



Extraction of cadmium from dilute solution using supported liquid membrane

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ABSTRACT

The extraction efficiencies of three phosphoric acid derivatives (D2EHPA, PC-88A and Cyanex 272) for Cd in supported liquid membrane (SLM) have been reported. The equilibrium study indicated the release of two moles of H⁺ ions from the extractant for extraction of one mole of cadmium ion and association of two moles of the extractants in the extracted species in each case. The diffusion constant of Cd–D2EHPA, Cd–PC-88A and Cd–Cyanex 272 complex through the membrane phase was found to be 2.53×10^{-9} , 5.435×10^{-9} and 11.22×10^{-9} m²/s, respectively. The effects of various parameters such as flow rate, pH of feed solution, concentration of extractants in membrane phase, concentration of H₂SO₄ in strip solution and concentration of Cd in feed solution on cadmium flux (J_{Cd}) have been investigated. At pH 7.5, the percentage of cadmium extraction was found to be maximum with 600 mol/m³ D2EHPA and PC-88A and 800 mol/m³ Cyanex 272. The extraction of cadmium using the phosphoric acid derivative follows the order D2EHPA > PC-88A > Cyanex 272.

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1. Introduction

The widespread use of cadmium in various industrial activities like metallurgy, electroplating, pigments, nuclear, Ni–Cd batteries and agricultural fields (fertilizer and pesticides) causes the cadmium release into the aquatic environment. Cadmium is considered to be a serious threat to the environment and human health due to its toxicity [1]. Efforts are being carried out to develop improved and efficient techniques to remove or reduce cadmium concentration in the wastewaters or effluents to protect the environment. Depending on the concentration of cadmium, nature of effluent/wastewater, associated ions and cost of treatment, several processes such as chemical precipitation (as hydroxide, carbonate, sulphide, etc.), physical treatment (ion exchange, adsorption, foam floatation) and separation processes (reverse osmosis, ultra-filtration, solvent extraction), are being currently used [2–6] for removal/separation of cadmium. Bioremediation of cadmium has also been studied in recent years [7–8]. The drawbacks of these processes are secondary waste generation, inconvenient operational condition, high cost, etc. The cadmium content in majority of wastewaters/effluents is less than 1 g/L and the conventional liquid–liquid extraction processes [9–14] using specific extractant are found unsuitable. Also the solvent extraction process suffers from inherent drawbacks such as loading limitation, losses of metal ions in interfacial third phase, organic contamination, etc. [15]. In

this context, different liquid membrane processes have been proved to be an effective alternative for treatment of cadmium containing effluents/wastewaters [16–21]. The supported liquid membrane (SLM) has edge over other membrane processes with respect to its high selectivity, low energy utilization [18] and has been a subject of number of recent investigations for separation of cadmium and other metal ions from wastewaters/effluents using a variety of extractants [22–28].

Phosphoric acid derivatives such as bis-(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) and bis-(2,4,4-trimethyl pentyl) phosphinic acid (Cyanex 272) have been used as extractants for extraction of cadmium ion by several workers [29,10]. However, the use of supported liquid membrane for treatment of cadmium containing wastewaters/effluents is scanty [30–32]. As the structure and nature of organic carriers present in the membrane play a vital role in determining the overall performance of SLM system, a comparative extraction efficiency of cadmium from its aqueous solution by SLM with D2EHPA, PC-88A and Cyanex 272 as extractants has been studied in the present investigation and the results are reported.

2. Experimental

2.1. Materials

All the reagents like CdSO₄·7H₂O, HCl, H₂SO₄, EDTA, etc. used were of analytical grade. Celgard 2400, a microporous polypropylene film supplied by Hoechst Celanese Inc., USA,

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Nomenclature

Nomenclature

A	area of the membrane (m^2)
C_0	initial concentration of the complex (mol/m^3)
\bar{D}	diffusion coefficient of the complex through the membrane (m^2/s)
D	distribution coefficient
d	thickness of the membrane (m)
J_{Cd}	flux of the cadmium ion ($\text{mol}/\text{m}^2 \text{ s}$)
Q_t	amount of metal complex transferred through membrane at time 't' (mol/m^3)
t	time (s)
V	volume of the solution taken (m^3)

Greek letter

ε	membrane porosity
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Subscripts

Org.	organic phase
Aq.	aqueous phase
f	feed phase
s	strip phase

was used as the solid support for the liquid membrane. This film was $25.4 \mu\text{m}$ thick, 41% porous with pore size of $0.04 \mu\text{m} \times 0.12 \mu\text{m}$ (WXL). The commercial extractants, bis-(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) and bis-(2,4,4-trimethyl pentyl) phosphinic acid (Cyanex 272) were supplied by Heavy Water Plant, Talcher, India; Daihachi. Chemical Industry Co. Ltd., Japan and Cytec Inc., USA, respectively. These extractants were used as received without any further purification. Distilled kerosene (b.p. $180\text{--}240^\circ\text{C}$) was used as the diluent. The membranes were prepared by absorbing the microporous polypropylene sheet in the organic phase prepared by diluting the required extractant in distilled kerosene for at least 24 h before starting of the experiments.

A stock solution of Cd ($8.896 \text{ mol}/\text{m}^3$) was prepared by dissolving $\text{CdSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water and analysed by titration with standard EDTA. The required working solution was prepared by dilution. The pH of the aqueous solution was adjusted to the desired values using dilute $\text{H}_2\text{SO}_4/\text{NaOH}$ solution. The pH of aqueous solutions was measured with a digital pH meter (Model LI 127) provided with a combined glass electrode. The meter was standardized with NBS buffers before any measurement.

All the experiments for extraction equilibrium and liquid membrane were carried out at room temperature ($30 \pm 1^\circ\text{C}$).

2.2. Extraction equilibrium

For equilibrium studies 10 cm^3 of the aqueous solution containing $1.014 \text{ mol}/\text{m}^3$ of cadmium was equilibrated with an equal volume of extractant in a separating funnel for 5 min. Tri-n-butyl phosphate (5%) was used as the phase modifier. After complete phase disengagement, the aqueous phase was separated and was analysed for Cd concentration. The concentration of Cd in the organic phase was calculated from the difference between the metal ion concentration in the aqueous phase before and after extraction. As and when required, the metal concentration in the organic phase was determined after filtration through 1PS phase separation paper and stripping a suitable aliquot of it with 2 M H_2SO_4 followed by dilution and analysis.

The percentage extraction of Cd was calculated as follows:

$$\text{Cd extraction (\%)} = \frac{[\text{Cd}]_{F(i)} - [\text{Cd}]_{F(e)}}{[\text{Cd}]_{F(i)}} \times 100 \quad (1)$$

where $\text{Cd}_{F(i)}$ is the initial metal concentration in the feed phase, while $\text{Cd}_{F(e)}$ is the metal concentration in the aqueous phase at equilibrium.

2.3. Membrane experiments

The supported liquid membrane experiments were carried out using a plate and frame type two-compartment permeation cell as described elsewhere [33]. The effective membrane area (geometrical membrane area \times porosity) of the cell was 0.0217 m^2 . The volumes of the strip solution and feed solution used were 100 cm^3 each. The feed solutions were adjusted to the desired pH using buffer solution before starting of each experiment. Both solutions were circulated through the membranes with a peristaltic pump (Watson Marlow 501 S). The feed solution continuously agitated using mechanical stirrers. Sampling were done by withdrawing 1.0 cm^3 of solution at desired time interval and analysed for metal ion concentration. The percentage of metal transported was determined by using:

$$\text{Cd transported (\%)} = \frac{[\text{Cd}]_{S(t)}}{[\text{Cd}]_{F(t)}} \times 100 \quad (2)$$

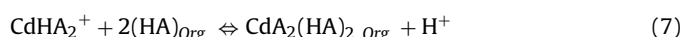
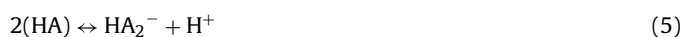
where $[\text{Cd}]_{F(t)}$ and $[\text{Cd}]_{S(t)}$ denote the metal concentration in the feed and strip compartments at an elapsed time 't'.

2.4. Analytical methods

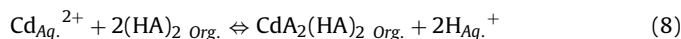
The concentration of Cd and other metal ions were determined using a Perkin-Elmer Model AAnalyst-200 Atomic Absorption Spectrophotometer (AAS) after proper dilution of samples with 10% HCl. The FT-IR spectra of the extractants and their complexes were recorded on a Varian 800 FT-IR (Scimitar Series) to assess the modes and extent of binding of extractants with Cd.

3. Theory

The formation of complex between cadmium and phosphoric, phosphonic or phosphinic acid involves several steps (Eqs. (3)–(7)): the dissociation of dimeric molecule into monomers, distribution of monomer between aqueous interface and organic medium, acid dissociation of monomer at the interface, and finally the formation of neutral Cd complex with ionized extractant. These steps are represented as follows:



where HA denotes phosphoric, phosphonic or phosphinic acid. Thus, the overall extraction process is governed by:



The equilibrium constant (K) is defined as (Eq. (9))

$$K = \frac{[\text{CdA}_2(\text{HA})_2]_{\text{Org.}} [\text{H}^+]_{\text{Aq.}}^2}{[\text{Cd}^{2+}]_{\text{Aq.}} [(\text{HA})_2]_{\text{Org.}}^2} \quad (9)$$

$$\text{Or, } K = \frac{D[H^+]_{Aq.}^2}{[(HA)_2]_{Org.}^2} \left(D = \frac{[CdA_2(HA)_2]_{Org.}}{[Cd^{2+}]_{Aq.}} \right) \quad (10)$$

$$\text{Or, } \log D = \log K + 2\text{pH} + 2 \log [(HA)_2]_{Org.} \quad (11)$$

The flat sheet liquid membrane used in the extraction study acts as the uniform barrier which supports the organic extractant for the Cd ion transport. The extraction reaction of Cd ions and the extractant at the feed/membrane interface is governed by equilibrium as depicted in equation (8).

The amount of metal ion transferred per unit area (V/A) [Cd]_{F(t)} was plotted against time 't' for all the experiments and the permeation rates per unit area or flux were calculated from the initial slopes of the (V/A) [Cd]_{F(t)} versus time plots.

$$J_{Cd} = \left(\frac{V}{A} \right) \frac{d[Cd]_{F(t)}}{dt} \quad (12)$$

where V is the volume of the aqueous phase, A is the active surface area of the membrane.

4. Results and discussion

4.1. Equilibrium study

Some preliminary experiments on liquid–liquid extraction of cadmium were carried out from an aqueous solution bearing 1.014 mol/m³ Cd with D2EHPA, PC-88A and Cyanex 272 (0.2 mol/dm³) to know the extraction mechanism of cadmium with different phosphoric acid derivative. This extraction was carried out in the pH range 1.5–8.0. The equilibrium pH after extraction of cadmium with D2EHPA, PC-88A and Cyanex 272 were found to vary in between 1.47 to 3.08, 1.52 to 3.28 and from 1.48 to 3.22, respectively. The percentage extraction of Cd with different extractants at different equilibrium pH was shown in Fig. 1, which showed substantial increase of extraction with increase of equilibrium pH. The percentage extraction was found to be maximum (65.61) with D2EHPA and minimum (6.8) with Cyanex 272. The extraction trend follows the order D2EHPA > PC-88A > Cyanex 272. This is due to availability of more and more extractant in dissociated form with increasing pH to form the neutral complex and also in agreement with the complexing ability of the extractants with Cd. The variation of distribution coefficient in terms of log D versus equilibrium pH was shown in Fig. 2. The slope values of these plots in the range 1.56–2.28 indicated that two moles of H⁺ were released from each of the extractant used for extraction of one mole of cadmium ion as proposed in Eq. (8). To provide further evidence

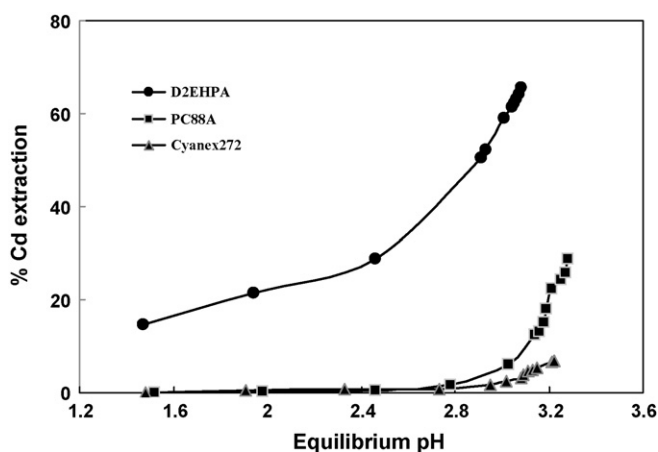


Fig. 1. Effect of equilibrium pH on percentage extraction of Cd with 0.2 M D2EHPA, PC-88A and Cyanex 272.

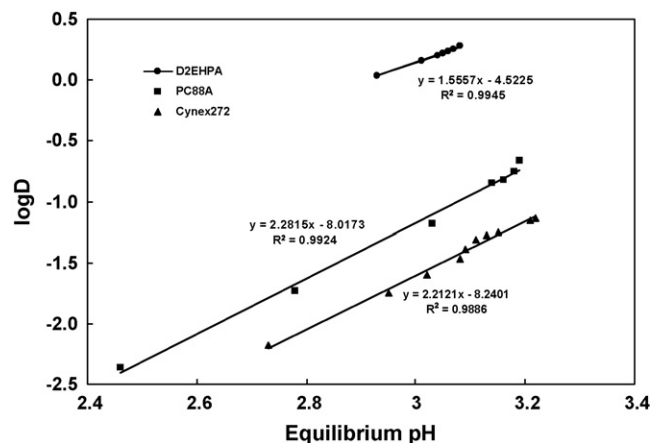


Fig. 2. Effect of equilibrium pH on log D. Experimental conditions: 0.2 M D2EHPA, PC-88A and Cyanex 272.

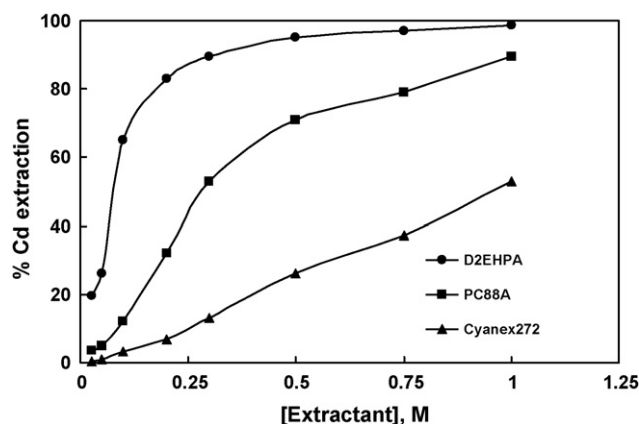


Fig. 3. Effect of [extractant] on percentage extraction of Cd at pH 7.5.

in this regard, the effect of extractant concentration on the extraction of cadmium was studied in the range 0.025–1.0 M keeping the phase ratio and initial pH constant at 1:1 and 7.5, respectively. The percentage extraction of Cd increased with increase of [D2EHPA] up to 0.5 M and there after remained practically constant. However in case of PC-88A and Cyanex 272, the percentage extraction of Cd increased even up to the extractant concentration of 1.0 M (Fig. 3). The slopes of the plots of log D versus log [extractant] (Fig. 4) was

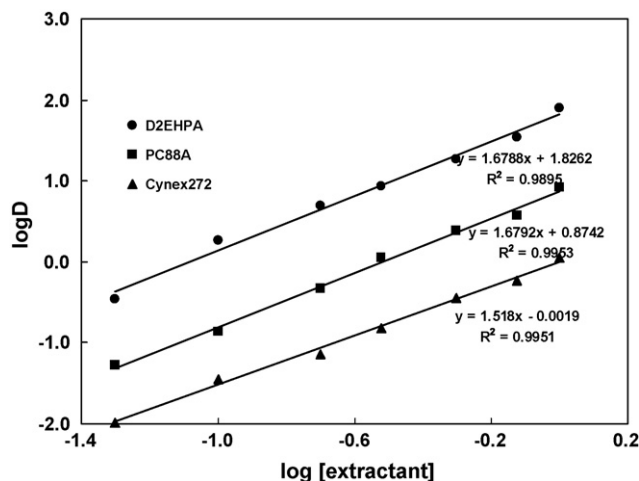


Fig. 4. Effect of log [extractant] on log D, pH 7.5.

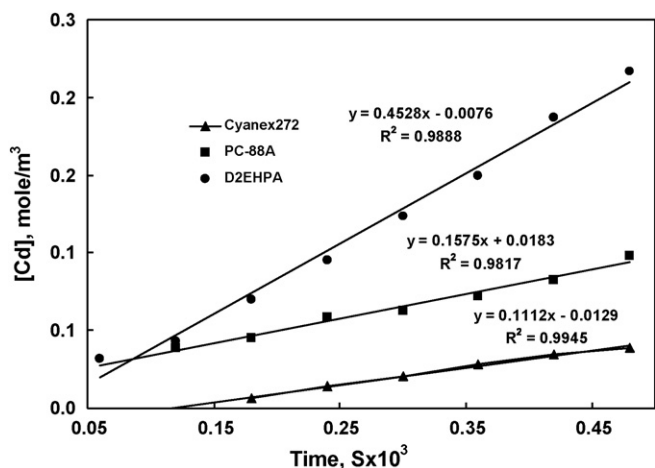


Fig. 5. Permeation of Cd complex at different time. Experimental conditions: compartment I—loaded organic of Cd–D2EHPA, Cd–PC-88A and Cd–Cyanex 272; compartment II—kerosene, stirring rate 500 rpm.

again found more than 1.5 (1.68 for both D2EHPA and PC-88A and 1.52 for Cyanex 272) indicating the association of two moles of each extractant for extraction of one mole of metal ion in the extracted species.

4.2. Supported liquid membrane study

The extraction of cadmium through supported liquid membrane system depends on several factors like diffusivities of Cd–extractant complex through membrane, flow rate of feed and strip solution, pH of the feed solution, extractant concentration in the membrane phase, acid concentration in strip solution and Cd concentration in feed solution, etc. and therefore need to be optimized.

4.2.1. Determination of diffusion coefficient

The transport of neutral complex, formed between the extractant and the cadmium ion at the feed solution–membrane interface to the other side of the membrane by diffusion process is an important step in SLM system and hence it is desirable to know the diffusion coefficient for different complexes through the membrane. Before starting this experiment the Cd–D2EHPA, Cd–PC-88A and Cd–Cyanex 272 complexes (loaded organic) were generated by equilibrating 125 mL of 1.014 mol/m³ Cd solution with 125 mL of 1 M D2EHPA, PC-88A and Cyanex 272 in kerosene separately at 1:1 phase ratio. The pH of the aqueous solution was 7.5. After phase disengagement, the organic phases were separated, filtered through IPS phase separation paper and used for the study. The microporous film was absorbed with kerosene and was clamped in between two half cells using PVC gaskets forming two compartments each having a capacity of 100 cm³ [33]. The active membrane area (geometric area × porosity) was 1.12 × 10^{−3} m². One compartment (compartment-I) of the cell was filled with the loaded organic (Cd–D2EHPA/Cd–PC-88A/Cd–Cyanex 272) and the other compartment (compartment-II) was filled with kerosene. The loaded organic diffused from compartment-I to the compartment-II. Both the compartments were kept under agitation using mechanical stirrers. Sampling was done by withdrawing 1.0 cm³ of loaded organic from both the compartments at desired time interval and the samples were filtered using IPS paper. The amount of cadmium ion transferred was determined by stripping a suitable aliquot of it with 2 M H₂SO₄ followed by dilution and analysis.

The diffusion coefficients were calculated from the slope of the linear plots (Fig. 5) based on Crank's equation [34]:

$$Q_t = \left(\frac{\bar{D}C_o}{d} \right) \left\{ t - \left(\frac{d^2}{6\bar{D}} \right) \right\} \quad (13)$$

The diffusion coefficients of Cd–D2EHPA, Cd–PC-88A and Cd–Cyanex 272 through the membrane phase were found to be 2.53 × 10^{−9}, 5.435 × 10^{−9} and 11.22 × 10^{−9} m²/s, respectively. Assuming the cadmium flux J_{Cd} , through the membrane follows the Fick's first law is represented by:

$$J = \frac{\bar{D}\varepsilon(D_f[Cd^{2+}]_f - D_s[Cd^{2+}]_s)}{d} \quad (14)$$

and as per Eq. (14) the flux increases with increase of diffusion coefficient (\bar{D}). But in this study a reverse trend was observed. This may be explained as follows: the permeation of metal ions through the supported liquid membrane is mainly controlled by (i) aqueous film diffusion, (ii) interfacial chemical reaction and (iii) membrane diffusion [35]. The equilibrium studies above showed higher percentage extraction of cadmium with D2EHPA than with PC-88A and Cyanex 272, which indicates a higher interfacial chemical reaction rate with D2EHPA. The higher percentage extraction of Cd with D2EHPA from a sulphate solution was also observed, in which the performance for extraction of cadmium with different extractants follows the order D2EHPA > Cyanex 272 > Cyanex 923 and D2EHPA > PC-88A > Cyanex 272 [36,29]. The higher interfacial chemical reaction rate of Cd with D2EHPA than PC-88A and Cyanex 272 may be the reason for higher flux with D2EHPA.

4.2.2. Effect of flow rate on the extraction of Cd

The flow rate of feed solution is an important hydrodynamic factor in the extraction of metal ions as it affects the aqueous film boundary layer and the residence time of metal ion at the feed solution–membrane interface. The effect of flow rate of feed solution containing 1.014 mol/m³ of Cd on the cadmium flux (J_{Cd}) was studied in the range 20–200 cm³/min keeping the pH of the feed solution, [extractant] in the membrane phase and [H₂SO₄] in the strip solution constant at 4.5, 500 and 900 mol/m³, respectively and was shown in Fig. 6. It was observed that cadmium flux increased from 0.61 × 10^{−5} to 1.132 × 10^{−5}, 0.43 × 10^{−5} to 0.95 × 10^{−5} and from 0.32 × 10^{−5} to 0.89 × 10^{−5} mol/m² s for D2EHPA, PC-88A and Cyanex 272, respectively with the increase of flow rate from 20 to 120 cm³/min and thereafter decreased on further increase of flow rate. The highest value of J_{Cd} with flow rate of 120 cm³/min indicated the least thickness of aqueous film boundary layer at this value. Further at lower flow rate, the flow of liquid is laminar

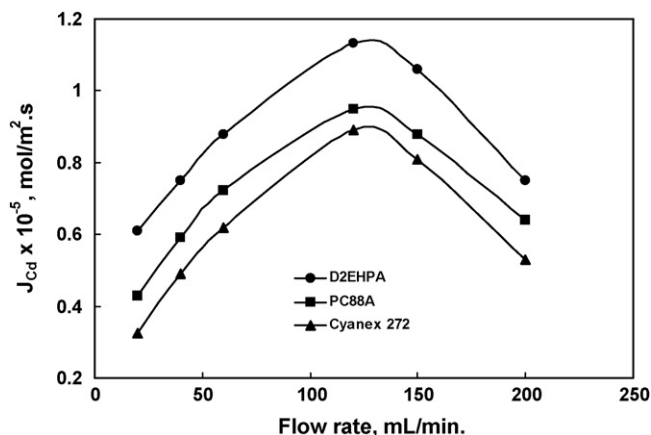


Fig. 6. Effect of flow rate on J_{Cd} . Experimental conditions: feed solution pH 4.5, 500 mol/m³ extractant in membrane phase, 900 mol/m³ H₂SO₄ in strip solution.

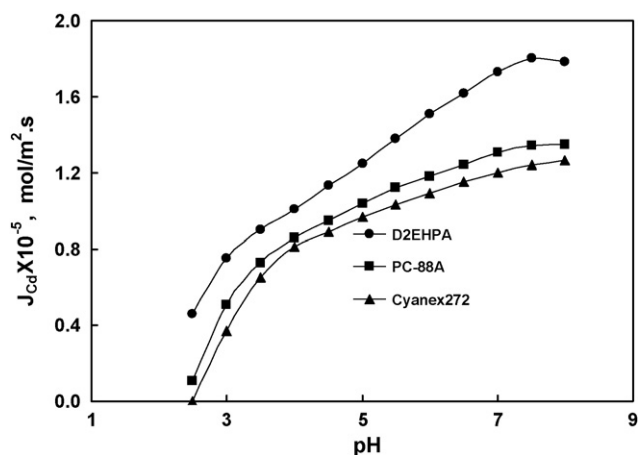


Fig. 7. Effect of pH on J_{Cd} . Experimental conditions: 500 mol/m³ extractant in membrane phase, 900 mol/m³ H₂SO₄ in strip solution, 120 mL/min flow rate.

while some turbulence gets associated with the flow of fluid leading to reduced aqueous boundary layer at higher flow rate. Also it is known that the residence time of cadmium ion at the feed solution–membrane interface is inversely proportional to the flow rate. These factors are presumably responsible for the decrease of J_{Cd} value at higher flow rate.

4.2.3. Effect of pH

The extraction of cadmium from sulphate media containing 1.014 mol/m³ of Cd was studied in the pH range 2.5–8.0 at constant extractant concentration (500 mol/m³) and flow rate (120 cm³/min) and the results are shown in Fig. 7. It was found that the J_{Cd} increased progressively with increase of pH up to 7.5 irrespective of the extractant and thereafter decreased or remained practically same on further increase of pH. However, the extent of increase of J_{Cd} was relatively more (0.46×10^{-5} to 1.805×10^{-5} mol/m² s) in case of D2EHPA than other extractants with increase of pH from 2.5 to 7.5. There was practically no extraction with Cyanex 272 at pH ~3.0. With increasing pH in the range 2.5–7.5, the dissociation of the extractants increases at the feed–solution membrane interface, which leads to increased formation of Cd–extractant complex and increase of J_{Cd} . Further increase of pH leads to marginal change in the concentration of dissociated extractants and hence a plateau was obtained at pH beyond 7.5.

4.2.4. Effect of the carrier concentrations

The effect of the carrier concentration (D2EHPA, PC-88A and Cyanex 272) in the membrane phase on the cadmium flux was studied in the range 50–1000 mol/m³. The Cd concentration and pH of the feed solution were kept constant at 1.014 mol/m³ and 7.5, respectively. Fig. 8 shows the relationship of J_{Cd} and extractant concentration in its dimeric form. The cadmium flux increased with increase of [extractant] up to ~600 mol/m³ ([HL]₂ = 300 mol/m³) but remained unaffected on further increase of extractant concentration. In accordance with Eq. (8), an increase of [extractant] increased the formation of Cd–extractant complex at the feed side–membrane interface. Moreover at lower [extractant], the interface was not saturated by the extractant and hence the flux increased with increase of [extractant]. The plateau region obtained at higher concentration of extractant (>600 mol/m³) is presumably due to the combined effect of saturation of feed–membrane interface with the complex and viscosity of the membrane phase.

The plots of time dependent percentage extraction of cadmium under the above set of conditions using different extractants (Fig. 9) revealed that D2EHPA is most effective among all and also the extraction of cadmium is highest with least extraction time. The

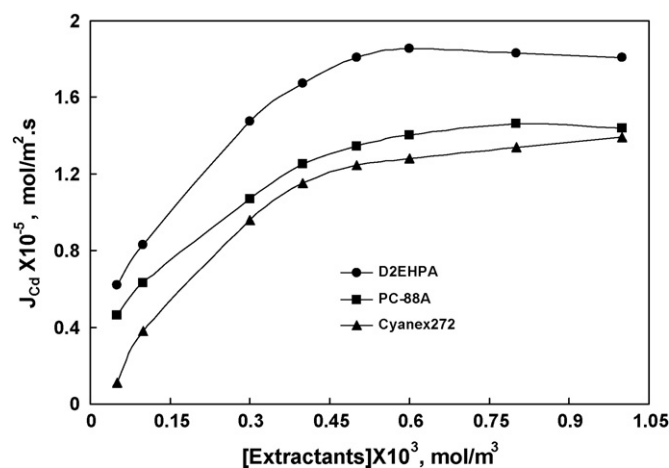


Fig. 8. Effect of [extractant] on J_{Cd} . Experimental conditions: pH of feed solution 7.5, 900 mol/m³ H₂SO₄ in strip solution, 120 mL/min flow rate.

percentage extraction of cadmium was found to decrease in the order D2EHPA > PC-88A > Cyanex 272. Same observation was also obtained for extraction of cadmium from sulphate solution using TOPS-99 (D2EHPA), PC-88A and Cyanex 272 by solvent extraction technique [29]. The percentage extraction increased from 4.3% to 85%, 0.5% to 83.4% and 1% to 82.2% with D2EHPA, PC-88A and Cyanex 272, respectively with increase of extractant concentration from 0.01 to 0.04 M and D2EHPA was found to be the efficient extractant than other two.

4.2.5. Effect of the acid concentration in strip solution

The stripping of cadmium complex from the membrane interface is an important step for effective use of SLM processes. Stripping reaction with respect to the Cd–extractant in the presence of an acid at membrane–strip side interface is very fast and the stripping kinetics was studied with different sulphuric acid concentration in the range 90–1800 mol/m³. The pH of feed solution, extractant concentration in the membrane phase and flow rate were kept constant at 7.5, 600 mol/m³ and 120 cm³/min, respectively. The variation of cadmium flux with acid concentration in strip solution (Fig. 10) showed an increasing trend of flux with increase of H₂SO₄ concentration up to 900 mol/m³ irrespective of extractant. With higher acid concentration a plateau was obtained indicating an acid concentration of ~900 mol/m³ is sufficient to strip out total cadmium from the membrane phase.

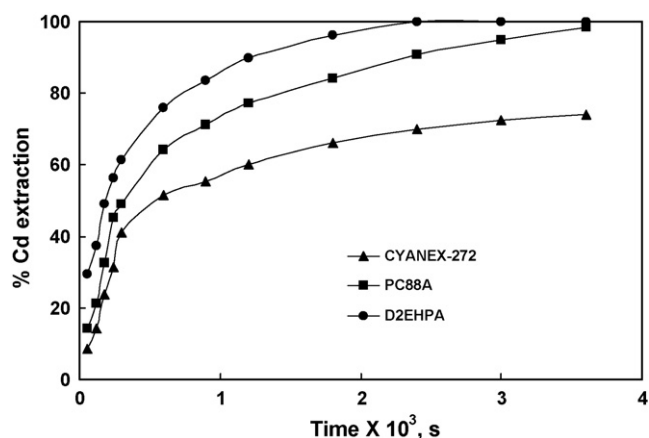


Fig. 9. Percentage extraction of Cd at different times with D2EHPA, PC-88A and Cyanex 272. Experimental conditions: pH 7.5, 600 mol/m³ extractant in membrane phase, 900 mol/m³ H₂SO₄ in strip solution, 120 mL/min flow rate.

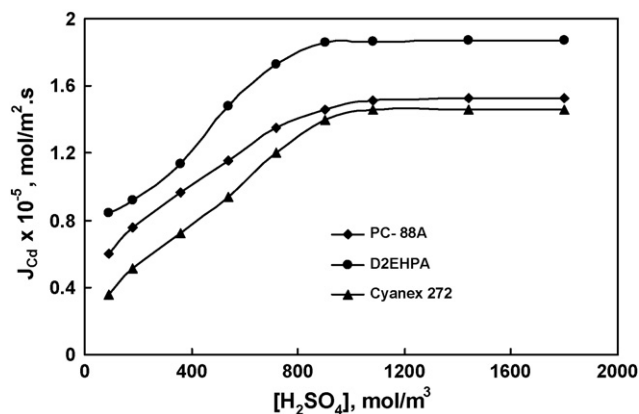


Fig. 10. Effect of strip solution concentration on J_{Cd} . Experimental conditions: pH of feed solution 7.5, 600 mol/m³ extractant in membrane phase, flow rate: 120 mL/min.

4.2.6. Effect of Cd ion concentration in feed solution

The concentration of Cd in the feed solution is important factor which strongly influence its extraction. The effect of Cd concentration on J_{Cd} was studied in the range 0.44–10.67 mol/m³ at pH 7.5 using all three extractants as the mobile carrier and the results were shown in Fig. 11. It was observed that the J_{Cd} increased sharply with the increase of Cd up to ~2.0 mol/m³ and thereafter increased rather slowly up to ~8.94 mol/m³. Within this range of [Cd] in feed solution the availability of Cd at the feed solution–membrane interface increased with increase of Cd concentration. As such the interfacial chemical reaction becomes faster, which led to increase in J_{Cd} according to Eq. (8). With further increase in Cd concentration, the membrane phase tends to get saturated with Cd–extractant complex leading to a plateau region of J_{Cd} at [Cd] above 8.94 mol/m³.

4.2.7. FT-IR spectra of cadmium complex

The formation of cadmium complexes with different extractants through phosphorous-hydroxyl group was evident from the FT-IR spectral studies. Fig. 12 shows the FT-IR spectra of carriers and their complexes after reaction with Cd. It was observed that the carrier as well as its corresponding Cd complex exhibits the characteristics peaks at 2970–2860 and 1460 cm⁻¹ for C–H stretching and bending vibrations of –CH₃ moiety, respectively [37,38]. The absence of low intensity characteristic peaks for P–(OH) in the region 2750–2550 cm⁻¹ is indicative of formation of Cd complexes. The shift of –OH deformation bands (~30 cm⁻¹) with reduced intensity with Cd–extractant complexes provides further evidence

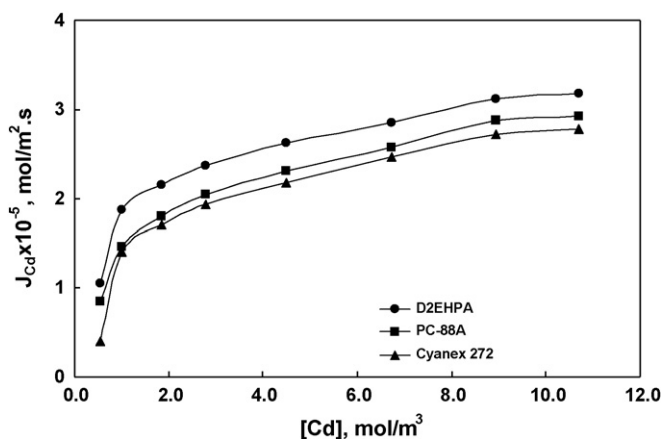


Fig. 11. Effect of Cd concentration in feed solution on J_{Cd} . Experimental conditions: pH of feed solution 7.5, 600 mol/m³ extractant in membrane phase, 120 mL/min flow rate.

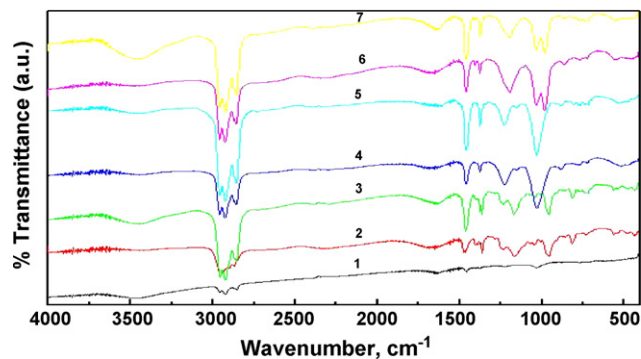


Fig. 12. FT-IR study of D2EHPA, PC-88A, Cyanex 272, Cd-D2EHPA, Cd-PC-88A and Cd-Cyanex 272.

in favour of complex formation through phosphorous-hydroxyl group. Marginal shift of characteristic band for P=O, appeared in the range 1140–1200 cm⁻¹, towards higher frequency also indicates the participation of P=O oxygen in complex formation through coordination. The remaining peaks are more or less same in both the cases.

5. Conclusions

The extraction of cadmium by supported liquid membrane using phosphoric acid derivative has been studied and following conclusions may be drawn from the above studies.

- The equilibrium studies indicated an increase of percentage extraction of cadmium with increase of equilibrium pH from 1.47 to 3.08, 1.52 to 3.28 and from 1.48 to 3.22, for D2EHPA, PC-88A and Cyanex 272, respectively. The percentage extraction with D2EHPA was maximum (65.61).
- The percentage extraction of Cd increased with increase of [D2EHPA] up to 0.5 M, but with PC-88A and Cyanex 272, the percentage extraction of Cd increased even up to 1.0 M.
- The slope values of log D versus pH plots for D2EHPA, PC-88A and Cyanex 272 were found in between 1.55 and 2.28 indicated the release of two moles of H⁺ from the extractant for extraction of a mole of cadmium ion. The slopes of log D versus log [extractant] were 1.68 for both D2EHPA and PC-88A and 1.52 for Cyanex 272 indicated the association of two moles of the extractant in the extracted species.
- The diffusion coefficient of Cd–D2EHPA, Cd–PC-88A and Cd–Cyanex 272 through the membrane phase was found to be 2.53×10^{-9} , 5.435×10^{-9} and 11.22×10^{-9} m² s⁻¹, respectively.
- J_{Cd} increased from 0.61×10^{-5} to 1.132×10^{-5} mol/m² s, 0.43×10^{-5} to 0.95×10^{-5} mol/m² s and from 0.32×10^{-5} to 0.89×10^{-5} mol/m² s for D2EHPA, PC-88A and Cyanex 272, respectively with the increase of flow rate from 20 to 120 cm³/min and thereafter decreased on further increase of flow rate.
- J_{Cd} increased with increase of feed solution pH up to 7.5 for all the three extractants used.
- With increase of extractant concentration, J_{Cd} increased up to 600 mol/m³ and with further increase of extractant concentration there was marginal increase of the cadmium flux.
- The optimum conditions for maximum cadmium flux were: pH 7.5; 600 mol/m³ [D2EHPA], 600 mol/m³ [PC-88A], 800 mol/m³ [Cyanex 272] and 900 mol/m³ H₂SO₄.
- The percentage cadmium extraction with these three extractants follows the order D2EHPA > PC-88A > Cyanex 272.

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