Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

EXTRACTION OF CADMIUM(II) BY SUPPORTED LIQUID MEMBRANE USING TOPS-99 AS MOBILE CARRIER

Sushree Swarupa Tripathy[a]; Kadambini Sarangi[a]; Radhanath Prasad Das[a]
[a] Regional Research Laboratory, Bhubaneswar, Orissa, India

To cite this Article Tripathy, Sushree Swarupa , Sarangi, Kadambini and Das, Radhanath Prasad(2002) 'EXTRACTION OF CADMIUM(II) BY SUPPORTED LIQUID MEMBRANE USING TOPS-99 AS MOBILE CARRIER', Separation Science and Technology, 37: 12, 2897 — 2911

To link to this Article: DOI: 10.1081/SS-120005472

URL: http://dx.doi.org/10.1081/SS-120005472

SEPARATION SCIENCE AND TECHNOLOGY, 37(12), 2897–2911 (2002)

EXTRACTION OF CADMIUM(II) BY SUPPORTED LIQUID MEMBRANE USING TOPS-99 AS MOBILE CARRIER

Sushree Swarupa Tripathy, Kadambini Sarangi,* and Radhanath Prasad Das

Regional Research Laboratory, Bhubaneswar 751 013,
Orissa, India

ABSTRACT

The permeation rate of Cd(II) from a dilute aqueous sulfate media using supported liquid membrane technique has been studied. The microporous polypropylene film celgard 2500 was used as solid support for the liquid membrane and TOPS-99 was used as mobile carrier. Effect of different parameters such as stirring rate, Cd(II) concentration in feed solution, pH of feed solution, extractant concentration in membrane phase, and acid concentration in strip solution on cadmium flux was studied. It was observed that stirring speed of 500 rpm was sufficient to minimize the resistance due to aqueous boundary layer. Cadmium flux, $J_{\mathrm{Cd(II)}}$ increases with increase in pH of feed solution from 3.0 to 6.0 as well as with increase of cadmium concentration in feed solution. Also with increase in TOPS-99 concentration in membrane phase up to 100 mol/m^3 $J_{\mathrm{Cd(II)}}$ increases and then becomes constant.

---

*Corresponding author. Fax: 91-674-581637; E-mail: kadambini_sarangi@yahoo.com

Key Words: Liquid membrane; Cadmium(II) transport; TOPS-99; Carrier

INTRODUCTION

Cadmium and its compounds are toxic and poisoning occurs through inhalation and ingestion. In spite of its toxicity, it is used in different industries such as electroplating, pigments, synthetic chemicals, ceramics, metallurgical products, and photographic products.[1] Most often cadmium enters the water system through industrial discharge necessitating its removal from effluents. Using precipitation methods, cadmium can be removed as carbonates (pH 7.5–8.5), as hydroxides (pH 8–11), and can also be removed by co-precipitation at pH 6.5 with $FeCl_3$ when a $Fe(OH)_3$ floc is formed.[1] Such precipitation processes have inherent problems of solid–liquid separation, high cost, and slow kinetics. As an alternative, removal of metal ions from dilute solutions/industrial effluents through supported liquid membrane (SLM) process offers operational simplicity, low solvent inventory, and low energy consumption over precipitation process. The SLM technique was first proposed by Bloach[2] and later used for extraction/separation of different metal ions such as Cr,[3–5] Au,[6] Cu, Zn,[7–9] Al,[10] Ce,[11] Pt,[12] and Fe(III).13 This technique is also used for the removal of organic compounds such as phenols,[14] amino acids, etc.[15]

The chemistry of metal extraction in liquid membrane process is similar to that of liquid–liquid extraction. A survey of the literature for liquid–liquid extraction of cadmium showed extensive use of a variety of extractants like alamine 336[16] and D2EHPA.[17] Studies have also been made using mixed extractants such as carboxylic acid and trialkyl phosphine sulfide.[18] Separation and recovery of Cd from systems like Zn–Cd–Co–Ni,[19] Zn–Cd,[20] Zn–Cd–Hg[21–23] have also been investigated.

Although considerable work has been reported for the liquid–liquid extraction of cadmium, studies concerning the liquid membrane extraction of cadmium are rare. The kinetics of Cd(II) transport through a bulk liquid membrane using tricaprylamine in xylene as mobile carrier has been reported.[24] Effect of paraffin and surfactant on coupled transport of Cd(II) through bulk liquid membrane was studied by He and Ma[25] Tri-octyl amine in xylene was used as an extractant and it was reported that transport of Cd(II) ions was coupled by the co-transport of protons.

Di-(2-ethylhexyl) phosphoric acid is a widely used extractant for the extraction of different metal ions and the extraction mechanism is well established.[26–29] It is also used as a mobile carrier for SLM.[7,30,31] The present work examines the possibility of using SLM technique to remove Cd(II) from dilute solutions using TOPS-99 as an extractant (TOPS-99 is di-2-ethyl hexyl phosphoric acid produced by Heavy Water Plant, Talcher, Orissa, India). The equilibrium studies were carried out to find out the extraction mechanism of Cd(II) with TOPS-99. In SLM studies, the various process variables include effect of stirring rate, effect of D2EHPA concentration, effect of Cd(II) concentration, effect of acid concentration in strip solution, and effect of Cd(II) in strip solution on cadmium flux.

THEORY

The formation of the Cd(II)–TOPS-99 complex at the feed side-membrane interface involves monomerization of $(\text{TOPS-99})_2$, distribution of monomer between aqueous interface and organic medium and acid dissociation of monomer at the interface. These reactions are represented as follows:

$$\overline{(\mathrm{HA})_2} \leftrightarrow \overline{2(\mathrm{HA})} \tag{1}$$

$$\overline{(2\mathrm{HA})} \leftrightarrow 2(\mathrm{HA}) \tag{2}$$

$$2(\mathrm{HA}) \leftrightarrow \mathrm{HA}_2^- + \mathrm{H}^+ \tag{3}$$

where, HA is TOPS-99 and —— designates the organic phase.

Then ionized TOPS-99 reacts with Cd(II) at the feed side-membrane interface, which is followed by formation of neutral Cd(II) species at the interface.

$$\mathrm{Cd}^{2+} + \mathrm{HA}_2^- \Leftrightarrow \mathrm{CdHA}_2^+$$

$$\mathrm{CdHA}_2^+ + 2(\mathrm{HA})_{\mathrm{org}} \Leftrightarrow \mathrm{CdA}_2(\mathrm{HA})_{2\,\mathrm{org}} + \mathrm{H}^+$$

So the mechanism by which a metal ion is extracted from an aqueous phase using TOPS-99 can be written as

$$\mathrm{M}^{2+}_{\mathrm{aq}} + 2(\mathrm{HA})_{2\,\mathrm{org}} \Leftrightarrow \mathrm{MA}_2(\mathrm{HA})_{2\,\mathrm{org}} + 2\mathrm{H}^+_{\mathrm{aq}} \tag{4}$$

The equilibrium constant, K of the reaction can be written as:

$$K = \frac{[\mathrm{MA}_2(\mathrm{HA})_2]_{\mathrm{org}}[\mathrm{H}^+]^2_{\mathrm{aq}}}{[\mathrm{M}^{2+}]_{\mathrm{aq}}[(\mathrm{HA})_2]^2_{\mathrm{org}}} \tag{5}$$

or,

$$K = \frac{D[\mathrm{H}^+]^2_{\mathrm{aq}}}{[(\mathrm{HA})_2]^2_{\mathrm{org}}} \tag{6}$$

where $D = [MA_2(HA)_2]_{org}/[M^{2+}]_{aq}$, or,

$$\log D = \log K + 2\text{pH} + 2\log[(HA)_2]_{org} \tag{7}$$

Analysis of the experimental value of distribution ratio (D) as a function of equilibrium pH and extractant concentration at constant value of other parameters, allows estimation of the number of extractant molecules associated with the extractant metal complex.

EXPERIMENTAL

Reagents

The commercial extractant TOPS-99 (di-(2-ethyl-hexyl) phosphoric acid) was supplied by Heavy Water Plant, Talcher, Orissa, India and was used as received. Distilled kerosene (bp 190–210°C) was used as the diluent. Tri-*n*-butyl phosphate (TBP) 5 vol% was used as modifier.

All other chemicals used such as $3CdSO_4 \cdot 8H_2O$, H_2SO_4, NaOH, etc., were of analytical reagent grade. Stock solution of $1\,kg/m^3$ Cd(II) was prepared and working solutions were prepared by dilution.

Membrane

Microporous polypropylene film Celgard 2500 supplied by Hoechest Inc., USA was used as the solid support for the liquid membrane. As per the specification provided by the supplier, the membrane has a porosity of 41%, thickness of 25.4 μm, and pore dimensions $(W \times L) = 0.04 \times 0.12\,\mu m$.

Methods

The microporous film was impregnated with TOPS-99 of desired concentration under vacuum and was clamped in between two half cells using PVC gaskets forming two compartments each having a capacity of $100\,cm^3$.[9] The active membrane area (geometric area × porosity) was $0.14735\,m^2$. The aqueous feed solution containing Cd(II) in the concentration range 0.44–44.48 mol/m^3 was adjusted to the desired pH value using dilute H_2SO_4 or NaOH before the start of the experiment. Sulfuric acid solution of 900 mol/m^3 concentration was used as strip solution in all experiments excepting those involving effect of concentration on the flux. The feed and strip solutions were kept under agitation using mechanical stirrers. Sampling was done by withdrawing 1.0 cm^3 of solutions from both the compartments at desired time interval and the samples were analyzed for Cd(II) concentration using atomic absorption spectrophotometer (AAS, Perkin Elmer, model 372, accuracy for cadmium is ±0.01 ppm).

RESULTS AND DISCUSSION

Equilibrium Study

For equilibrium studies 10 cm^3 of the aqueous solution containing 0.88 mol/m^3 of cadmium was equilibrated with an equal volume of TOPS-99 in a separating funnel for 10 min. After complete phase disengagement, the aqueous phase was separated and was analyzed for Cd(II) concentration. The concentration of Cd(II) in the organic phase was calculated from the difference between the metal-ion concentration in the aqueous phase before and after extraction. The TBP (5 vol%) was used as modifier. There may not be any synergic extraction for cadmium using TBP, as there was no literature found on this.

Effect of Equilibrium PH

The extraction of cadmium from sulfate media containing 0.88 mol/m^3 of Cd(II) was studied using TOPS-99 (30 mol/m^3) within the equilibrium pH range 3.0–3.4. Percentage extraction increases with the increase in equilibrium pH (Fig. 1). There was no extraction below equilibrium pH 3.0. Figure 2 shows the plot of $\log D$ vs. equilibrium pH. The plot is linear with a slope of 2.2, indicating the exchange of 2 mol of H^+ with 1 mol of the extracted metal species, which supports the reaction mechanism shown in Eq. (7)

Effect of Extractant Concentration

The effect of TOPS-99 concentration on the extraction of cadmium (0.88 mol/m^3) was studied in the range 0.5–20 mol/m^3. It was observed that percentage extraction of Cd(II) increased with increase of extractant concentration (Fig. 3). The $\log D$ vs. log[extractant] plot shown in Fig. 4 is a straight line with slope 2.15. This indicates that 2 mol of extractant is associated with the extracted metal species.

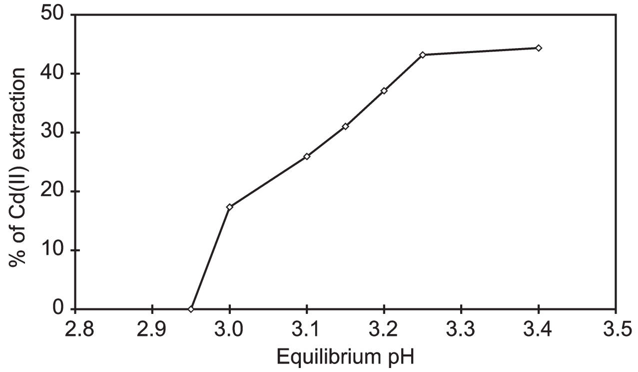

Figure 1. Effect of equilibrium pH on the extraction of cadmium.

Transport of Cd(II) by Supported Liquid Membrane

Effect of the following parameters was studied on transport of Cd(II) by liquid membrane using TOPS-99 as mobile carrier: (a) stirring speed, (b) pH of the feed solution, (c) TOPS-99 concentration in the membrane, (d) concentration of Cd(II) in feed solution, and (e) acid concentration in strip solution. It was observed that Cd(II) concentration decreases in the feed compartment linearly with time for 2 hr and increases with time in the strip compartment at the same

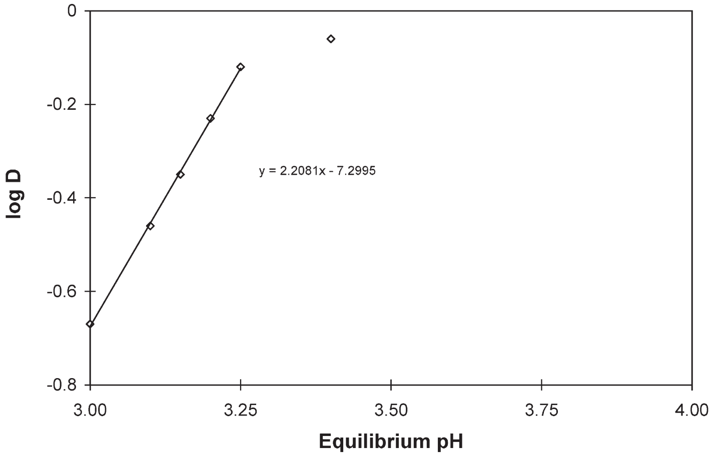

Figure 2. Plot of equilibrium pH vs. log D.

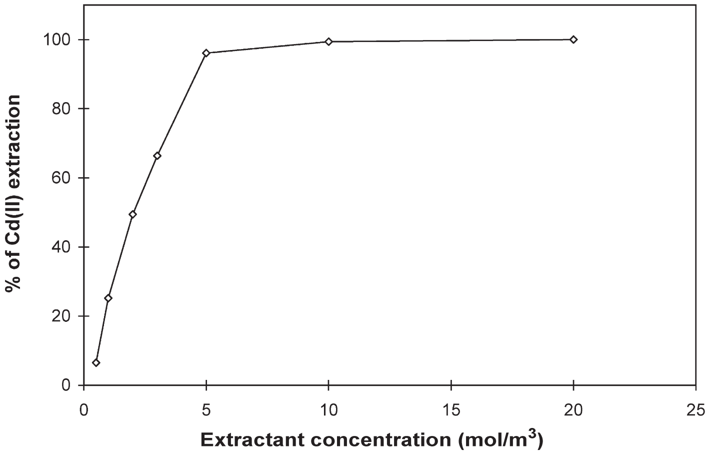

Figure 3. Effect of extractant concentration on the extraction of cadmium.

rate as it decreases in feed solution. (V/A)d[Cd(II)] was plotted against dt for each experiment and from the slope of the initial straight line, flux of the cadmium ($J_{Cd(II)}$) was calculated:

where, V is the volume of the solution on each side of the membrane, (m^3); A, the effective membrane area, (m^2); t, the time, (sec).

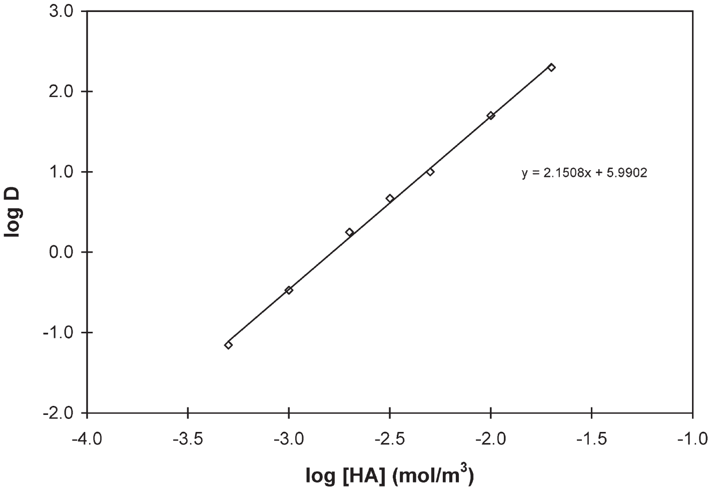

Figure 4. Plot of log [HA] vs. log D.

Effect of Stirring Rate

Permeation of metal ions through aqueous boundary layer is one of the major resistances in liquid membrane technique. To minimize this resistance, solutions in both the compartments were kept under agitation. The impeller of diameter 1.5 cm was used for stirring. The stirring rate was varied between 50 and 600 rpm and the effect of stirring speed on cadmium flux is shown in Fig. 5. It was observed that cadmium flux increases with increasing stirring rate between 50 and 500 rpm and the flux remains constant thereafter. So it was assumed that a stirring rate of 500 rpm is sufficient for this experimental set up to achieve minimum resistance due to aqueous film boundary layer and further experiments were carried out with the above stirring rate.

Effect of pH

The effect of pH in the feed solution on the transport of cadmium was studied at two different TOPS-99 concentration (50 and 300 mol/m^3) in the membrane phase. The cadmium concentration in feed solution was kept constant at 0.88 mol/m^3. The value of log $J_{\mathrm{Cd(II)}}$ was plotted against pH in Fig. 6, which shows that with 50 mol/m^3 TOPS-99, cadmium flux increases with the increase in pH from 3.0 to 4.0 and a plateau region is obtained at higher pH values. There was no extraction of cadmium below pH 3.0. With an increase in pH (3.0–4.0), dissociation

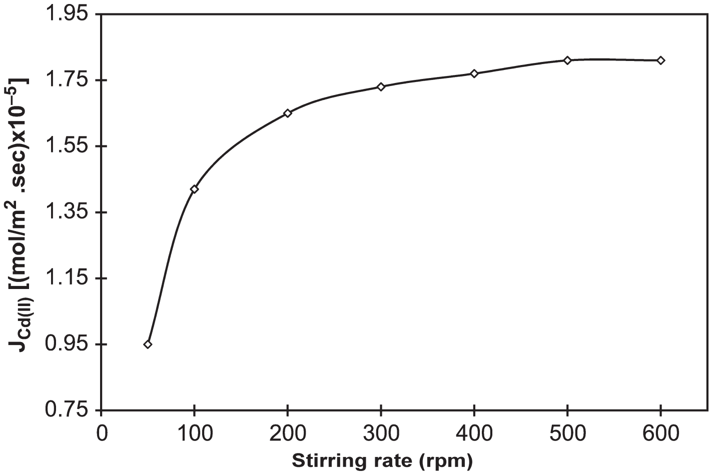

Figure 5. Effect of stirring rate on $J_{\mathrm{Cd(II)}}$.

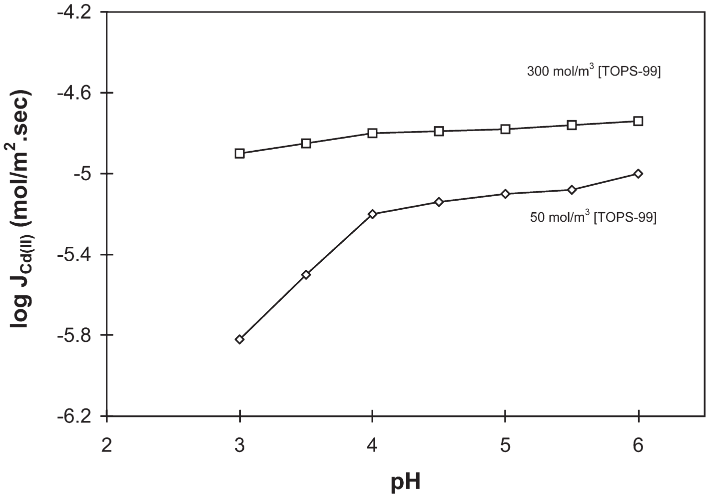

Figure 6. Effect of pH on $J_{\mathrm{Cd(II)}}$.

of TOPS-99 molecule increases at the feed-membrane interface, which leads to increased formation of Cd(II)–TOPS-99 complex and increase of $J_{\mathrm{Cd(II)}}$. Between pH 4.0 and 6.0, further dissociation of TOPS-99 and formation of Cd(II)–TOPS-99 complex is very small, because the dissociation of TOPS-99 and complex formation have already attained maximum. Therefore, a plateau was obtained at pH region of 4.0–6.0. However at higher concentration of TOPS-99 (300 mol/m^3), the feed-membrane interface was saturated with TOPS-99–Cd(II) complex even at pH 3.0 and so a plateau was obtained for the whole pH region.

Effect of Extractant Concentration

The effect of the concentration of TOPS-99 in the membrane phase on the cadmium flux was studied in the range 25–400 mol/m^3. The Cd(II) concentration and pH of the feed solution was kept constant at 0.88 mol/m^3 and 6.0, respectively. Figure 7 shows the log–log relationship of $J_{\mathrm{Cd(II)}}$ and concentration of TOPS-99 in its dimeric form. Cadmium flux increases with increase in TOPS-99 concentration up to 100 mol/m^3 ($[\mathrm{HL}]_2 = 50\,\mathrm{mol/m^3}$) and further increase in extractant concentration has no significant effect on permeation rate of cadmium. As per Eq. (4) with increase in TOPS-99 concentration, the formation of Cd(II)–TOPS-99 complex increases at the feed side-membrane interface and since at a lower extractant concentration, the same interface is not saturated by the extractant, the flux increases with an increase in extractant concentration. The

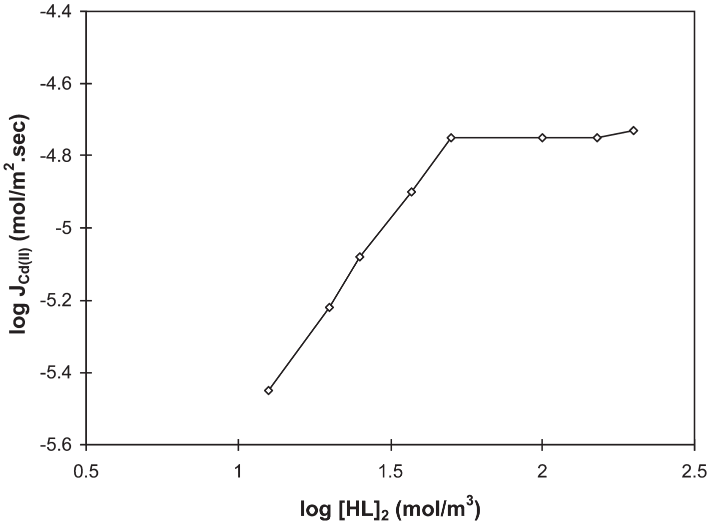

Figure 7. Effect of extractant concentration on $J_{\mathrm{Cd(II)}}$.

plateau region beyond 100 mol/m^3 TOPS-99 can be explained as the combined effect of saturation of feed-membrane interface with the complex and viscosity of the membrane phase.

Effect of Cd(II) Concentration in Feed Solution on $J_{\mathrm{Cd(II)}}$

Effect of Cd(II) concentration on $J_{\mathrm{Cd(II)}}$ was studied in the range 0.444–44.48 mol/m^3 with three different TOPS-99 concentration (25, 100, and 300 mol/m^3) in the membrane phase, keeping the pH of feed solution constant at 6.0. Figure 8 shows the log–log relationship between the metal flux $J_{\mathrm{Cd(II)}}$ and the feed concentration of Cd(II). It can be observed from the figure that up to 8.89 mol/m^3 of Cd(II) concentration, a linear relationship is obtained with slope value of 0.4. Within this concentration range of Cd(II) in feed solution, the availability of Cd(II) at the feed side-membrane interface increases with increase in the Cd(II) concentration. So interfacial chemical reaction becomes faster, which leads to increase in J_{Cd}(II). With further increase in Cd(II) concentration, the membrane phase tends to get saturated with Cd(II)–TOPS-99 complex. In addition, the concentration gradient between bulk feed phase and the feed-membrane interface diminishes sharply. All these factors lead to the plateau region of $J_{\mathrm{Cd(II)}}$ across the membrane at higher concentration of Cd(II) (beyond 8.89 mol/m^3) in the feed compartment.

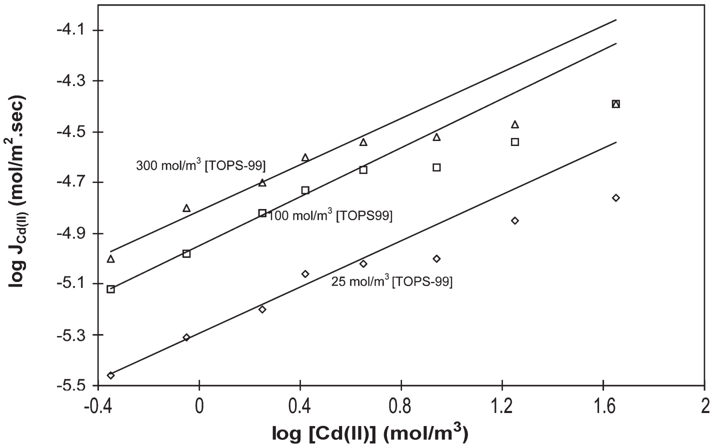

Figure 8. Plot of log [Cd(II)] vs. log $J_{\mathrm{Cd(II)}}$.

Effect of Acid Concentration in Strip Solution

Stripping reaction with respect to the metal–TOPS-99 in the presence of an acid at membrane-strip side interface is very fast. The stripping kinetics was studied with different concentrations of acid solutions (180, 360, 900, and 1800 mol/m^3). Figure 9 shows the effect of acid concentration on $J_{\mathrm{Cd(II)}}$. It was observed that $J_{\mathrm{Cd(II)}}$ increased with increase in the acid concentration from 180 to 900 mol/m^3. The percentages of stripping with H_2SO_4 of 900 and 1800 mol/m^3 concentration were identical, which indicates that a strip solution having 900 mol/m^3 H_2SO_4 is sufficient for this stripping study.

Effect of [Cd(II)] in Strip Solution on $J_{\mathrm{Cd(II)}}$

Liquid membrane is a process, where permeation of metal ions from feed solution to strip solution can take place against concentration gradient. The maximum extent to which the metal ions can be concentrated in strip solution depends on the concentration difference in the coupled ion across the membrane. According to Donnan Equilibrium, for ion M^{n+}, where n is the valency of the metal ion, transfer of metal ion from feed solution to strip solution will be continued until the equilibrium (8) is attained.[32]

$$\frac{[M^{n+}]_f}{[M^{n+}]_s} = \frac{[H^+]_f}{[H^+]_s} \tag{8}$$

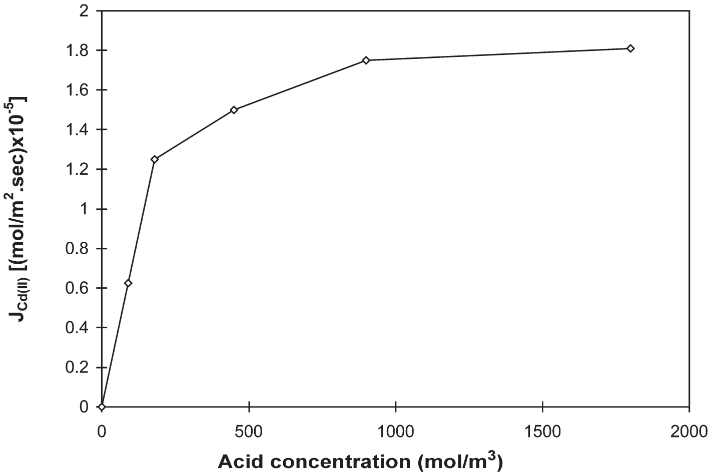

Figure 9. Effect of acid concentration in strip solution on $J_{\mathrm{Cd(II)}}$.

where, f and s designate the feed and strip compartment respectively. Therefore, experiments were carried out with strip solutions having 900 mol/m^3 H_2SO_4 and different concentrations of cadmium (4.44–88.96 mol/m^3). It was observed that with increase in the cadmium concentration in strip solution from 4.44 to 88.96 mol/m^3, there is no change in cadmium flux and cadmium ion continues to be transferred from feed side to strip side.

CONCLUSIONS

Extraction of Cd(II) was carried out by liquid membrane technique using TOPS-99, produced by Heavy Water Plant, Talcher, India, as mobile carrier. In addition, equilibrium studies with shake flask were carried out. Following conclusions may be drawn from the studies.

(a) For equilibrium studies, the percentage extraction of Cd(II) increased with increase in extractant concentration. The slope analysis studies of log D vs. log (HA) indicates that 2 moles of the extractant was involved with 1 mol of the extracted metal species.

(b) The stirring rate of 500 rpm was found to be sufficient for minimizing the resistance due to aqueous boundary layer.

(c) The cadmium flux increases with increase in pH from 3.0 to 4.0 and then forms a plateau. There was no extraction below pH 3.0.

(d) Also J_{Cd} increases with increase in extractant concentration up to 100 mol/m^3 and then remains constant.

(e) It was observed that 900 mol/m^3 H_2SO_4 is sufficient for the stripping studies. The cadmium ion could be concentrated in strip solution against its concentrated gradient which is according to Donnan equilibrium equation.

ACKNOWLEDGMENTS

The authors wish to thank Dr. P. V. R. Bhaskara Sarma, Scientist, RRL, Bhubaneswar for his valuable suggestion and Dr. Vibhuti N. Misra, Director, Regional Research Laboratory, Bhubaneswar, for his kind permission to publish this paper. One of the authors (SST) is thankful to Heavy Water Board, Department of Atomic Energy, Government of India for awarding a research fellowship during the course of investigation. This work was supported by Heavy Water Board, Government of India.

REFERENCES

1. Cheremisinoff, Paul N. *Handbook of Water and Wastewater Treatment Technology*; Marcel Dekker Inc.: New York, 1995; 418.
2. Bloach, R. Hydrometallurgy Separations by Solvent Membranes. In *Membrane Science and Technology*; Flinn, J.E., Ed.; Plenum: New York, 1970; 171.
3. Youn, I.J.; Harrington, P.J.; Stevens, G.W. Long Term Performance of Hollow Fibre Membrane Solvent Extraction Modules Used for Cr(VI) Recovery from Electroplating Rinse Water. SX Ion Exch. **2000**, *18* (5), 933.
4. Vincent, T.; Guibal, E. Non-Dispersive Liquid Extraction of Cr(VI) by TBP/Aliquot 336 Using Chitosan Made Hollow Fibre. SX Ion Exch. **2000**, *18* (6), 1241.
5. Alguacil, F.J.; Coedo, A.C.; Dorado, M.T. Transport of Chromium (VI) Through a Cyanex 923 Xylene Flat Sheet Supported Liquid Membrane. Hydrometallurgy **2000**, *57*, 51.
6. Sastree, A.M.; Madi, A.; Alguacil, F.J. Solvent Extraction of $Au(CN)_2^-$ and Application to Facilitated Supported Liquid Membrane Transport. Hydrometallurgy **2000**, *54*, 71.
7. Ilias, S.; Schimmel, K.A.; Yezek, P.M. Non-Dispersive Liquid Liquid Extraction of Copper and Zinc from an Aqueous Solution by D2EHPA and LIX 984 in a Hollow Fibre Membrane Module. Sep. Sci. Technol. **1999**, *34* (6 and 7), 1007.

8. Yang, X.J.; Fane, A.G. Facilitated Transport of Copper in Bulk Liquid Membranes Containing LIX984N. Sep. Sci. Technol. **1999**, *34* (9), 1873.
9. Sarangi, K.; Bhaskara Sarma, P.V.R. Extraction of Copper (II) in the Presence of Cobalt (II), Nickel (II), Manganese (II) and Iron (II) Using Supported Liquid Membrane. Indian J. Chem. **1992**, *31A*, 379.
10. Berends, A.M.; Witkamp, G.J.; Van, G.M. Rosmalen Extraction of Aluminium from Piching Bath with Supported Liquid Membrane Extraction. Sep. Sci. Technol. **1999**, *34* (6 and 7), 1521.
11. Kedari, C.S.; Pandit, S.S.; Ramanujam, A. Studies of the In Situ Electrooxidation and Selective Permeation of Cerium (IV) Across a Bulk Liquid Membrane Containing Tributyl Phosphate as the Ion Transporter. Sep. Sci. Technol. **1999**, *34* (9), 1907.
12. Fontas, C.; Salvado, V.; Midalgo, M. Solvent Extraction of Pt(IV) by Aluqiat 36 and Its Application to a Solid Supported Liquid Membrane System. SX Ion Exch. **1999**, *17* (1), 149.
13. Alguacil, F.J.; Alonso, M. Iron(III) Transport Using a Supported Liquid Membrane Containing Cyanex 921. Hydrometallurgy **2000**, *58*, 81.
14. Tompkins, C.J.; Michaels, A.S.; Paretti, S.W. Removal of *p*-Nitrophenol from Aqueous Solution by Membrane Supported Solvent Extraction. J. Membr. Sci. **1992**, *75*, 277.
15. Shinbo, T.; Yamaguchi, T.; Yanagishite, H.; Sakaki, K.; Kitamoto, D.; Sugiura, M. Selective Transport of Amino Acid Mediated by Chiral Crown Ether Effect of Membrane Stability. J. Membr. Sci. **1993**, *84*, 241.
16. Stenstrom, S. Extraction of Cadmium from Phosphoric Acid Solutions with Amines. Part III. A Thermodynamic Extraction Model. Hydrometallurgy **1987**, *18*, 1.
17. Casas, I.; Miralles, N.; Sastree, A.; Aguilar, M. Extraction of Cadmium (II) by Organophosphorous Compounds. Polyhedron **1986**, *5* (12), 2039.
18. Preston, J.S. The Selective Solvent Extraction of Cadmium by Mixtures of Carboxylic Acids and Trialkylphosphine Sulphides. Part I. The Origin and Scope of the Synergistic Effect. Hydrometallurgy **1994**, *36*, 61.
19. Owusu, G. Selective Extractions of Zn and Cd from Zn–Cd–Co–Ni Sulphate Solution Using Di-2-Ethylhexyl Phosphoric Acid Extractant. Hydrometallurgy **1998**, *47*, 205.
20. Verhaege, M. Influence of the Chloride Concentration on the Distribution and Separation of Zinc and Cadmium by Means of Solvent Extraction with Carboxylic Acids. Hydrometallurgy **1975**, *1*, 97.
21. Singh, J.M.; Gogia, S.K.; Tandon, S.N. Study on the Extraction of Zinc (II), Cadmium (II) and Mercury (II) with Caprylic Acid. Hydrometallurgy **1982**, *9*, 97.

22. Rice, N.M.; Smith, M.R. Recovery of Zinc, Cadmium and Mercury (II) from Chloride and Sulphate Media by Solvent Extraction. J. Appl. Chem. Biotechnol. **1975**, *25*, 379.
23. Noguira, C.A.; Delmas, F. New Flow Sheet for the Recovery of Cadmium, Cobalt and Nickel from Spent Ni–Cd Batteries by Solvent Extraction. Hydrometallurgy **1999**, *52*, 267.
24. He, D.; Ma, M. Kinetics of Cadmium (II) Transport Through a Liquid Membrane Containing Tricapryl Amine in Xylene. Sep. Sci. Technol. **2000**, *35*, 1573.
25. He, D.; Ma, M. Effect of Paraffin and Surfactant on Coupled Transport of Cadmium (II) Ions Through Liquid Membranes. Hydrometallurgy **2000**, *56*, 157.
26. Sastree, A.M.; Muhammed, M. The Extraction of Zn(II) from Sulphate and perchlorate Solutions by Di-(2-Ethyl-hexyl) Phosphoric Acid Dissolved in Isopar-H. Hydrometallurgy **1984**, *12*, 177.
27. Dreisinger, D.B.; Copper, W.C. The Kinetics of Zinc, Cobalt and Nickel Extraction in the D2EHPA–Heptane–$HClO_4$ System Using the Rotating Diffusion Cell Technique. Solvent Extr. Ion Exch. **1989**, *7*, 335.
28. Sarangi, K.; Reddy, B.R.; Das, R.P. Extraction Studies of Cobalt (II) and Nickel (II) from Chloride Solutions Using Na-Cyanex 272 Separation of Co(II)/Ni(II) by the Sodium Salt of D2EHPA, PC88A and Cyanex 272 and Their Mixtures. Hydrometallurgy **1999**, *52*, 253.
29. Thakur, N.V. Separation of Dysprosium and Yttrium from Yttrium Concentrate Using Alkyl Phosphoric Acid (DEHPA) and Alkylphosphoric Acid (EDEHPA-PC88A) as Extractants. Solvent Extr. Ion Exch. **2000**, *18* (5), 853.
30. Rezvanianzadeh, M.R.; Yamini, Y.; Khanchi, A.R.; Ashtari, P.; Marajheh, M.G. High Selective and Efficient Membrane Transport of Molybdenum Using Di-(2-Ethyl-hexyl) Phosphoric Acid as Carrier. Sep. Sci. Technol. **2000**, *35* (12), 1939.
31. Huang, T.C.; Tsai, T.H. Separation of Cobalt and Nickel Ions in Sulphate Solutions by Liquid–Liquid Extraction and Supported Liquid Membrane with D2EHPA Dissolved in Kerosene. J. Chem. Eng. (Jpn) **1991**, *29* (1), 126.
32. Babcock, W.C.; Kelly, D.J.; Lachapeller, E.D.; Smith, K.L.; Baker, R.W. Coupled Transport Membranes in Hydrometallurgy. Hydrometallurgy **1981**, *D2/1*, 81.

Received July 2001
Revised December 2001