RSC Advances

RSC Advances

www.rsc.org/advances

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

Separation of toxic heavy metals from its aqueous solution using environmentally benign vegetable oil as liquid membrane

Kamal Kumar Bhatluri,[*] Sushma Chakraborty,[*] Mriganka Sekhar Manna,[*†] Aloke Kumar Ghoshal[*] and Prabirkumar Saha[*‡]

This paper presents an experimental investigation of simultaneous extraction and recovery of harmful heavy metals from the industrial wastewater through Bulk Liquid Membrane (BLM) based technology. The selective extraction and stripping are achieved through the transportation of two such heavy metals *viz*., lead and cadmium. The environmentally benign coconut oil is selected as solvent of the Liquid Membrane (LM) through two phase equilibrium studies. Same studies are performed to optimize various physico-chemical parameters, such as pH of feed phase, concentrations of feed and strip phases, temperature, speed of stirring of feed phase, run time (duration of extraction), concentration of carrier *etc*., on the extraction of cadmium. The performance of LM is enhanced with respect to run time by the use of a suitable extracting agent i.e. carrier. Three phase transportation studies are thereby conducted through BLM at the same optimized operating parameters obtained in two phase studies. The extraction and recovery are found to be 72% and 64%, respectively. Further experimentations through BLM were conducted for transportation of lead with the same set of operating parameters. Both the extraction (82%) and recovery (77%) are found comparatively higher for lead as opposed to that of cadmium.

1 Introduction

The streams of industrial wastewater contain many toxic compounds such as non-biodegradable and highly toxic heavy metals *viz*. cadmium and lead which cause serious damage to the environment and the human health in particular.[1] Industries such as pulp and paper, battery, fertilizer, chlor-alkali, alloy and steel, paints and pigments, petrochemicals and mining activities include the major source of these toxics.[2,3] These heavy metals tend to bio-accumulate and bio-magnify in the food chain causing severe health problems.[1–4] The allowable limits of lead and cadmium in drinking water, as guided by World Health Organization (WHO), are 3 ppb and 10 ppb respectively.[5] Hence, these heavy metals should be removed from wastewater, at least to their permissible limits, before their disposal to the larger aquatic environment.

Conventional methods are available for separation of heavy metals such as chemical precipitation, coagulation, electrodialysis, solvent extraction, reverse osmosis, adsorption, ion exchange and chemical oxidation and reduction. However, each of these conventional techniques have got some inherent disadvantages such as loss of solvent, high cost, high energy consumption, *etc*. involved in their processing.[1–6] In recent times, LM techniques are extensively studied by researchers in various fields *viz*. organic, inorganic and analytical chemistry, biomedical engineering and biotechnology, chemical engineering and wastewater treatment *etc*. due to certain advantages such as the scope of simultaneous extraction and recovery of solute, simplicity of process, high separation factor and most importantly requirement of less amount of solvent and carrier. Out of the various types of LM configurations, *viz*., BLM, Emulsion Liquid Membrane (ELM) and Supported Liquid Membrane (SLM), BLM has the simplest design for performing LM processes.[7–12]

Castro *et al*.[13] used the BLM configuration for separation and pre-concentration of Cd ions in natural water using 2-acetylpyridine benzoylhydrazone as the mobile carrier, toluene as the organic solvent and nitric acid as the stripping agent. He *et al*.[14] studied the kinetics of transport of cadmium through BLM

‡ *Author for correspondence*
* *Department of Chemical Engineering, Indian Institute of Technology Guwahati, Assam 781039, INDIA. Fax: +91.361.2582291; Tel: +91.361.2582257; E-mail: p.saha@iitg.ac.in*
† *Presently at National Institute of Technology Agartala (Tripura, India)*

employing 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.[15–18] Tripathy *et al.*[17] used H_2SO_4 as a stripping agent. They achieved the maximum flux of cadmium with 0.1M carrier in the membrane phase. Bidari *et al.*[18] 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.*[19] used the alkaline carrier, Aliquat 336 as a carrier 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.*[20] also studied the performance of Aliquat 336 for the separation of lead using EDTA as stripping agent and achieved 80% extraction. Altin *et al.*[21] 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 and achieved 82% transportation efficiency.

Nevertheless, most of the experiments for the separation of heavy metals were conducted using conventional organic solvents which are flammable, highly toxic and volatile in nature. On the other hand, vegetable oils are very good alternative to such hazardous organic solvents. They possess all the properties of good extractants, yet they are non-toxic and non-volatile. Moreover they are inexpensive too. Very few researchers conducted LM experiments using environmentally benign solvents such as vegetable oils. Chakraborty *et al.*[6] used coconut oil as the solvent for the separation of Hg(II) from aqueous solution using SLM configuration. Trioctylamine (TOA) as the carrier, coconut oil as the solvent and PVDF as the membrane support were employed for the study. Coconut oil was also used as a solvent by Venkateswaran *et al.*[22] with D2EHPA as the carrier, PTFE as the membrane support and H_2SO_4 as the stripping agent to separate copper ions via SLM. In our previous work[1], LM based technology was developed for the separation of Cd(II) from wastewater using low cost environmentally benign coconut oil as the solvent.

In the present work, coconut oil is explored as solvent in the BLM for simultaneous separation of two heavy metals lead and cadmium. Aliquat 336 is used as the carrier in the LM. The separation feasibility is checked by two phase equilibrium studies for extraction only prior to three phase transportation studies. Various parameters for the transportation are optimized initially for cadmium. Later, those conditions are employed for the transportation of lead also and compared with that of cadmium. The preferential transportation of lead over the cadmium is found out experimentally.

2   Materials and Method

2.1   Chemicals and reagents

The chemicals and reagents used for this research were all of Guaranteed Reagent (GR) grade. Disodium ethylenediaminetetraacetate (Na$_2$-EDTA) and cadmium chloride monohydrate (CdCl$_2$. H$_2$O) were obtained from Merck (India), Lead chloride (PbCl$_2$) was procured from Loba Chemicals Pvt. Ltd. (India), Aliquat 336 (methyl-tri-capryl ammonium chloride) was procured from Sigma Aldrich (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. Accutrace® reference standard cadmium and lead solutions (1000 ppm) for Atomic Absorption Spectrophotometer (AAS) analysis were procured from AccuStandard (USA).

The stock solution (1000 ppm) of cadmium (Cd) and lead (Pb) were prepared by dissolving of 1.6308 g of CdCl$_2$.H$_2$O and 1.342 g of PbCl$_2$ in one liter volumetric flasks. The solutions were shaken well and required amount of this 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 required quantity of the stock solution with water up to the desired concentration. The stripping phase was prepared by Na$_2$-EDTA by dissolving the required amount of stripping agent in 500 ml of Milli-Q® deionized water. In order to prepare the membrane phase, appropriate amount of carrier agent (*i.e.*, Aliquat 336) was dissolved in various organic solvents (*viz.*, toluene, chloroform, 1,2-dichloroethane, isooctane and $n-$heptane) or vegetable oils (*viz.*, coconut oil, sunflower oil, mustard oil and soybean oil).

2.2   Analytical instruments

Concentrations of the solutes, *viz.*, lead and cadmium in feed and strip phases were measured by AAS (Varian Australia, Model: AA240FS) in flame mode. For the two phase equilibrium study, thorough mixing of the aqueous and the organic phases were accomplished in shaking incubator (Daihan Labtech Co. Ltd, LSI 3016R). The pH of the solutions was measured using a digital pH meter (Eutech Instruments, EUTECH 510). The viscosity and interfacial tension were measured by a rheometer (Thermo Electron Corporation, HAAKE Rheostress RS1) and a tensiometer (Kruss Germany, K9), respectively.

2.3   Two phase equilibrium distribution

Two phase equilibrium studies were performed in order to check the feasibility of extraction of solute by the organic phase. The whole experiment was designed in sequential steps. First the organic phase is selected, then the influential parameters for efficient extraction are optimized. For easy reference of metals, we represent them with a common symbol 'M' in the rest of the document, where M refers to either of lead and cadmium. Equal amounts (20 mL) of the individual aqueous phase of M and the organic phase were taken in a 100 mL conical flasks and the mixtures were agitated for 6 h at a speed of 200 rpm in a shaker. The mixtures were taken out from the shaker and allowed to settle in beakers until two separate layers of the aqueous and organic phases were obtained. The experiments were conducted at room temperature (25°C). Samples from the aqueous phases were collected with the help of a syringe and were analyzed by AAS. Concentrations of cadmium and lead in the aqueous phases

were measured at a wavelength of 228.3 nm and 283.3 nm, respectively. All the experiments were performed thrice and the results were reported with the help of error bar.

2.4 Solute transport methodology

Stripping agent plays an important role for re-extraction of metal ions from LM. From our previous studies of BLM[1] and SLM[2] configurations, we reported that Na_2-EDTA is an efficient stripping agent for the stripping of M from the membrane phase due to its metal chelating capacity. We used Na_2-EDTA as stripping agent in this study too. In the feed solution, metal chloride (MCl_2) salts are transformed into anion (MCl_4^{2-}) in presence of HCl. Solute-carrier complex of $(R_4N^+)_2MCl_4^{2-}$ 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, whereby the solute-carrier complex undergoes decomplexation in presence of stripping agent. The schematic diagram for the transportation of M in the co-transport mode is reported in Fig. 1.
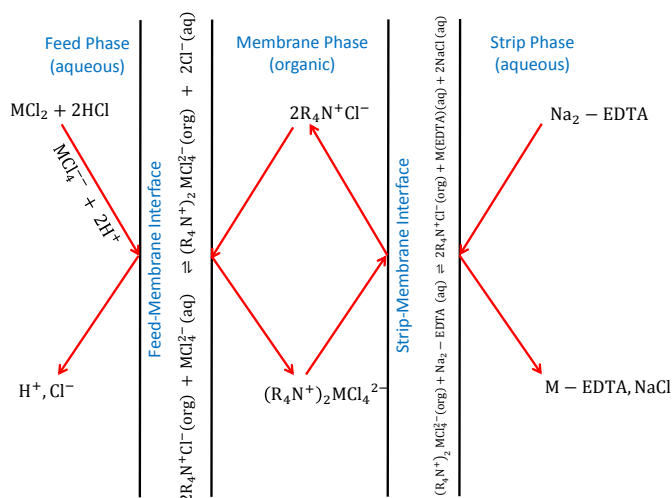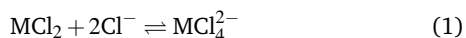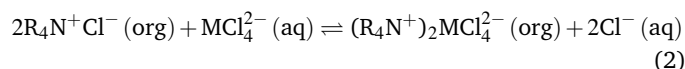

Fig. 1 Schematic diagram of transport of heavy metals, viz. Cd(II) and Pb(II), through liquid membrane

The reaction mechanism for the transportation of M is as follows:
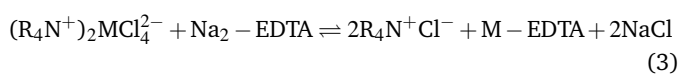
Complexation of M by chloride ions in the feed solution:[23]

$$MCl_2 + 2Cl^- \rightleftharpoons MCl_4^{2-} \qquad (1)$$

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

$$2R_4N^+Cl^- (org) + MCl_4^{2-} (aq) \rightleftharpoons (R_4N^+)_2MCl_4^{2-} (org) + 2Cl^- (aq) \qquad (2)$$

The stripping reaction:

$$(R_4N^+)_2MCl_4^{2-} + Na_2-EDTA \rightleftharpoons 2R_4N^+Cl^- + M-EDTA + 2NaCl \qquad (3)$$

2.5 Experimental setup and procedure

Fig.2 shows the schematic of experimental setup. This setup had already been used in our previous work and hence the detailed description has been provided elsewhere.[1] The feed and strip phases were poured carefully and slowly into the respective compartments and the membrane phase being lighter than aqueous phases was placed on the top of both the aqueous phases. Both the aqueous phases were stirred by magnetic stirrer. The height of the separating plate is such that chance of accidental mixing of feed and the strip phases (due to stirring) is greatly reduced, yet there is no hindrance of transport of solute through membrane phase. The working volume of each of the aqueous phases were 65 mL and that of membrane phase was 30 mL. Area of membrane-aqueous phase interfaces at both sides of the LM was about 19.5 cm^2.
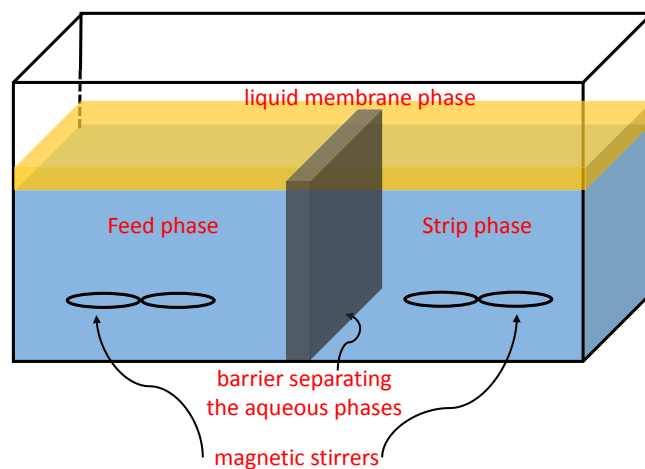

Fig. 2 Schematic of the experimental set up

Experiments were performed in order to study the effects of operating conditions on extraction and recovery of M. The performance of the LM is reported in terms of % extraction and % recovery calculated by following equations:

$$\%Extraction = \frac{C_{f_{in}} - C_f}{C_{f_{in}}} \times 100 \qquad (4)$$

$$\%Recovery = \frac{C_s}{C_{f_{in}}} \times 100 \qquad (5)$$

where, $C_{f_{in}}$ and C_f are the initial and final concentrations of M in the feed phase whereas C_s is the final concentration of M in stripping phase.

3 Results and discussions

3.1 Two phase equilibrium study

The two phase studies were carried out in order to measure the extent of solute extraction capability of LM with various physico-chemical conditions of aqueous phase. The operating parameters for extraction were optimized prior to the BLM study. 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 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 1).

Table 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 (in %)	Extraction (in %)
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

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 (92.1%) 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 lower extraction capacity, as 63.90%, 5.33%, 3.61%, 2.76%, 19.50% and 17.92%, respectively.

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.[24] It has 45.9%–50.3% lauric acid $(CH_3(CH_2)_{10}COOH)$. Chen et al.[25] described the mechanism of metal ion complexation with fatty acid by the following equation:

$$M^{++} + 2CH_3(CH_2)_{10}COOH \rightleftharpoons M[CH_3(CH_2)_{10}COO]_2 + 2H^+ \quad (6)$$

In other words, fatty acid itself serves the purpose of an extractant in this case and facilitates the highest extraction of metal cations in absence of any conventional extractant/carrier. Hence the coconut oil is the best alternative to conventional extractant among the tested solvents.

Table 2 Surface tension and interfacial tension of various vegetables oils

Name of the sample	Surface tension at 25°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

Moreover the interfacial tension of coconut oil (with Milli-Q® deionized water) is minimum too (Table 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, coconut oil was chosen as the suitable solvent for further studies.

3.1.2 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 increases with increase in pH up to 6.5 and decreases thereafter as shown in Fig. 3.
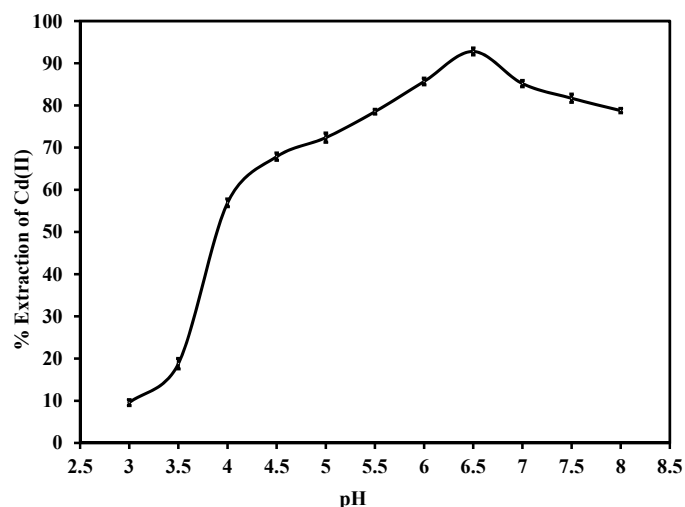

Fig. 3 Effect of pH on the equilibrium distribution of Cd(II) in absence of extractant: initial concentration of aqueous phase = 5 ppm, Volume of aqueous phase = 20 mL, Volume of organic phase = 20 mL, stirring speed = 200 rpm, duration of extraction = 6 h and Temperature = 25 °C

The experiments were performed in absence of any extractant in the organic phase. In the mildly acidic condition (pH = 6.5), cadmium is ionized and cations (Cd^{++}) are available in the aqueous 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 extractants[25] of Cd^{++} as described in Sec. 3.1.1. The extraction of cadmium increased at higher pH since cadmium stays in cationic form at mild acidic condition.[1] In higher acidic condition of aqueous phase, extraction decreases because cadmium forms H$_2$CdCl$_4$ 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.[2] Formation of cation ceases towards the neutrality and/or alkalinity of aqueous phase. Hence, pH of aqueous phase was maintained at 6.5 in the subsequent experiments.

3.1.3 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 yields formation of complex at the aqueous-organic interface which subsequently diffuses in the organic phase. The diffusivity is enhanced through the complexation. Experimental findings pre-

sented in this section substantiate the justification of addition of extractant. 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 reached equilibrium (maximum 90%) in 2 h in presence of extractant. On the other hand, equilibrium (maximum 88%) is reached after 6 h when no extractant was added to the organic phase (Fig. 4). Hence, further experiments were carried out in presence of extractant and for 2 h only.
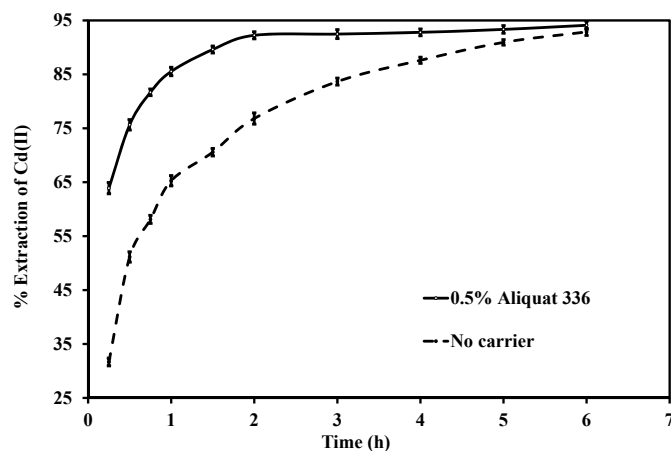
Fig. 4 Role of extractant on the time to reach the equilibrium: initial concentration of aqueous phase = 5 ppm, Volume of aqueous phase = 20 mL, Volume of organic phase = 20 mL, stirring speed = 200 rpm, pH of aqueous phase = 6.5 and Temperature = 25 °C.

3.1.4 Effect of concentration of extractant

The experiments were carried out with various concentrations of extractant in the range of 0 to 2% (v/v). Results are reported in Fig. 5. 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
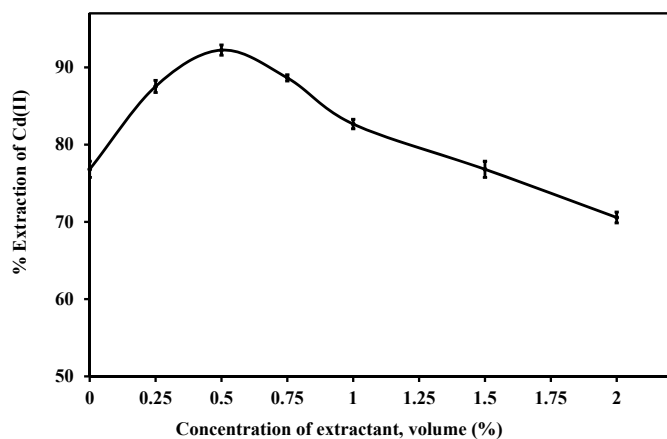

Fig. 5 Effect of concentration of extractant on the extraction of Cd(II): initial concentration of aqueous phase= 5 ppm, Volume of aqueous phase = 20 mL, Volume of organic phase = 20 mL, stirring speed = 200 rpm, pH of aqueous phase = 6.5, duration of extraction = 2 h and Temperature = 25 °C
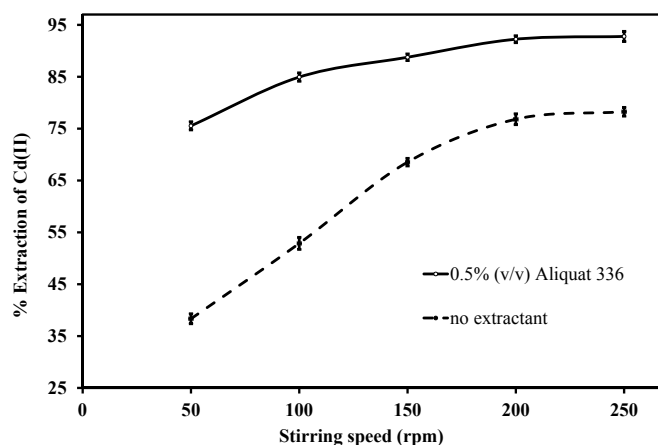

Fig. 6 Effect of stirring speed on the extraction of Cd(II): initial concentration of aqueous phase = 5 ppm, Volume of aqueous phase = 20 mL, Volume of organic phase = 20 mL, concentration of exractant = 0.5%(v/v) Aliquat 336, pH of aqueous phase = 6.5, duration of extraction = 2 h and Temperature = 25 °C

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.

3.1.5 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 aqueous-membrane interface. The higher the speed of stirring higher was the reduction of concentration polarization. However at very rigorous stirring the emusion is formed between the organic and aqueous phases. Hence, the speed of stirring is 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 are reported in Fig. 6.

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.

3.1.6 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. 4 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
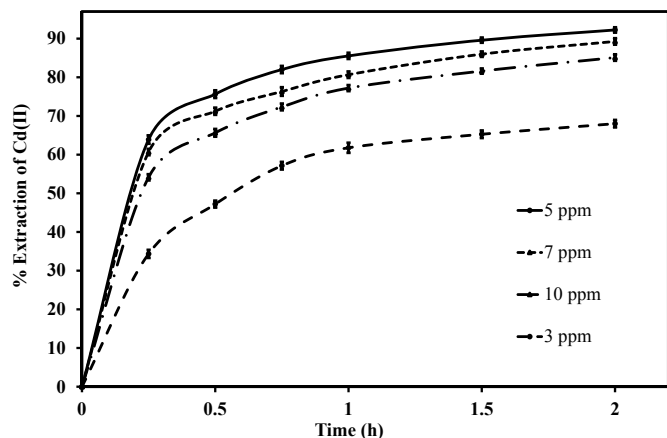
Fig. 7 Effect of initial concentration of Cd(II) in two phase study: Volume of aqueous phase = 20 mL, Volume of organic phase = 20 mL, stirring speed = 200 rpm, pH of aqueous phase = 6.5, concentration of extractant = 0.5% (v/v) Aliquat 336, duration of extraction = 2 h and Temperature = 25 °C

reported in Fig. 7. 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 lower driving force for the transportation of solute between the aqueous and organic phases. The flux of cadmium increases with increasing concentration in the feed phase due to higher concentration gradient. However, an optimality 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.

3.1.7 Effect of temperature

The temperature range of 25°C to 50°C was chosen for studying the effect of temperature for the extraction of cadmium. The experiments were conducted both in presence and absence 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°C and subsequently decreases significantly with further rise in temperature beyond 35°C (Fig. 8).

Such behavior is due to combination of various facts with temperature such as different aqueous/organic interfacial reactions in absence of a Aliquat as mentioned elsewhere.[10] The properties of the fatty acid change with the change of temperature that affects 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.

3.2 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). In addition, concentration of EDTA in stripping phase was optimized for efficient transportation of solute from LM to strip phase. As opposed to the two phase study where an extractant is needed for complexation purpose, three phase BLM involves a de-complexation phenomena 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 is possible. Moreover, the ratio of organic phase to feed phase was less compared to two phase equilibrium studies. Hence, the requirement of carrier in BLM should be different than extractant in two phase studies. Finally, transportation efficiencies were compared for two different metals, cadmium and lead for the identical operational parameters.

3.2.1 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, EDTA is used as a stripping agent taking the reference of previous research work.[12] EDTA is a well-known metal chelator and it re-extracts cadmium at the membrane-strip interface and forms Cd-EDTA complex (Eq. 3). Experiments were conducted with different concentrations of EDTA in stripping phase ranging from 0.005M to 0.03M. Other operating conditions were as follows: initial concentration of feed phase = 5 ppm, pH of feed phase = 6.5 and concentration of carrier 0.5% (v/v) Aliquat 336 in solvent (coconut oil). The results are reported in Fig. 9.

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 EDTA in the strip phase and back extraction of cadmium ions to the membrane phase were the major reasons behind their reduc-
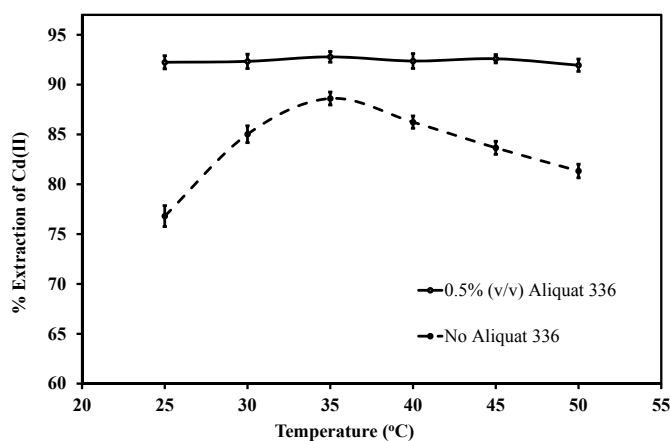

Fig. 8 Effect of temperature on the separation of Cd(II) in two phase study: Volume of aqueous phase = 20 mL, Volume of organic phase = 20 mL, stirring speed = 200 rpm, pH of aqueous phase = 6.5 and duration of extraction = 2 h

Table 3 Summary of optimum condition for transport of Cd(II) in two phase equilibrium study

| Parameter	Range studied	Optimum value
Solvent	Various vegetable oils	Coconut oil
pH of aqueous phase	3–8	6.5
Concentration of extractant	0–2% (v/v) Aliquat 336	0.5% (v/v) Aliquat 336
Duration of extraction	0–6 h	In absence of extractant: 6 h In presence of 0.5% (v/v) Aliquat 336: 2 h
Initial concentration of Cd(II) in aqueous phase	1–10 ppm	5 ppm
Temperature	25–50°C	In absence of extractant: 35°C In presence of 0.5% (v/v) Aliquat 336: significant variation
Speed of stirring	50–250 rpm	200 rpm
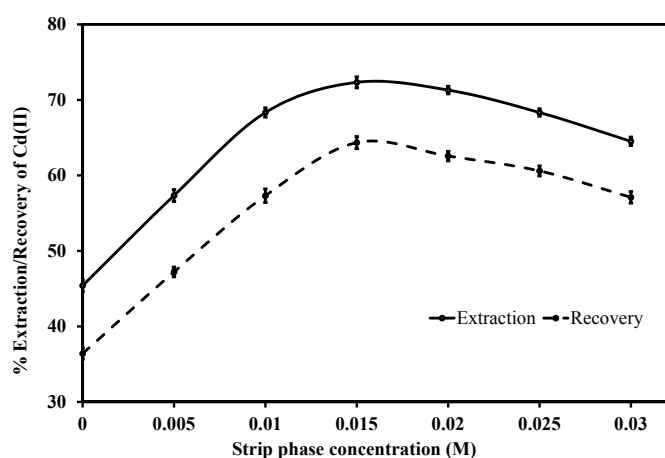
Fig. 9 Effect of concentration of EDTA in strip phase on the recovery of Cd(II): initial concentration of feed phase = 5 ppm, Volume of each aqueous phase = 65 mL, Volume of organic phase = 30 mL, concentration of carrier = 0.5%(v/v) Aliquat 336, pH of feed phase = 6.5, duration of three phase operation = 6 h
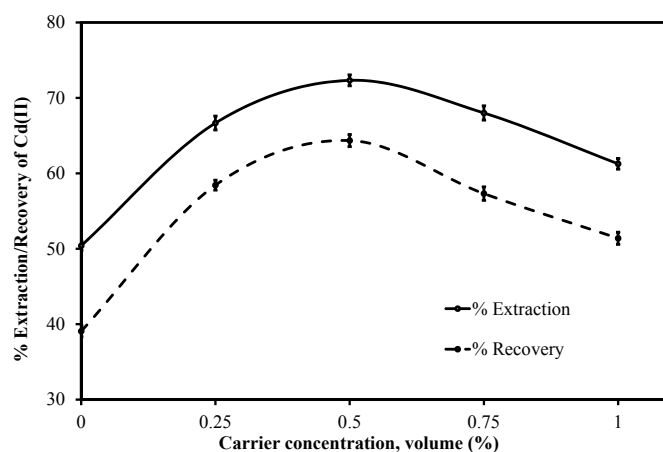

Fig. 10 Effect of concentration of carrier in organic phase on the transport of Cd(II): initial concentration of feed phase = 5 ppm, Volume of each aqueous phase = 65 mL, Volume of organic phase = 30 mL, concentration of EDTA in strip phase = 0.015 M, pH of feed phase = 6.5, pH of strip phase = 4.76, duration of three phase operation = 6 h

tion. These behaviors were observed also by Altin et al.[21] Hence, 0.015 M EDTA was chosen as the optimum concentration of the stripping solution.

3.2.2 Effect of carrier concentration

Concentration of carrier in the organic phase was re-optimized in the range 0-1% (v/v). The results are reported in Fig. 10. According to Eq.3, 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 with 0.5% (v/v) Aliquat 336 and yielded the maximum extraction of 72%. The carrier Aliquat 336 being very viscous (1500 mPa.s at 30°C) increases the viscosity of the organic phase when added in higher concentration. The rate of diffusion of the cadmium complex through the LM becomes lower and the recovery decreases with the increase in the concentration of carrier. The optimum 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 oeration.

3.2.3 Individual transportation of cadmium and lead

It is desired to examine whether the operating conditions/parameters, standardized as above, are relevant in case of some other solute, lest a condition of binary pollutants is detected in the wastewater in question. In view of this, lead has been selected as the second heavy metal that is widely available in the wastewater emanating from the industries that are targeted for Cd mitigation. The selected LM and the various parameters optimized for the transport of cadmium were employed for the transport of Pb(II). Identical conditions of feed and stripping phases were maintained. Higher extraction (82%) and recovery (77%) were observed for transportation of lead. The accumulation (5%) of metal in the organic phase at equilibrium *i.e.* at the end of the batch experiments was lesser in case of transportation of lead as compared to that of cadmium (8%). Experimental results were reported in Fig. 11.

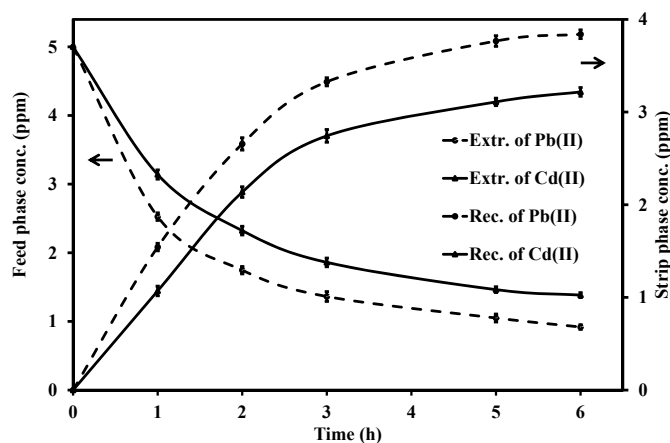The reasons could be explained by the difference in the elec-

Fig. 11 Transportation of individual metals through BLM: initial concentration of feed phase = 5 ppm, Volume of each aqueous phase = 65 mL, Volume of organic phase = 30 mL, concentration of EDTA in strip phase = 0.015 M, pH of feed phase = 6.5, pH of strip phase = 4.76, temperature = 25°C

tronic configurations of lead and cadmium and the consequent differences in their chemical properties for the complexation and de-complexation as well as in stability criterion. Pb(II) has an atomic number of 82 with electronic configuration as $[Xe]4f^{14}5d^{10}6s^16p^3$, whereas, the atomic number of Cd(II) is 48 with electronic configuration as $[Kr]\,5s^24d^{10}$. The stability of Pb-EDTA complex is higher 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 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).[26,27] 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.[28] Hence, the designed LM can be used to remove both the heavy metals with preferential removal of Pb(II).

4 Conclusion

An efficient BLM comprising of environmentally benign coconut oil has been used for the simultaneous extraction and recovery of hazardous heavy metals, *viz.* Cd(II) and Pb(II), from the industrial wastewater. Certain physico-chemical parameters related to aqueous and organic phases were optimized in equilibrium studies. The parameters were then employed for the recovery of Cd(II) in BLM configuration with additional variable such as concentration of stripping phase. The conditions, so obtained, were employed for the transportation of another heavy metal, Pb(II) and the results were compared. The optimized parameters for efficient extraction are tabulated in Table 3. Maximum recovery of metals was observed with the 0.5 % (v/v) Aliquat 336 in coconut oil in organic phase and 0.015 M EDTA in stripping phase. The efficacy of coconut oil as an useful extractant has been substantiated with the performance. The maximum extraction and recovery of Cd(II) are 72% and 64% respectively whereas the same for Pb(II) are 82% and 77% with same optimum conditions. The transportation of lead is relatively higher due to their favorable
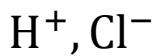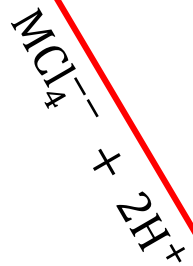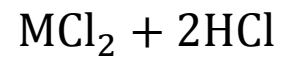
electronic configuration.

References

1 K. K. Bhatluri, M. S. Manna, P. Saha and A. K. Ghoshal, *Asia-Pacific Journal of Chemical Engineering*, 2013, 775–785.

2 K. K. Bhatluri, M. S. Manna, P. Saha and A. K. Ghoshal, *Journal of Membrane Science*, 2014, 256–263.

3 I. Zawierucha, C. Kozlowski and G. Malina, *Waste Management (New York, N.Y.)*, 2013, **33**, 2129–36.

4 P. K. Mohapatra, D. S. Lakshmi, a. Bhattacharyya and V. K. Manchanda, *Journal of Hazardous Materials*, 2009, **169**, 472–479.

5 WHO, *World Health Organization: Guidelines for Drinking-water Quality*.

6 K. Chakrabarty, P. Saha and A. K. Ghoshal, *Journal of Membrane Science*, 2010, **350**, 395–401.

7 R. Gill, N. Bukhari, S. Safdar and S. M. Batool, Proceedings of the 16th International Conference on Heavy Metals in the Environment (2012), 2013, pp. 1–5.

8 S. Suren, U. Pancharoen and S. Kheawhom, *Journal of Industrial and Engineering Chemistry*, 2014, **20**, 2584–2593.

9 R. Anupama and K. Palanivelu, *Indian Journal of Chemical Technology*, 2005, **12**, 436–440.

10 J. C. Aguilar, E. Rodr, D. S. Miguel and J. D. Gyves, *Journal of Membrane Science*, 2001, **190**, 107–118.

11 V. S. Kislik, *Liquid Membranes: Principles & Applications in Chemical Separations & Wastewater Treatment*, Elsevier, London, UK.

12 K. Chakrabarty, *PhD thesis*, Indian Institute of Technology Guwahati, India, 2010.

13 M. D. Granado-Castro, M. D. Galindo-Riaňo and M. Garcia-Vargas, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2004, **59**, 577–583.

14 D. He and M. Ma, *Separation Science and Technology*, 2000, **35**, 1573–1585.

15 A. Babakhani, F. Rashchi, A. Zakeri and E. Vahidi, *Journal of Power Sources*, 2014, **247**, 127–133.

16 F. Asrafi, A. Feyzbakhsh and N. E. Heravi, *International Journal of ChemTech Research*, 2009, **1**, 420–425.

17 S. S. Tripathy, K. Sarangi and R. P. Das, *Separation Science and Technology*, 2002, **37**, 2897–2911.

18 E. Bidari, M. Irannajad and M. Gharabaghi, *Hydrometallurgy*, 2014, **144-145**, 129–132.

19 K. Grudpan and C. G. Taylor, *Analyst*, 1984, **109**, 585–588.

20 C. McDonald, M. M. Mahayni and M. Kanjo, *Separation Science and Technology*, 1978, **13**, 429–437.

21 S. Altin, S. Alemdar, A. Altin and Y. Yildirim, *Separation Science and Technology*, 2011, **46**, 754–764.

RSC Advances Accepted Manuscript

22 P. Venkateswaran, a. N. Gopalakrishnan and K. Palanivelu, *Journal of Environmental Sciences*, 2007, **19**, 1446–1453.

23 N. Dalali, H. Yavarizadeh and Y. Agrawal, *Journal of Industrial and Engineering Chemistry*, 2012, **18**, 1001 – 1005.

24 J. B. Rossel, B. King and M. J. Downes, *Journal of the American Oil Chemists' Society*, 1985, **62**, 221–230.

25 L. Chen, H. Meng, L. Jiang and S. Wang, *Chemistry—An Asian Journal*, 2011, **6**, 1757–1760.

26 G. H. Jeffery, J. Bassett, J. Mendham and R. C. Denney, *VO-GEL's Textbook of Quantitative Chemical Analysis*, Longman Scientific & Technical, Essex, UK, 5th edn, 1989, pp. 55–60.

27 M. R. Dudzinska and D. A. Clifford, *Reactive Polymers*, 1991/1992, **16**, 71–80.

28 S. C. Datta, N. K. Johar and S. M. Bhola, *Foundation Course in Chemistry (Eds)*, Ane books, India, 2010, pp. 94–97.
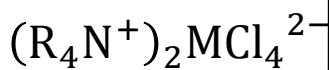
RSC Advances Accepted Manuscript

Feed Phase (aqueous)

$MCl_2 + 2HCl$

$MCl_4^{2-} + 2H^+$

H^+, Cl^-

Feed-Membrane Interface

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

Membrane Phase (organic)

$2R_4N^+Cl^-$

$(R_4N^+)_2MCl_4{}^{2-}$

Strip-Membrane Interface

$(R_4N^+)_2 MCl_4^{2-}(org) + Na_2 - EDTA \ (aq) \rightleftharpoons 2R_4N^+Cl^-(org) + M(EDTA)(aq) + 2NaCl \ (aq)$

Strip Phase (aqueous)

$Na_2 - EDTA$

$M - EDTA, NaCl$