Recovery of cadmium (II) by supported liquid membrane using triethanolamine as mobile carrier

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ABSTRACT

The transport of cadmium ions through a supported liquid membrane containing triethanolamine (TEA) as mobile carrier has been studied. The effects of Cd(II) concentration, HCl in feed and carrier concentration in membrane has been studied. Cd(II) concentration increase in feed leads to an increase in flux from 2.1×10^{-7} to 8.4×10^{-7}mol-cm^{-2}-sec^{-1} within Cd(II) ions concentration range (2.7×10^{-4}M-16.37×10^{-4}M) at 2.0M HCl in the feed and 3.0M triethanolamine in the membrane. Increase in H$^+$ ion concentration from 0.5M to 3.0M results in an increase in Cd(II) ions flux but a decrease is observed beyond 2.0M HCl concentration in feed. Increase in carrier concentration in the liquid inside the membrane enhances the flux with its maxima at 3.0M carrier. Further increase in the concentration of TEA leads to a decrease in transport due increase in viscosity of membrane liquid. The optimum conditions for Cd(II) ions transport are, 2.0M HCl in feed, 3.0M TEA in membrane, 0.1M NaOH as strip solution. Similar transport characteristics have been observed for Cd-EDTA complexed anions across TEA-cyclohexanone based SLM, thus indicating a cadmium anion transport coupled with protons and chloride or EDTA co-ions.

INTRODUCTION

Heavy metals often appear in high concentrations in all kinds of industrial effluents giving rise to hazards of pollution because of their high toxicities and wide environmental spreading. Small quantities of cadmium occur naturally in air, water and soil. It can leach into water bodies from pipes and solder, or may enter water from chemical waste disposal sites[1-2]. In industry, cadmium uses vary from an electrode component in alkaline batteries to a stabilizer in plastics. Production of nickel-cadmium batteries, paint pigments, anti-corrosive coatings, manufacturing of electronic components

and select metal alloys, are to name a few. The clean-up of polluted waters requires the development and use of cost effective and efficient technologies.

Facilitated transport of cations from an aqueous solution using supported liquid membranes (SLM) represents a powerful tool in separation science. The liquid membrane technology is based on inserting a selective immiscible organic liquid barrier between two miscible liquid phases. The separation of the compound of interest is accomplished by the transport of solute through the liquid membrane from the aqueous feed to the aqueous stripping phase. The importance of these processes has been shown by a number of research-

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ers[3–10], with a variety of carrier agents incorporated into the membrane. Their high specificity and potential for industrial-scale processes with economic advantages made them useful to solve some important problems, such as processing dilute metal ions solutions for recovery of the metals ions of metallurgical importance. In addition, separation by this technique offers several advantages over the classical solvent extraction processes, due to reduced inventory of organic carrier for extraction. Hence, highly selective and expensive extractants can also be used, which would not be economical in conventional solvent extraction. In this paper coupled transport of cadmium ions using triethanolamine-cyclohexanone liquid membranes have been studied. Previously, we have investigated the SLM extraction of Cr(VI) ions from aqueous solution by using commercial amine, Alamine 336[11]. The EDTA-complexed Cd ions were also studied to see the behaviour of complexed metal ions across the TEA-cyclohexanone SLM. The SLM study was extended to Cd battery industrial wastes to recover cadmium ions to indicate the practical and environmental importance of this work.

Theoretical aspects

A number of mathematical models, which describe the behaviour of supported liquid membrane separation processes, have been worked out by other authors[12–15]. The system in the present study consists of two aqueous phases and an organic phase, which contains the carrier, triethanolamine (TEA), confined within the membrane pores by capillary action. The membrane serves both as a support for the organic phase and as a barrier between the two aqueous phases. This results in two aqueous-organic interfaces with well-defined transfer area. Figure 1 shows the expected mechanism of transport of Cd ions.
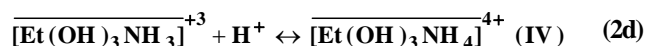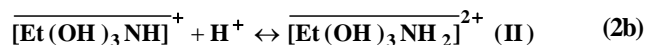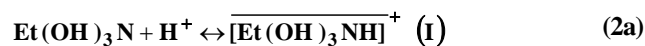
The extraction of cadmium (II) ions by TEA is supposed to be based on the formation of Cd(II) anionic complex in the membrane interface. The transport of the metal ions through the supported liquid membrane system is considered to be composed of many elementary steps[16–18]. In our theoretical considerations the following three steps are taken into account, i.e.: (i) diffusion of metals ions from feed bulk solution into membrane face; association of Cd(II) ions with TEA molecule, (ii) diffusion of complex in the organic membrane phase to the other side of membrane through membrane liquid and (iii) dissociation of Cd(II) ions after coming in contact with stripping solution

The reaction taking place between the metal ions and the carrier on the membrane interface is governed by the equilibrium:

$$Cd(II)_{aq} + (2+n)Cl^-_{aq} + nH^+_{aq} + nEt(OH)_3N \leftrightarrow \overline{[Et(OH)_3NH_n]CdCl_{2+n}} \quad (1)$$
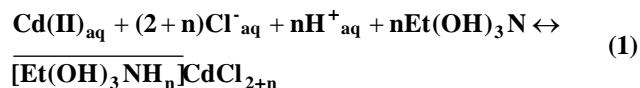
Following are the main possibilities of protonation of TEA molecule at N and O sites under the acidic conditions;

$$Et(OH)_3N + H^+ \leftrightarrow \overline{[Et(OH)_3NH]}^+ \ (I) \quad (2a)$$

$$\overline{[Et(OH)_3NH]}^+ + H^+ \leftrightarrow \overline{[Et(OH)_3NH_2]}^{2+} \ (II) \quad (2b)$$

$$\overline{[Et(OH)_3NH_2]}^{+2} + H^+ \leftrightarrow \overline{[Et(OH)_3NH_3]}^{3+} \ (III) \quad (2c)$$

$$\overline{[Et(OH)_3NH_3]}^{+3} + H^+ \leftrightarrow \overline{[Et(OH)_3NH_4]}^{4+} \ (IV) \quad (2d)$$

or in generalized form,

$$Et(OH)_3N + nH^+ \leftrightarrow \overline{[Et(OH)_3NH_n]}^{n+} \ (V) \quad (2e)$$

Species I, II, III, IV and V may be formed as a result of protonation of TEA, which will associate with cadmium ions in the anionic form associated with chloride ions. Species with overbear represent the organic phase entities.

$$Cd^{2+} + 2Cl^- \leftrightarrow CdCl_2 \quad (3a)$$
$$CdCl_2 + Cl^- \leftrightarrow [CdCl_3]^{1-} \quad (3b)$$

and complexes can be formed as;

$$CdCl_2 + nCl^- \leftrightarrow [CdCl_{2+n}]^{n-} \quad (3c)$$

Now species taking part in ions pair formation may be I, II, III and IV and in general form V, having 1, 2, 3, 4 or 'n'protons and the ions-pair complexes will be $Et(OH)_3N[H\eta.CdCl_{2+n}]$, which is the same species as
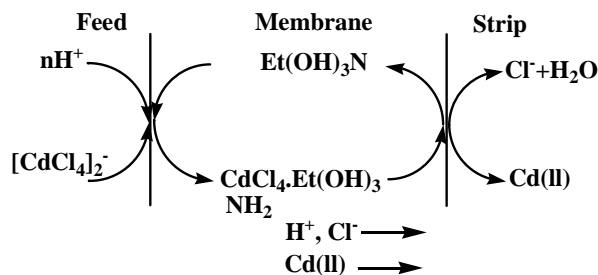

Figure 1: Coupled co-ion transport of Cd(II) ions

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indicated by reaction (1).

On the stripping side, this complex will break to release the $(EtOH)_3N$ carrier. The mechanism of cadmium ion transport is, therefore, coupled co-ion transport type, with the complexing of H^+ and Cl^- ions both moving to the stripping phase through membrane phase along with Cd(II) ions.

The relationship which correlates the membrane flux (J) to concentration (C), to the aqueous feed volume V, and to membrane area A is given below.

$$J = -\frac{d[Cd(II)]}{dt}\frac{V}{A} \qquad (4)$$

the integrated form of flux equation is

$$\ln\frac{[Cd(II)]_{f,t}}{[Cd(II)]_{f,0}} = -\frac{A}{V}Pt \qquad (4a)$$

where $[Cd(II)]_{f,0}$ is initial cadmium concentration in feed; $[Cd(II)]_{f,t}$ is total concentration of Cd(II) at time t and P is permeability. A linear dependence of the feed solution with time is obtained, and the permeability can be calculated from the slope of the straight line that fits the experimental data[19].

EXPERIMENTAL

Membranes

The support for the organic phase was a Durapore microporous PVDF film. This support has porosity 75%, thickness 125μm, pore diameter 0.2μm and tortuosity 1.67. This is a chemically stable and hydrophobic synthetic polymer support. The supported liquid membrane has an organic phase that contains the carrier, in the polymeric porous medium. In the present study, triethanol amine was selected as carrier because it is a good extracting agent of divalent transition metals. Cyclohexanone was used as organic solvent/diluent. The organic solvent containing the carrier was incorporated into the support membrane by capillary action, by soaking the film in the carrier/diluent solution for 24 hours.

Liquid membrane cell

The permeation cell used for SLM experiments consisted of 2 compartments separated by the membrane. Each compartment, feed and strip, had a maximum volume of 140mL. A membrane of effective surface area 14.2cm² could be fixed amid the two cham-
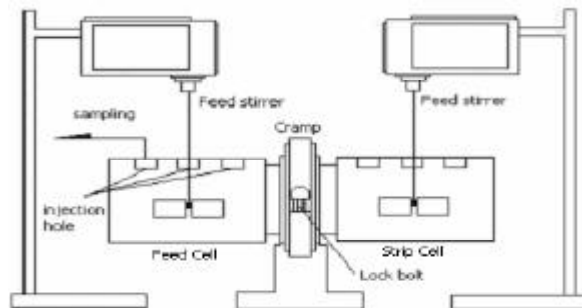

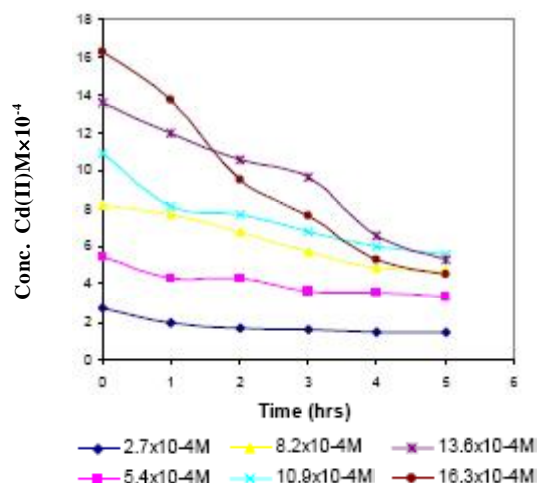**Figure 2: Schematic diagram of the permeation cell**

Figure 3: Decrease in Cd²⁺ ions concentration in feed vs. time, with NaOH as stripping solution. [NaOH]=0.5M, [TEA]=3.0M, [HCl]=2.0M, [Cd²⁺]=2.7×10⁻⁴-16.3×10⁻⁴M

bers. The agitation of the solutions was carried out by 2 synchronized motors that relied on variable power supply with a stirring rate of 1000 rpm. The stirring rate was high enough to minimize boundary layer resistances. The experimental temperature was 25 ± 0.5^0C. Figure 2 shows the schematic diagram of the permeation cell.

Flux measurement

The feed and stripping solutions were filled in their respective cell compartments with the membrane separating the two chambers. The solutions were kept agitated with stirrers at a speed greater than 1500 rpm to avoid concentration polarization at the membrane interfaces. Samples from feed and strip solutions were taken after regular intervals of time and analyzed on an atomic absorption spectrophotometer (Solaar M6 thermo elemental).
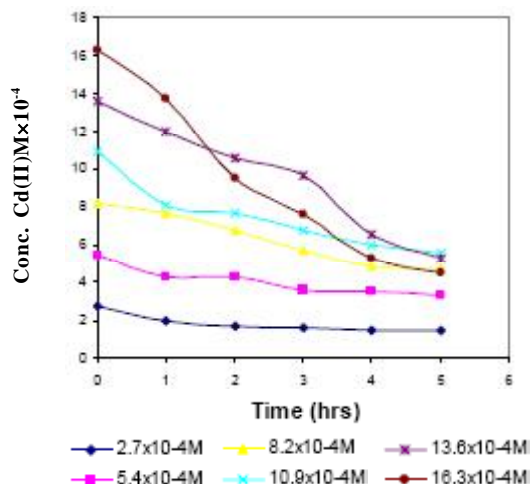
Reagents

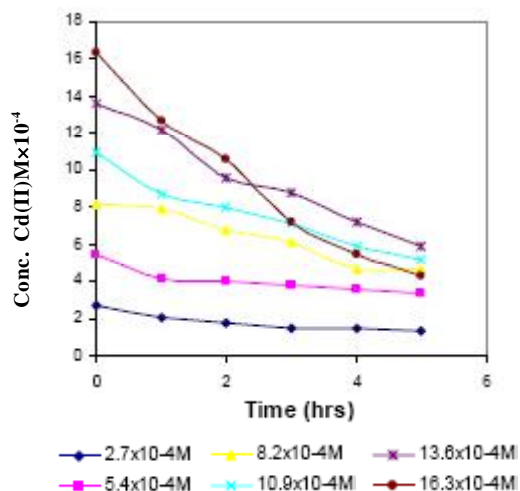**Figure 4: Decrease in Cd²⁺ ions concentration in feed vs. time, with NaOH as stripping solution. [NaOH]=1.0M, [TEA]=3.0M, [HCl]=2.0M, [Cd²⁺]=2.7×10⁻⁴- 16.3×10⁻⁴M**

Figure 5: Decrease in Cd²⁺ ions concentration in feed vs. time, with NaOH as stripping solution. [NaOH]=2.0M, [TEA]=3.0M, [HCl]=2.0M, [Cd²⁺]=2.7×10⁻⁴ – 16.3×10⁻⁴M

Figure 6: Effect of Cd²⁺ concentration on flux with different strip concentrations

Figure 7: Decrease in Cd²⁺ ions concentration in feed vs. time, with different HCl concentration in feed. [NaOH] =1.0M, [TEA]=3.0M, [HCl]=0.1-3.0M, [Cd²⁺]=16.3×10⁻⁴M

Following chemicals were used during this study. $CdCl_2$(AR grade, Fluka), triethanolamine (Fluka), NaOH (Extra Pure grade), E.Merck, HCl 37% pure from E. Merck. All other chemicals used were of analytical reagent grade or better. Deionized water was used to make the solutions.

RESULTS AND DISCUSSION

A series of permeation experiments were performed to investigate the effect of feed concentration (Cd²⁺), carrier concentration (TEA), acid concentration (HCl)

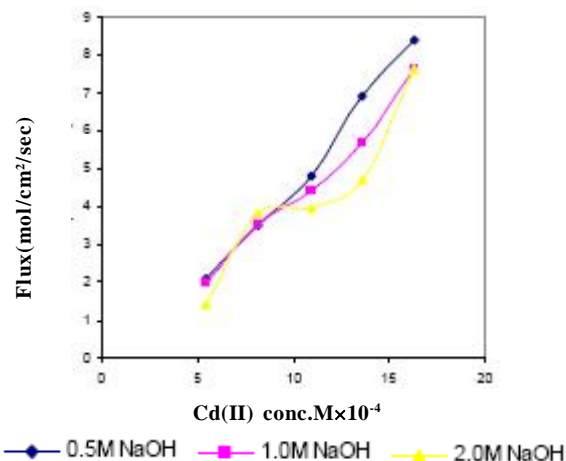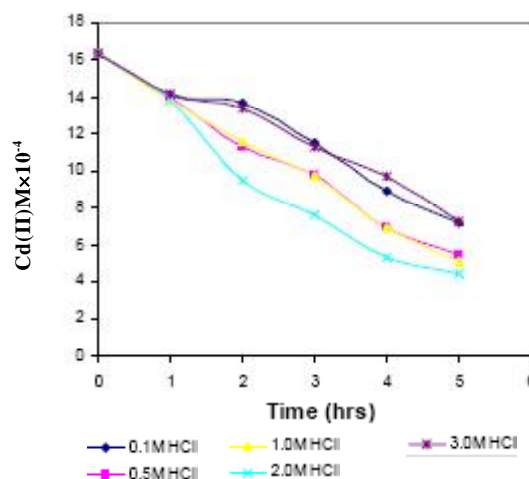and stripping solution (NaOH), on metal transport.

Effect of cadmium ion concentration

The effect of cadmium(II) concentration in the feed solution, as a function of time is depicted in figures 3 to 6. It is clear that the transport is affected by the concentration of cadmium ions present on the feed side of the membrane. The stripping solutions used are 0.5M, 1.0M and 2.0M NaOH. As the concentration of feed solution is increased, the extraction of cadmium(II) ions also increases. It can also be seen that Cd(II) ions are transported uphill across the membrane, even when the concentration of Cd ions in the feed solution is less than that in the stripping phase. It is possible due to the higher
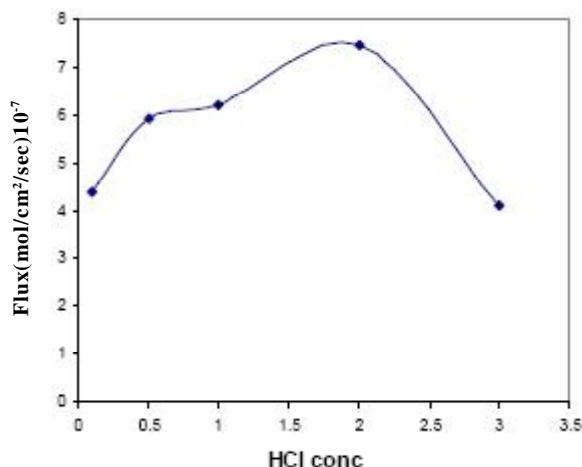
Figure 8: Effect of Cd^{2+} concentration on flux with different HCl concentrations in feed

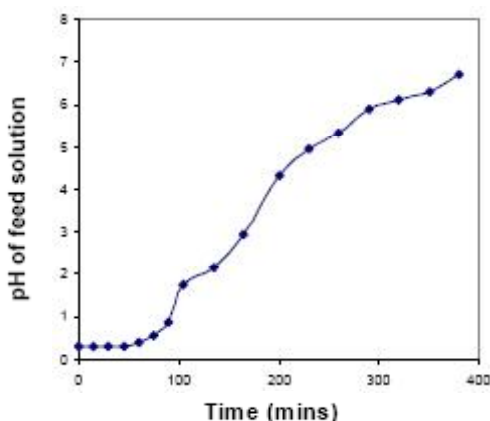**Figure 9: Variation of pH in feed solution vs. time. [NaOH] =1.0M, [TEA]=3.0M, [HCl]=2.0M, [Cd^{2+}]=16.3×10^{-4}M**

membrane phase concentration on the feed side face of the membrane.

Figure 5 shows the effect of feed solution concentration on the transport of cadmium(II) ions through the membrane using 2.0M NaOH as a stripping solution. It is clear from Figure 6 that there is a marked increase in flux with increase in cadmium concentration and maximum flux is found when 16.3×10^{-4}M cadmium concentration is used. This is in accordance with reaction (1). The amount of strippent (NaOH) concentration slightly influence the flux. About 0.5-2M NaOH concentration is sufficient to strip cadmium ions.

Effect of HCl concentration

Figures 7-8 represent the effect of HCl concentration in the feed on the transport of cadmium ions through the present membrane. It is seen that the flux of metal

ions increases up to 2M HCl concentration and then deceases. The concentration range studied for HCl is from 0.1 to 3.0M. According to Equations 2a to 2d, the cadmium ions get converted into [CdCl$_{2+n}$]$^{n-}$ in the presence of HCl. So the cadmium anions associates with TEA ions in the presence of protons to form a (EtOH)$_3$NH]$_n$CdCl$_{2+n}$ type complex which diffuses towards the other side of the membrane, resulting in Cd(II) transport.

From figure 8, it is quite obvious that the flux of cadmium ions first increases with an increase in HCl concentration and then decreases after passing through a maximum value.

This observation is in accordance with the theory, according to which flux is directly proportional to square of hydrogen ion concentration[20].

$$\log J = A + \log T - \log \eta + \log[H^+]^2 + 2\log[R_3N]^2 + \log C^o \quad (5)$$

where J is flux, A is a constant, η and T are viscosity and absolute temperature at which transport takes place and C^o is concentration of Cd in feed.

To study the transport of hydrogen ions with time, pH of feed solution was measured at regular intervals of time. It was observed that pH of feed solution increases with time (Figure 9). The reason can be attributed to transport of hydrogen ions from feed to strip solution.

Cadmium (II) chloride in the presence of HCl in feed solution is changed to H$_2$CdCl$_4$ specie which react with triethanolamine on the surface of membrane on feed side to form an ionic complex of approximate composition of [(EtOH)$_3$NH]CdCl$_3$ which diffuses in the membrane to the stripping side resulting in Cd(II) ions transport.

To see the transport of Cd(II) ions complexed with a chelating agent, EDTA, an experiment was conducted with 0.01M EDTA in the feed solution with 6.31×10^{-4}M Cd(II) ion concentration and 1.0M HCl in the feed solution and 0.50M NaOH as stripping solution. The results are depicted in figure 9. It is clear from results that Cd(II) ions have been transported to stripping solution showing that EDTA is also complexed like other anions with Cd ions to make the transport of these metal ions possible. The results can be explained as follows;

EDTA is the molecule with four acetic acid groups, and in the aqueous medium it ionizes to furnish four hydrogen ions as follows[21]:
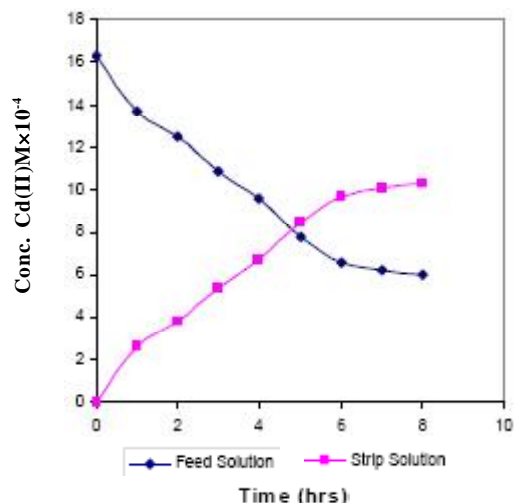
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Figure 10: Cd²⁺ concentration in feed and strip solutions vs. time with 0.05M EDTA solution in feed. [NaOH]=1.0M, [TEA]=3.0M, [HCl]=2.0M,[Cd²⁺]=16.3×10⁻⁴M
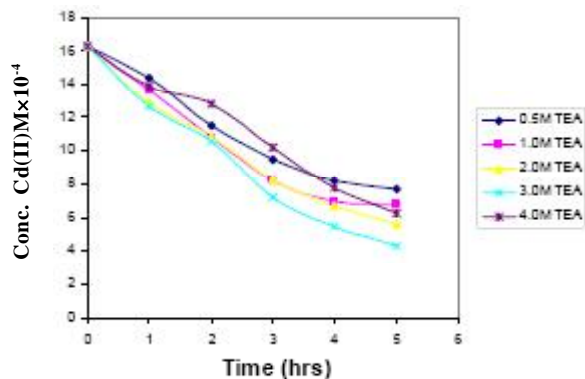

Figure 11: Decrease in Cd²⁺ concentration in feed vs. time with different TEA concentrations in SLM. [NaOH]=1.0M, [TEA]=0.5-4.0M, [HCl]=2.0M,[Cd²⁺]=16.3×10⁻⁴M
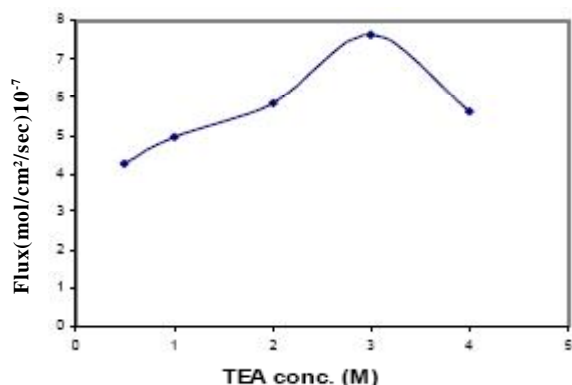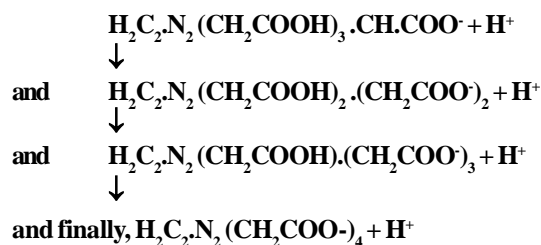

Figure 12: Effect of different TEA concentrations on the flux of Cd²⁺ ions through the SLM. [NaOH]=1.0M, [TEA]=0.5-4.0M, [HCl]=2.0M, [Cd²⁺]=16.3×10⁻⁴M

$$H_2C_2.N_2(CH_2COOH)_3.CH.COO^- + H^+$$
$$\downarrow$$
and $$H_2C_2.N_2(CH_2COOH)_2.(CH_2COO^-)_2 + H^+$$
$$\downarrow$$
and $$H_2C_2.N_2(CH_2COOH).(CH_2COO^-)_3 + H^+$$
$$\downarrow$$

and finally, $H_2C_2.N_2(CH_2COO-)_4 + H^+$

and if $(CH_2COOH) = XH$, the EDTA can be represented as $ED(XH)_4$ and this may associate with Cd ions either as $[CdED(XH)_2X_2]$ or as $[CdED.X_3.XH]^-$ or as $[CdED.X_4]^{2-}$ and the complex formed with protonated TEA molecule represented as $[EtOH)_3NH]^+$ or $[EtOH)_3NH_2]^{2+}$ or $[EtOH)_3NH_n]^{n+}$ to form the complex like $[(EtOH)_3NH).CdEDX_3.X]$ or $[(EtOH)_3NH)_2 \cdot CdEDX_3.X_2]$ which is neutral and extractable into the organic membrane. This complex diffuses to the other face of the membrane and is stripped off the protons by OH^- ions present in the stripping phase, dissociating this neutral complex, resulting into back diffusion of TEA molecules to the membrane feed side to once again complex with Cd ions. Cd ions are stripped to stripping phase along with EDTA associated ions. The Cd ions are transported as such coupled with EDTA ions and protons. The mechanism of transport is, therefore, will be a coupled co-ion transport type.

EDTA is a strong chelating agent for heavy metal ions, the relative position of the unshared pair of electrons on the four carboxylate ions and the two nitrogen atoms being such that it can form stable five membered chelate rings with the metal ions. With six unshared pairs of electrons available, EDTA is expected to complex with Cd(II) ion having a co-ordination number 6. Usually only four rings are formed due to steric hindrance and the sixth pair of electrons is supplied by the water molecule as shown below.
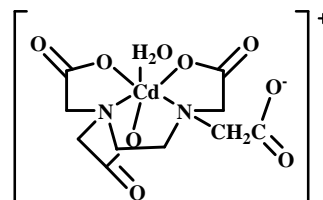
Effect of carrier concentration

The concentration of the TEA in the organic solution has a marked effect on the cation flux. Figures 11-12 show that, with the increasing TEA concentration in
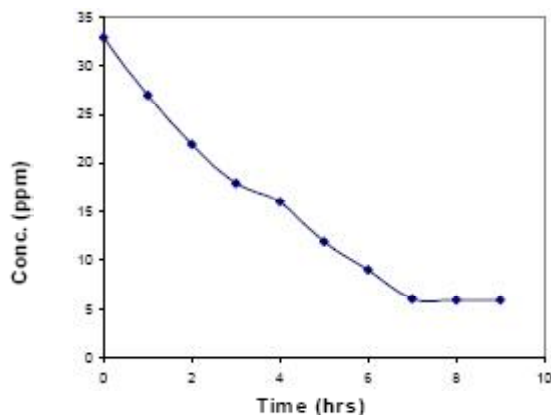
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Figure 13: Decrease in concentration of Cd²⁺ ions in feed vs. time for aqueous effluent. [NaOH]=0.5M, [TEA]=3.0M, [HCl]=2.0M, [Cd²⁺]=33ppm

TABLE 1 : Analysis of the effluent

Metal	Concentration (μg/mL)
Cd	33.0
Ni	17.4
Cu	3.5
Fe	11.2
Sn	BDL
Pb	2.1

membrane, Cd(II) transport gradually increases, reaching a maximum value at approximately 3.0M and then decreases. This effect can be accounted for by considering the influence of increasing viscosity of TEA solution upon the diffusion of the metal complex in the SLM.

Figure 12 shows that the flux increases with increasing triethanolamine concentration in the liquid membrane reaching an optimum value at 3.0M triethanolamine. It drops continuously with further increase in its concentration.

This may be explained keeping in view the increasing availability and formation of extractable complex with Cd(II) ions and hence its extraction into membrane (organic) phase, at the feed solution membrane.

Increase in triethanolamine concentration will lead to more $CdCl_3(EtOH)_3NH$ anionic complex formation and hence increase in its concentration gradient within the membrane along the membrane thickness but the viscosity of the organic phase also increases resulting into decrease in its diffusion through membrane phase. The flux of Cd(II) ions through the membrane as a function of triethanolamine concentration is shown in figure 12. Maximum flux under optimum conditions is observed at 3.0M triethanolamine concentration.

Extraction of cadmium(II) ions from a cadmium battery plant effluent

To apply the SLM for Cd(II) removal, one experiment was carried out with the cadmium alkaline battery plant waste solution in the feed compartment and 0.5M NaOH as the strip solution. All other conditions were kept the same as optimized above. It was clearly shown that almost all the cadmium ions transferred to the stripping solution within 7 hours of experiment (Figure 13). Analysis of the waste effluent was performed on atomic absorption spectrophotometer, results are given in TABLE 1.

Analysis of stripping solution shows that along with cadmium, nickel ions are also transported at the completion of experiment, which means that removal of cadmium and nickel can be made simultaneously from cadmium alkaline battery waste effluent.

CONCLUSIONS

1. The cadmium ions are transported across TEA-cyclohexanone membrane by coupled co-ion transport mechanism.
2. The optimum conditions of transport are 3.0 M TEA in the membrane and 2.0M HC1 in the feed.
3. Increase in Cd(II) concentration in the feed enhances the flux, so transport of Cd(II) ions are fast.
4. EDTA molecules also help to form complexed Cd(II) ions and facilitate the transport of this metal ions.
5. TEA is a useful carrier for cadmium extraction by using SLM systems.

ACKNOWLEDGMENTS

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