to the negative electrode *i.e.* cathode plate is more compared to that of Cd^{2+}. Hence, the electrodeposition of lead (II) is preferred to that of cadmium (II) on the same cathode plate copper.

Table 6.5: Summary of optimum condition for simultaneous transport and electro-deposition of Cd(II) and Pb(II) in three phase FS-SLM study

S. No.	Parameter	Range studied	Optimum value
1	Strip phase pH	2−12	4
2	Material of cathode plate	Copper and stainless steel	Copper (88% deposition)
3	Voltage for metal deposition	0.5−3.5 V	2.5 V
4	Cathode surface area	4.05, 16.20 and 36.45 cm^2	16.20 cm^2
5	Duration of extraction/stripping	0−10 h	10 h
6	**% Extraction** **% Recovery** Cd: 87.34% Cd: 84.74% or 72% deposition Pb: 98.80% Pb: 97.00% or 88% deposition	---	At the optimum conditions

6.4. Summary of the FS-SLM based simultaneous separation and electro deposition of Pb(II) and Cd(II)

- Electrodeposition integrated simultaneous extraction and stripping of Pb(II) and Cd (II) in SLM. The electrodeposition is carried out in the stripping section of an FS-SLM system.
- The carrier-solvent combination of "D2EHPA (4% v/v) in environmentally benign coconut oil" was used as the organic solution.
- Copper plate is found to be an ideal cathode for this purpose.

- At the optimum operating conditions: feed phase pH is 5 and stripping phase pH is 4, electric potential of 2.5 V and area of cathode electrode plate of 16.20 cm^2 to facilitate deposition and recovery of 72% cadmium (II) as compared to 88% of lead (II) simultaneously.
- The change in efficiency of individual transportation due to interaction effect was investigated.
- The maximum deposition based recovery of Pb(II) and Cd(II) from wastewater was attained at Cd(II):Pb(II)::1:4 (mass ratio).
- Lead (II) is being preferentially transported/electroplated over cadmium (II).

CHAPTER-VII

Conclusion

CHAPTER-VII

This chapter summarizes the inferences drawn from the present research work and provides recommendations towards future direction for the separation of toxic heavy metals from industrial effluents.

7.1. Conclusion

The performance of LM based processes for extraction and recovery of heavy metal pollutants from wastewater has been investigated in this thesis. The pollutants, *viz.* cadmium (II) and lead (II), were separated from aqueous solution by using different techniques. Two phase equilibrium studies as well as three phase transportation studies using BLM and FS-SLM were carried out. The operating parameters were optimized for achieving maximum yield. The efficiencies of separation processes of heavy metals in various configurations of LM were then measured and compared through a series of experiments. Stripping agent was so selected that the recovered heavy metals in the stripping phase were converted to solid waste either by precipitation or electroplating and waste management became easier. Thereby a novel technique has been proposed and implemented in which the LM based separation has been integrated with electroplating of separated metals on the cathode (copper) plate; and the resulting technique produces value-added products *i.e.* lead(II) and cadmium(II) electroplated copper plate. The major conclusions of this thesis are summarized below:

- The SLM based technique is applicable for simultaneous separation of cadmium (II) and lead (II) from wastewater
- Coconut oil has been found to be an ideal green solvent for the LM based the separation process of heavy metals.

Conclusion

- The two phase studies demonstrate that the optimum extraction of heavy metals can be obtained at the following operating conditions: pH of feed phase = 6.5, temperature of operation = 25˚C, concentration of extractant in the membrane phase = 0.5% (v/v) Aliquat 336, initial concentration of feed phase = 5 ppm, duration of extraction = 2 h.
- BLM is, in general, useful only for lab scale study. The up-gradation of the technique to a pilot/commercial scale is ineffective due to much lower value of surface area to volume ratio of LM. Hence, the efficiency of FS-SLM module was investigated in the separation of heavy metals.
- Although DMOA is the best extractant for extraction of cadmium, the extent of recovery of solute in the stripping side was very less. The second best extractant, *viz.* Aliquat 336, was found to be a suitable alternative.
- The FS-SLM combination "PVDF-Coconut oil-Aliquat 336-Na_2–EDTA" is found to be suitable for separation of heavy metals.
- Na_2–EDTA has been proved to be an excellent stripping agent to form a metal-EDTA complex in stripping phase.
- A fed batch type arrangement ensured the possibility of complete separation and pre-concentration of heavy metals with a relatively small amount of stripping agent.
- The LM system "PVDF-coconut oil-D2EHPA-Na_2CO_3" has been found to be substantially stable for 100 h but with reduction of extraction from 93% to 85% only.
- Transportation of the lead (II) from its nitrate salt is favorable compared to its chloride salt.
- The transportation of lead (II) is favored to that of cadmium (II) in all strategies of transportation through LM.
- Na_2CO_3 was found as a good stripping agent for the precipitation of Pb(II) and Cd(II) in the stripping chamber.

- Application of electric potential combined with LM based separation provided the opportunity to convert the liquid waste to concentrated solid ones. Moreover, metal salts in wastes are recovered as useful metallic form and for the production of value added substances.

7.2. Recommendations for future work

FS-SLM based separation is still an emerging area and there is huge scope for work in future. Extraction using multiple extractants needs greater focus for multiple heavy metals and their synergistic effects can be studied in detail; some other topics related to the ones presented in this thesis that needs to be addressed in future are the following:

- Development of mathematical modeling of the entire extraction process including process chemistry, speciation dynamics and metal recovery etc. would be a useful exercise.
- The SLM study was carried out for the separation of only two metals *i.e.* cadmium (II) and lead (II). This work can be extended to separate multiple numbers of metal ions from the industrial effluents with employment of multiple carriers and their synergistic effect on the transportation efficiency can be evaluated.
- The FS-SLM configuration, used in the present work, yielded promising results for separation of heavy metals. Therefore, similar studies using other configurations such as hollow fiber SLM, spiral wound SLM and series of two or more SLMs can be carried out.
- Detailed stability criteria of SLMs may be studied.
- In the present research work, electroplating was done only for lead (II) and cadmium (II). However, the same electroplating technique can be used for separation of other metals also.

Conclusion

- All the experiments in this research work were carried out in batch mode. The efficiency of a continuous mode SLM can be studied in future.

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Visible Research Output

Patent

[1] K.K. Bhatluri, M.S. Manna, A.K. Ghoshal, P. Saha, Separation of heavy metals from waste water by electrodeposition integrated supported liquid membrane, filed for Indian Patent, Application No. 733/KOL/2015 dated July 7, 2015.

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APPENDIX

Appendix-I

Composition of common coconut oil

Coconut oil is basically long and medium chain triglycerides [1]. The typical fatty acid composition [2] of coconut oil is given in Table AI.1

Table AI.1 Composition of fatty acids in coconut oil [2]

Name of components	Saturation	Quantity (%)
Caprylic Acid (C8)	saturated	7.0
Capric Acid (C10)	saturated	5.4
Lauric Acid (C12)	saturated	48.9
Myristic Acid (C14)	saturated	20.2
Palmitic Acid (C16)	saturated	8.4
Stearic Acid (C18)	saturated	2.5
Oleic Acid (C18)	mono-saturated	6.2
Linoleic Acid (C18)	poly-saturated	1.4

References

[1] R.L. Holliday, J.W. King, G.R. List, Hydrolysis of vegetable oils in sub- and supercritical water, Ind. Eng. Chem. Res., 36, (1997) 932-935.

[2] A.G. Gopala Krishna, G. Raj, A.S. Bhatnagar, P.K.P. Kumar, P. Chandrashekar, Coconut oil : Chemistry, production and its applications - A review, Indian Coconut J. 73 (2010) 15-27.

Appendix-II

Leakage test for BLM set-up

The BLM cell as described in Chapter-II was tested for probable leakage in the following manner.

- ✓ The cell was first filled up with carbon tetrachloride (CCl_4) to few mm above the bottom clearance.
- ✓ Then one compartment of the cell was filled with clear water and the other with a colored (crystal violet) solution.
- ✓ Both the aqueous phases were stirred continuously for 6-7 hours at a stirring speed of 500 rpm.
- ✓ The intensity of color in the aqueous phases was then measured with UV-vis spectrophotometer at a wavelength of 584 nm.

The results of the leakage test are furnished in the Table-AIII.1 below:

Table AII.1 Result of leakage test of BLM set-up

Time, h	Absorbance of clear water	Absorbance of colored water
0	0	0.0176
7	0	0.0171

The zero absorbance of the clear water confirmed that there was no leakage in the set-up.