

SEPARATIONS

E-Waste Management via Liquid Emulsion Membrane (LEM) Process: Enrichment of Cd(II) from Lean Solution**Mangesh S. Talekar and Vijaykumar. V. Mahajani****Chemical Engineering Department, Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai-400019, India*

E-waste management via liquid emulsion membrane (LEM) process for the extraction and enrichment of cadmium(II) has been studied using di-2-ethylhexyl phosphoric acid (D2EHPA) dissolved in *n*-dodecane as carrier and methane sulfonic acid (MSA) as a strip phase. The complexation stoichiometric coefficient (n) and equilibrium constant (K_{ex}) were determined by carrying out conventional liquid–liquid extraction studies. The factorial design method was used to see the importance of parameters. Emulsion preparation parameters such as carrier concentration, surfactant concentration, and internal strip phase (MSA) concentration were determined to get maximum extraction and enrichment. The influence of operating process parameters on the performance of LEM process, i.e., residence time, speed of agitation, and treat ratio, has been studied. A realistic simple model to aid the process design of LEM process has been developed.

1. Introduction

E-waste management is very important in the field of electronics. The main focus is not only to treat the solid waste generated for discharge but also to recover valuable elements for recycling. In this context, the recovery and recycle of cadmium assumes significant importance because this toxic element (permissible limit in drinking water as per WHO is 5 ppb) is used in batteries (Ni–Cd). The spent Ni–Cd batteries discarded as waste to the environment form one of the important sources of Cd and Ni.

The processes envisaged for the recovery of these metals consist of the leaching of spent waste with acid followed by the concentration of the element via conventional extraction or ion exchange processes. The concentrate is then used to recover the element via electrowinning.

Methane sulfonic acid (MSA) is ideally suitable for the extraction of metals. Many metal salts of MSA exhibit very high solubility in aqueous solutions. For instance, the solubility of an anhydrous salt of MSA, $\text{Cd}(\text{CH}_3\text{SO}_3)_2$, is 150 g/100 g of water at 293 K.¹ Furthermore, MSA is a green acid in a sense that it is biodegradable. For electroplating applications, it is reported to be better than sulfuric acid.¹ Therefore, the application of MSA is expected to grow in the field of E-waste management as an extracting agent for metallic elements, from solid waste. Keeping the above potential in mind, it was thought desirable to concentrate on treatment process involving MSA. The dilute acidic stream used for leaching is then concentrated by conventional liquid–liquid extraction followed by stripping.

The process intensification in the conventional enrichment system is achieved via the liquid emulsion membrane (LEM) system originally developed by Li in 1965.²

Several studies have been published concerning the recovery and separation of cadmium(II). Reddy et al.³ have studied the separation of cadmium(II) from a mixture of cadmium(II), cobalt(II), and nickel(II) sulfate leach liquor of spent Ni–Cd

batteries using phosphorus-based extractants. Among all phosphorus-based extractants, they found that cyanex 301 gives the selective separation of cadmium(II). Juang et al.⁴ used solid supported liquid membrane for the separation of Zn(II) and Cd(II) from sulfate media using di-2-ethylhexyl phosphoric acid (D2EHPA) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A), and they found that under comparable conditions, PC-88A revealed superior separation ability. Rodriguez et al.⁵ have studied the extraction of cadmium from chloride solution using solid supported membrane using cyanex 923 as a carrier. Szejner and Marmur⁶ have studied the removal of cadmium(II) ions by LEM, using D2EHPA as a carrier and HNO_3 as a strippant.

There is practically no published information available on the enrichment of Cd from a dilute solution of MSA, used for the leaching of Cd. Also, there is practically no information available in the published literature on the stripping of Cd by MSA. The spent Ni–Cd battery when subjected to acid leaching will contain respective salts of Ni and Cd in the solution. Knowledge with respect to the behavior of individual elements is desirable to develop an enrichment process from such a leaching solution. Kulkarni et al.⁷ have studied the enrichment of Ni using MSA as a strippant. Therefore, we have focused our attention on the enrichment of Cd from a Cd–MSA solution by the use of the LEM technique as a process intensification tool. The easily available D2EHPA was used as a shuttle vehicle to transport Cd from a membrane–salt solution interface to a membrane–stripping interface. The conventional extraction studies were performed to establish the stoichiometric coefficient for the complexation of cadmium with D2EHPA. The pH level has a pronounced effect on the extraction of metallic elements. Some experiments have been performed to ascertain this effect.

2. Experimental Section

2.1. Chemicals. Methane sulfonic acid (MSA) was obtained from s.d. fine chemicals (P) Ltd., Mumbai, India, and di-2-ethylhexyl phosphoric acid (D2EHPA) was obtained from Sisco Research Laboratories (P) Ltd., Mumbai, India. Surfactant

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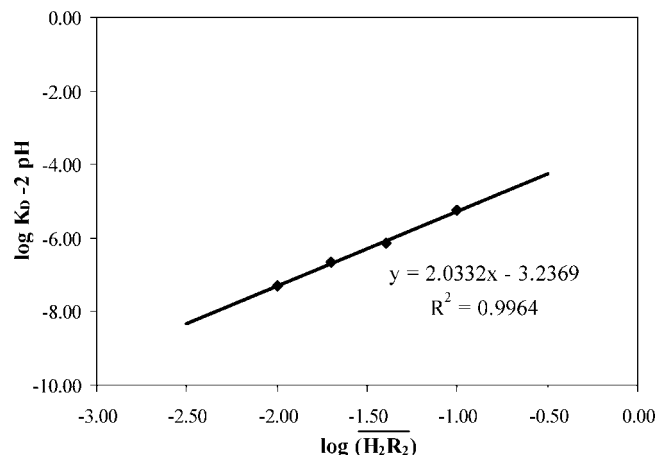


Figure 1. Plot of $\log K_D - 2 \text{ pH}$ vs $\log [(H_2R)_2]$ (diluent = *n*-dodecane; $(A_{\text{ex},0}) = 0.89 \times 10^{-3} \text{ kmol} \cdot \text{m}^{-3}$; $T = 303 \text{ K}$; equilibrium time = 3 h).

“Monemul-80” (sorbitan mono-oleate) was obtained as a gift sample from Mohini Organics (P) Ltd., Mumbai, India. D2EHPA and Monemul-80 were used as such without any further purification. All other reagents were obtained from local suppliers and used as is, without further purification.

A stock solution of cadmium(II) was prepared by dissolving cadmium hydroxide $\text{Cd}(\text{OH})_2$ in $0.1 \text{ kmol} \cdot \text{m}^{-3}$ MSA. Cadmium hydroxide was prepared by the precipitation of cadmium salt ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$) with sodium hydroxide followed by water washing and drying. The pH level of the aqueous phase was adjusted using sodium hydroxide. The standard cadmium(II) solution was procured from the Merck Co. (Germany). We used this solution containing $10\,000 \text{ mg} \cdot \text{L}^{-1}$ Cd for calibration purposes.

2.2. Apparatus and Procedure. The emulsion was prepared by emulsifying an aqueous acidic solution of strip phase with an organic phase. The organic phase (membrane phase) consisted of a surfactant monemul-80, a carrier reagent D2EHPA, water suppressing agent, cyclohexanone, and an organic diluent, *n*-dodecane. The internal strip phase (MSA) was added dropwise into a glass reactor containing the organic phase.

A predetermined volume of 1:1 was maintained for the organic phase to the internal strip phase. The reactor contents were stirred at 3000 rpm for 10 min with a six-blade turbine impeller of 30 mm diameter in a baffled glass vessel of 70 mm diameter where a stable milky-white emulsion was obtained, with the mean diameter of the encapsulated droplets varying from 1 to $5 \mu\text{m}$ as measured by a Coulter particle size analyzer (model LS 230). The emulsion was dispersed in the feed phase containing cadmium(II) from which cadmium(II) was extracted. It was possible to neatly separate the emulsion phase from the feed phase quickly in a separator before the emulsion started breaking. Emulsion stability was tested by observing the phase separation over time. The extraction was performed in the same reactor at a speed of 350 rpm.

An aqueous phase sample was taken after separating the emulsion from the aqueous phase in a separating funnel. The emulsion was then broken down by heating it to about 353 K for the analysis of the strip phase.

The conventional extraction equilibrium experiments were carried out by mixing 20 mL of organic phase and 20 mL of aqueous phase and then agitating by magnetic stirrer for 3 h. It was observed that this time was adequate for reaching equilibrium. The samples were analyzed to find the equilibrium distribution coefficient (K_D). Liquid–liquid extraction studies were carried out at different extractant concentrations to obtain

Table 1. Effect of Temperature on Distribution Coefficient (K_D)

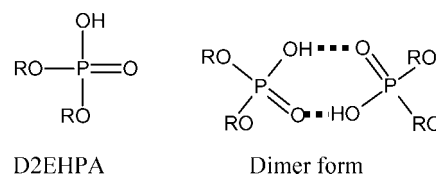
$T \text{ (K)}$	distribution coefficient (K_D)
293	3.41
303	2.85
313	2.71
318	2.42

the stoichiometric constant (n) and equilibrium constant (K_{ex}). All experiments were carried out at $303 \pm 1 \text{ K}$, and the reproducibility was checked at least twice.

2.3. Analytical. Cadmium(II) concentration in aqueous and strip phases was determined with the help of a high-performance ion chromatograph (DIONEX, USA) equipped with a GS50 gradient pump, ion-pac CS2 (2 mm) column, post column reactor and a AD25 absorbance detector operating at a wavelength of 520 nm. The strip phase droplet size and emulsion globule size were measured before and after extraction by a Coulter LS 230 laser particle size analyzer, where xylene was used as a background phase for the strip phase droplet size measurement and distilled water as a background phase for the emulsion globule size measurement. Cadmium(II) retained in organic phase was calculated by mass balance. The analytical techniques were validated from time to time, and the observed results were reproduced with an error of less than $\pm 3\%$.

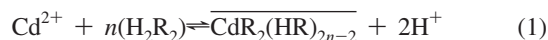
3. Results and Discussion

3.1. Extraction Equilibria. In order to comprehend extraction process by LEM, one must have an idea of the stoichiometry of complexation and the effect of temperature on extraction. The extractant used is D2EHPA. It is known to exist in dimer form in nonpolar solvents, such as the *n*-dodecane used in this study. The respective chemical structures are depicted below,



where R = 2-ethylhexyl group.

The extraction of cadmium(II) by D2EHPA can be expressed as follows:



The over bar refers to the organic phase. The structure of the cadmium complex is $(\text{R}_2\text{PO}_4)_2\text{Cd}$.

The extraction equilibrium constant K_{ex} is expressed as

$$K_{\text{ex}} = \frac{[\overline{\text{CdR}_2(\text{HR})_{2n-2}}] \times [\text{H}^+]^2}{[\text{Cd}^{2+}] \times [(\text{H}_2\text{R}_2)]^n} \quad (2)$$

The distribution coefficient of cadmium(II) K_D is defined as follows:

$$K_D = \frac{[\overline{\text{CdR}_2(\text{HR})_{2n-2}}]}{[\text{Cd}^{2+}]} \quad (3)$$

From the above expressions, after appropriate rearrangement and definitions, we have

$$\log K_D - 2\text{pH} = \log K_{\text{ex}} + n \log [(\text{H}_2\text{R}_2)] \quad (4)$$

3.1.1. Complexation Stoichiometry. The extraction equilibrium constant K_{ex} and the complexation stoichiometry n can be calculated using eq 4, by observing K_D values at different

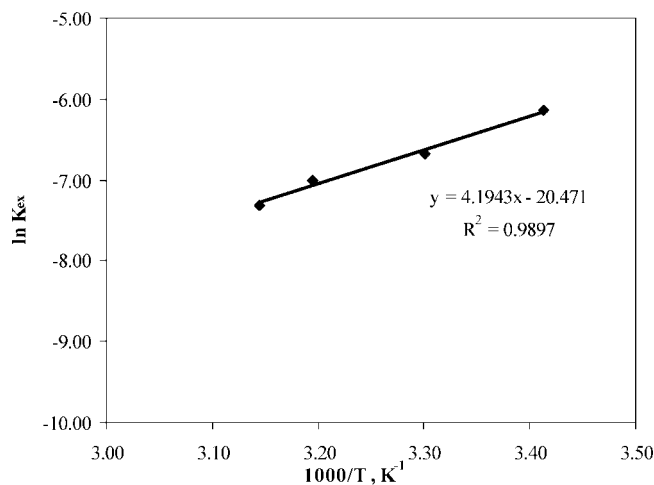


Figure 2. Plot of $\ln K_{\text{ex}}$ vs $1/T$ (diluent = *n*-dodecane; $(B_o) = 0.09 \text{ kmol} \cdot \text{m}^{-3}$; $(A_{\text{ex},0}) = 0.89 \times 10^{-3} \text{ kmol} \cdot \text{m}^{-3}$; equilibrium time = 3 h).

Table 2. Effect of pH on Extraction

initial pH	equilibrium pH	% extraction of cadmium(II)
1.5	1.25	3.5
3.5	2.7	59
4	2.9	61
5	2.93	67

concentrations of D2EHPA (HR) as an independent variable, as shown in Figure 1. From the values of n and K_{ex} obtained experimentally from the least-squares fit technique, we have $n = 2.03$ which can be deemed as $n = 2$ and $K_{\text{ex}} = 5.80 \times 10^{-4}$. The K_{ex} value observed by us is slightly higher than earlier reported by Juang et al.⁴ probably because the diluent used in our case is *n*-dodecane instead of kerosene.

3.1.2. Temperature. The distribution coefficient K_D for the extraction of cadmium(II) with $0.09 \text{ kmol} \cdot \text{m}^{-3}$ in *n*-dodecane was found to decrease with increase in temperature, in the range of 293–318 K, as depicted in Table 1. It is thus possible to infer the K_{ex} extraction equilibrium constant from eq 4. There is a relationship between K_{ex} and the heat and entropy of the complexation equilibrium, as given by the Van't Hoff equation as follows:

$$\ln K_{\text{ex}} = \left[\left(\frac{-\Delta_r H^\circ}{RT} \right) + \left(\frac{\Delta_r S^\circ}{R} \right) \right] \quad (5)$$

A plot of $\ln K_{\text{ex}}$ against $1/T$, as shown in Figure 2, gave the heat of reaction (change of enthalpy $\Delta_r H^\circ$) = $-34.87 \text{ kJ} \cdot \text{mol}^{-1}$, and the entropy of reaction is $(\Delta_r S^\circ) = -0.170 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. The $\Delta_r H^\circ$ negative means an exothermic reaction, and hence, K_{ex} will be higher at a lower temperature. The interaction between Cd and D2EHPA forming a complex results in a more orderly structure, thereby resulting in a negative change of entropy.⁸

3.1.3. Effect of pH. Some equilibrium experiments were carried out at a constant extractant concentration of $0.09 \text{ kmol} \cdot \text{m}^{-3}$ to see the effect of aqueous phase pH, varied in the range of 1.5–5 on the extraction of cadmium(II) depicted in Table 2. The change in the initial pH of the aqueous phase was measured once the equilibrium was attained. The acid extractant undergoes the dissociation process at the aqueous–organic interface, releasing the hydrogen ions to the aqueous phase. This fact causes the reduction of its equilibrium pH. Basualto et al.⁹ have also noted a similar effect in their studies.

3.2. LEM Extraction of Cadmium(II). The extraction of cadmium(II) from a dilute MSA solution by LEM is a series of

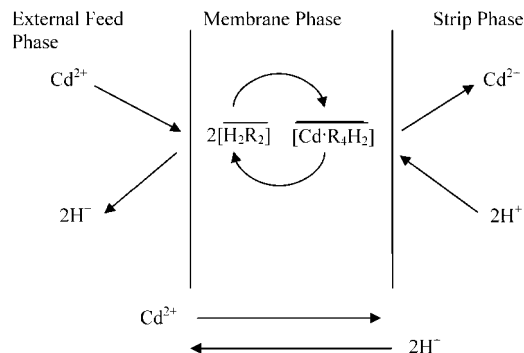


Figure 3. Mechanism of facilitated transport of cadmium(II).

Table 3. 2³ Factorial Design for the Extraction of Cadmium

variable	low level (−1)	high level (+1)
surfactant concentration, $\text{kmol} \cdot \text{m}^{-3}$ (χ_1)	0.02	0.07
D2EHPA concentration, $\text{kmol} \cdot \text{m}^{-3}$ (χ_2)	0.02	0.09
strip phase MSA concentration, $\text{kmol} \cdot \text{m}^{-3}$ (χ_3)	1	2

various transport processes, as shown in Figure 3, namely: (i) mass transfer of cadmium(II) ions from bulk of aqueous feed phase to the external interface of the emulsion globule; (ii) interfacial complexation reaction between Cd(II) ions and D2EHPA at the external interface; (iii) diffusion of D2EHPA–Cd(II) complex into emulsion globule; and (iv) stripping reaction between D2EHPA–Cd(II) complex and internal MSA at the interface of the stripping phase.

The strip phase encapsulated in organic membrane, being small in size ($<5 \mu\text{m}$), behaves as a rigid sphere. The strength of the acid in the strip phase played an important role during extraction. The major parameter influencing the extraction was the intensity of turbulence (speed of agitation) in the external phase. An increase in the level of agitation in the external (phase 3) phase resulted in a decrease in the mass transfer resistance, in the feed phase. However, it also resulted in the breakage of the membrane (phase 2) phase, thereby reducing overall efficiency of the extraction. Thus, there is an optimum speed of agitation to balance the two opposing effects. The other parameters affecting the rate and extent of extraction are the concentration of surfactant used in the organic phase and the volume ratio of the emulsion phase to aqueous phase (V_o/V_1). In order to have better understanding of dynamics of LEM technique, these parameters were studied.

The performance of the LEM extraction technique was measured with the help of the following terms: fractional extraction (Ex), enrichment (En), treat ratio (TR), and % swelling (Sw), defined elsewhere.¹⁰

The success of the LEM process depends upon the stability of the emulsion. If the emulsion is highly stable, the demulsification to separate the strip phase becomes difficult. Therefore, the process parameters in emulsion formulation and extraction need to be carefully selected.

3.3. Emulsion Preparation Parametric Study. **3.3.1. Factorial Design Study.** Experiments were designed using factorial design technique to see the main and interaction effects of the factors on the emulsion preparation. The effect of variable is the change in response produced by varying the level of the factor. When the effect of a factor depends on the level of another factor, the two factors are said to interact. In the present investigation, three variables at two levels (Table 3) were taken into consideration, based on the previous work experience on

Table 4. Experiment Design and Extraction, Enrichment, and Swelling of Cadmium

experiment	χ_1	χ_2	χ_3	$y_{\%Ex}$	y_{En}	$y_{\%sw}$
1	-1	-1	-1	35.2	4.3	2
2	+1	-1	-1	42.59	4.98	20
3	-1	+1	-1	75	6.4	4
4	+1	+1	-1	85.76	5.8	25
5	-1	-1	+1	30.2	2.9	10
6	+1	-1	+1	40.1	3.97	25
7	-1	+1	+1	65.3	4.8	15
8	+1	+1	+1	72.2	5.1	30

LEM systems, namely, surfactant concentration (χ_1), carrier (D2EHPA) concentration (χ_2), and strip phase MSA concentration (χ_3) to evaluate their main and interaction effects on the percent extraction, enrichment, and percent swelling of the emulsion. The 2^3 full factorial unreplicated experiments were carried out, and the results are tabulated in Table 4. Results were analyzed using Yates' technique described by Walpole and Myers.¹¹

Statistical models were developed of the following form for percent extraction, enrichment, and percent swelling.

$$y = b_0 + b_1\chi_1 + b_2\chi_2 + b_3\chi_3 + b_{12}\chi_{12} + b_{13}\chi_{13} + b_{23}\chi_{23} + b_{123}\chi_{123}$$

where y is the response, i.e., % extraction, enrichment, and % swelling; χ_1, χ_2, χ_3 are coded variables (surfactant, carrier, and strip phase concentration) from +1 to -1; $\chi_{12}, \chi_{13}, \chi_{23}, \chi_{123}$ are coded variables of the interaction parameters, χ_{12} means interaction between χ_1 and χ_2 , and so on; and b_0, b_1, b_2 , etc. are the coefficients of equation determined using Yates' technique.

For percent extraction, the model formed using the effects of the variable significant at the 95% confidence level ($F_{(0.95,1,8)} = 5.32$) is given below,

$$y_{\%Ex} = 55.793 + 4.369\chi_1 + 18.771\chi_2 - 3.84375\chi_3 - 1.971\chi_{23}$$

Similarly, for enrichment and percent swelling, the model equations with their significant effects at the 95% confidence level are

$$y_{En} = 4.781 + 0.181\chi_1 + 0.743\chi_2 - 0.589\chi_3 - 0.256\chi_{12} + 0.161\chi_{13}$$

$$y_{\%SW} = 16.375 + 8.625\chi_1 + 2.125\chi_2 + 3.625\chi_3 - 1.125\chi_{13}$$

Thus, from coefficients of model equations we can infer that extraction for cadmium(II) increases with an increase in surfactant and carrier (D2EHPA) concentrations in the range studied (positive value of coefficient) and it decreases (negative value of coefficient) with an increase in strip phase MSA concentration in the range of 1 to 2 kmol m^{-3} . Similarly, the percent swelling of the emulsion increased with an increase in the surfactant, carrier (D2EHPA), and strip phase MSA concentrations, which is in line with the positive values of the coefficients.

Furthermore, to have better insight into the emulsion preparation studies, some experiments were carried out as follows.

a. Organic Membrane Phase (Diluent). The selection of diluent is very important in LEM technique because of membrane stability. The organic diluent used to make membrane should have reasonably good viscosity, as otherwise, viscosity improvers are required. Also, the diluent must satisfy safety, health, and environmental compliance requirements. The chemical oxygen demand imparted to the aqueous phase by the diluent must be as low as possible. We have found that *n*-dodecane meets these requirements adequately. Recently Kulkarni and

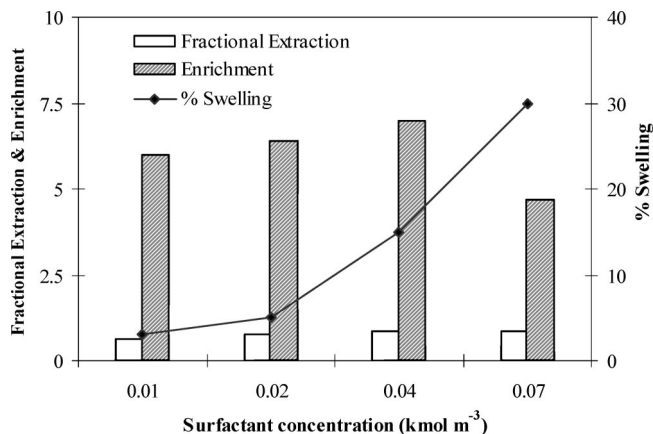


Figure 4. Effect of surfactant concentration (residence time = 5 min; speed of agitation = 350 rpm; TR = 1:10); $A_{ex,0} = 0.89 \times 10^{-3} \text{ kmol} \cdot \text{m}^{-3}$; $B_0 = 0.09 \text{ kmol} \cdot \text{m}^{-3}$; (M) = 1 $\text{kmol} \cdot \text{m}^{-3}$; (C) = 0.4 $\text{kmol} \cdot \text{m}^{-3}$; diluent = *n*-dodecane).

Mahajani¹² have used this diluent advantageously in the recovery of molybdenum. So, *n*-dodecane was selected as a diluent for the further study.

b. Surfactant Concentration. The surfactant (Monemul-80) was used to stabilize the w/o emulsion based on its hydrophilic–lyophobic balance value. Higher surfactant concentration resulted in higher emulsion stability but also increased swelling. The mechanism of water transport in LEM is via the diffusion of hydrated surfactant. The hydrophilic portion of the surfactant molecule picks up water at the aqueous feed phase–membrane phase interface and shuttles it through the membrane phase and becomes dehydrated by releasing water at the strip phase interface.¹³ With an increase in surfactant concentration, the process of hydration and dehydration is enhanced, leading to higher emulsion swelling. A higher concentration of surfactant increased emulsion swelling, and it adversely affected strip phase enrichment. To fix the surfactant concentration, which provides minimum swelling and membrane stability, experiments were carried out in the range of 0.01–0.07 $\text{kmol} \cdot \text{m}^{-3}$ depicted in Figure 4. It was observed that 0.04 kmol m^{-3} of surfactant concentration was a good tradeoff between two opposing effects.

c. Water Transport Suppressing Agent. The swelling phenomenon observed in LEM due to water transport explained above can be minimized if not eliminated by adding cyclohexanone as a water-repelling agent. The addition of cyclohexanone to the membrane phase alters the micellization mechanism such that surfactant molecules cover cyclohexanone over strip phase droplets during micellization. When cyclohexanone concentration is increased, micelle formation proceeds until reaching a fixed value, and any further increase in concentration tends to reverse encapsulation. Optimum concentration of the cyclohexanone¹⁰ is in the range of 0.3–0.4 $\text{kmol} \cdot \text{m}^{-3}$. Therefore, further studies were conducted with 0.4 $\text{kmol} \cdot \text{m}^{-3}$ of the cyclohexanone in the membrane phase.

d. Carrier Concentration. The carrier or extractant D2EHPA facilitates metal transport through the membrane phase by shuttling the complex formed with metal ion from the aqueous phase–membrane interface to the membrane–strip phase interface. The effect of carrier concentration on cadmium(II) transport was studied in the range of 0.02–0.12 $\text{kmol} \cdot \text{m}^{-3}$ of D2EHPA. Figure 5 shows the effect of carrier concentration on fractional extraction, enrichment, and percent swelling. It was observed that the extraction of cadmium(II) as well as enrichment increased with the increase in carrier concentration from 0.02 to 0.09 $\text{kmol} \cdot \text{m}^{-3}$. Furthermore, when the concentra-

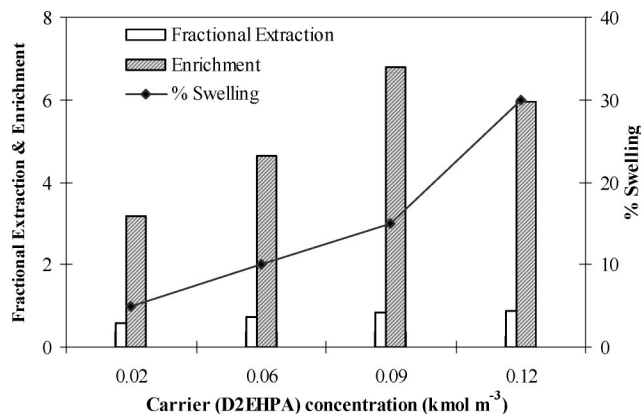


Figure 5. Effect of carrier (D2EHPA) concentration (residence time = 5 min; speed of agitation = 350 rpm; TR = 1:10; $A_{\text{ex},0} = 0.89 \times 10^{-3} \text{ kmol} \cdot \text{m}^{-3}$; $(S) = 0.04 \text{ kmol} \cdot \text{m}^{-3}$; $(M) = 1 \text{ kmol} \cdot \text{m}^{-3}$; $(C) = 0.4 \text{ kmol} \cdot \text{m}^{-3}$; diluent = *n*-dodecane).

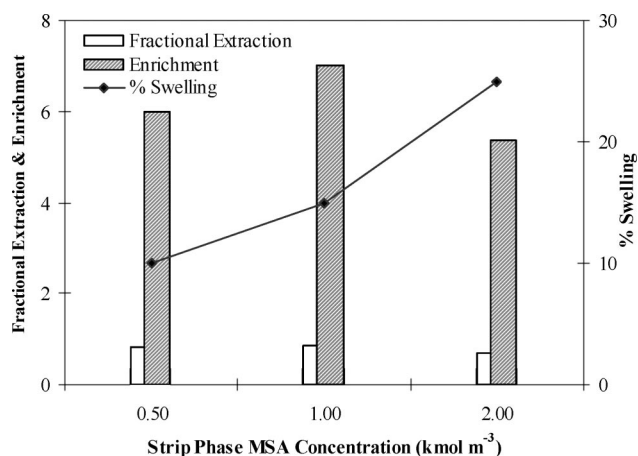


Figure 6. Effect of strip phase (MSA) concentration (residence time = 5 min; speed of agitation = 350 rpm; TR = 1:10; $A_{\text{ex},0} = 0.89 \times 10^{-3} \text{ kmol} \cdot \text{m}^{-3}$; $B_0 = 0.09 \text{ kmol} \cdot \text{m}^{-3}$; $(S) = 0.04 \text{ mol} \cdot \text{m}^{-3}$; $(C) = 0.4 \text{ kmol} \cdot \text{m}^{-3}$; diluent = *n*-dodecane).

tion was increased from 0.09 to $0.12 \text{ kmol} \cdot \text{m}^{-3}$, the extraction, enrichment and % swelling got affected. This observation is in line with Lee et al.¹⁴ Reduction in extraction may be because of the increased viscosity of the membrane phase, which reduces the diffusion coefficient of the complex in the membrane phase. So further, experiments were carried out at 0.09 kmol m^{-3} of D2EHPA concentration, unless otherwise stated.

e. Concentration of Stripping Agent. Figure 6 shows the effect of strip phase concentration studied in the range from 0.5 to $2 \text{ kmol} \cdot \text{m}^{-3}$ on the fractional extraction, enrichment of cadmium(II) and swelling of the emulsion. Swelling increased with the acidity of internal droplets, because of the increased osmotic pressure difference between feed and strip phase¹³. It was found that the extraction and final enrichment increased when the acid concentration was varied from 0.5 to 1 kmol m^{-3} . However, when the concentration of acid in the strip phase was varied from 1 to 2 kmol m^{-3} both extraction and enrichment were adversely affected. It was as a result of increase of swelling which caused more amount of water to permeate through the membrane causing the internal droplet to swell and coalesce. Thus, a concentration of 1 kmol m^{-3} was found to be appropriate.

Thus, for the LEM system under consideration, the following parameters have been fixed:

- diluent, *n*-dodecane,
- surfactant concentration, $0.04 \text{ kmol} \cdot \text{m}^{-3}$,

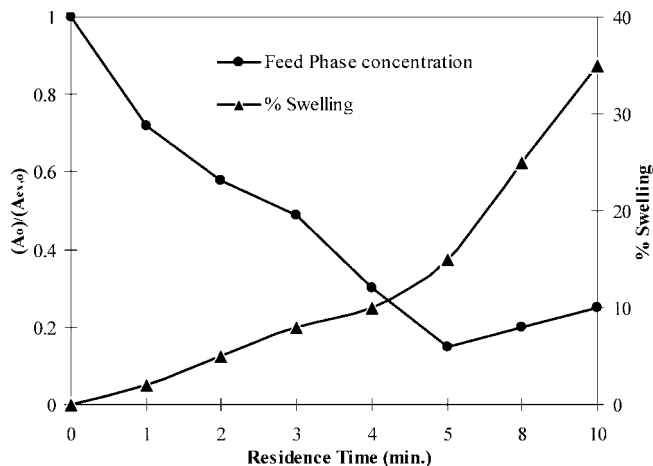


Figure 7. Residence time selection for the cadmium extraction with respect to swelling ($A_{\text{ex},0} = 0.89 \times 10^{-3} \text{ kmol} \cdot \text{m}^{-3}$; speed of agitation = 350 rpm; TR = 1:10).

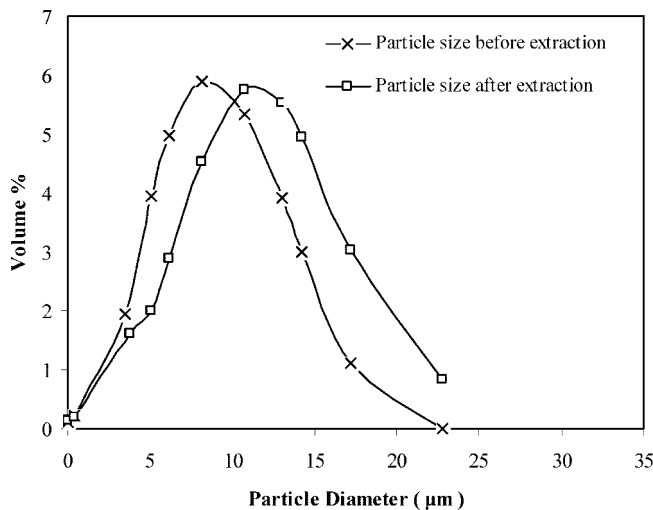


Figure 8. Swelling of the emulsion measured by Coulter particle size analyzer.

- water transport suppressing agent concentration, $0.4 \text{ kmol} \cdot \text{m}^{-3}$,
- carrier concentration, $0.09 \text{ kmol} \cdot \text{m}^{-3}$,
- strip phase MSA concentration, $1 \text{ kmol} \cdot \text{m}^{-3}$. The other process operating parameters such as residence time, speed of agitation, and treat ratio were studied with the above fixed parameters.

3.4. LEM Process Operating Parametric Study. The process parameters, which mainly affect the performance of LEM extraction process, are residence time, speed of agitation during extraction, and treat ratio.

3.4.1. Residence Time. The residence time (contact time) plays an important role for the LEM extraction. The longer residence time resulted in more transfer of water inside the internal phase, which caused the membrane to swell, and subsequently might have initiated the breakage of the emulsion phase. Figure 7 exhibits the fraction of original metal remaining in the aqueous feed phase and the swelling as a function of residence time. The swelling of the internal phase was also analyzed by Coulter particle size analyzer, as depicted in Figure 8. At the end of 5 min, the extraction observed was 85% and the resultant enrichment was 7. The higher residence time resulted in the higher concentration of cadmium(II) in the aqueous feed phase. This is due to leakage of cadmium(II) in

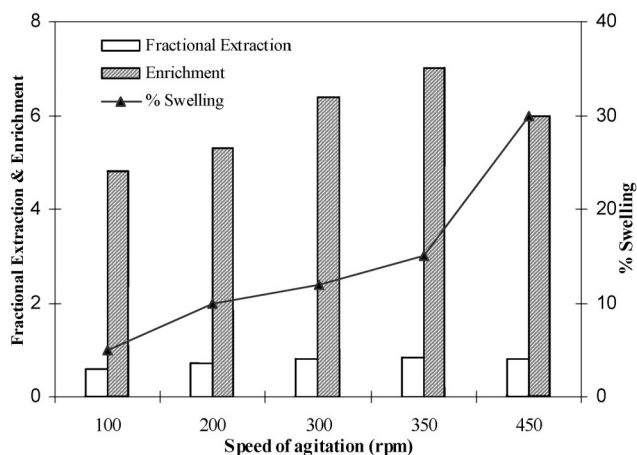


Figure 9. Effect of speed of agitation ($A_{ex,0} = 0.89 \times 10^{-3} \text{ kmol} \cdot \text{m}^{-3}$; residence time = 5 min; TR = 1:10).

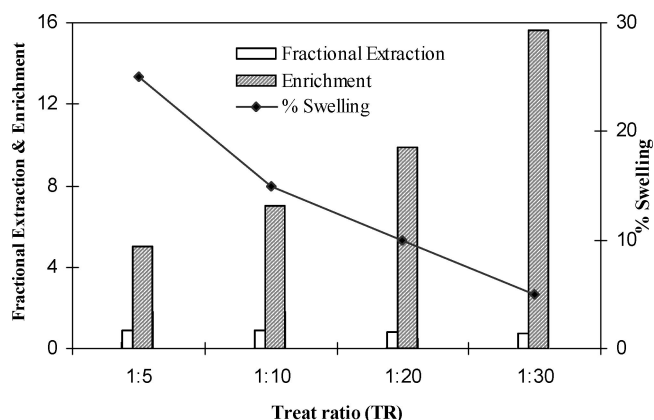


Figure 10. Effect of treat ratio (TR) ($A_{ex,0} = 0.89 \times 10^{-3} \text{ kmol} \cdot \text{m}^{-3}$; residence time = 5 min; speed of agitation = 350 rpm).

the aqueous feed phase owing to breakage of the internal strip phase. Therefore, we decided to carry out all the remaining LEM experiments using a residence time of 5 min.

3.4.2. Speed of Agitation. The effect of agitation speed was studied in the range of 100–450 rpm and is shown in Figure 9. While an increase in the level of agitation would increase interfacial area and the mass transfer coefficient, there is some level of agitation beyond which an increase in agitation level is likely to break the emulsion droplets, thereby reducing overall enrichment and extraction.

It was observed that increasing the speed of agitation from 100 to 350 rpm increased the extraction and enrichment. This was due to an increase in volumetric mass transfer coefficient, $k_{LA}a$, in the aqueous feed phase, but further increase in speed of agitation from 350 to 450 rpm resulted in the reduction in the extraction as well as enrichment due to an increase in swelling; similar behavior was reported by Kulkarni et al.¹⁵ and Thien et al.¹⁶ Thus, the 350 rpm speed of agitation was selected for further study.

3.4.3. Effect of Treat Ratio (TR). The treat ratio is defined as the ratio of emulsion phase volume (V_e) to aqueous phase volume (V_i). The treat ratio was varied by changing the amount of feed phase (V_i) added to the emulsion phase (V_e) by keeping the volume of the latter constant. The treat ratio was varied from 1:5 to 1:30, as shown in Figure 10. Fractional extraction of cadmium(II) decreased with decreasing the values of V_e/V_i . With a decrease in the treat ratio, the volumes of both carrier and stripping agent, i.e., the volume of the emulsion as a whole.

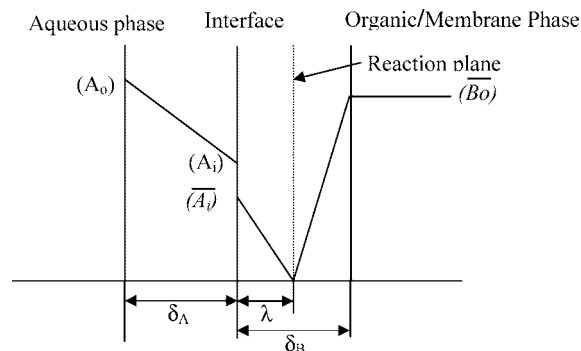


Figure 11. Mass transfer with instantaneous chemical reaction with aqueous side resistance (film theory).

Table 5. Overall Mass Transfer Coefficient ($K_{L,a}$) as a Function of Speed of Agitation (rpm)

speed of agitation (rpm)	$K_{L,a} \times 10^4 \text{ (s}^{-1}\text{)}$
100	1.05
200	1.26
300	1.41
350	1.50

decreased. Therefore, the surface area for the mass transfer owing to the formation of a large number of emulsion globules decreased. As a result, a lower degree of extraction was obtained, but the enrichment was greater. The lower treat ratio means less emulsion is required to extract cadmium(II), which is desired from a process point of view to have maximum enrichment with respect to feed phase cadmium(II). Thus there exists a trade-off between the fractional extraction and the enrichment of metal in the strip phase.

3.4.4. Model Development. Recently, Yadav and Mahajani¹⁰ have developed a very simple and realistic model to aid in the process design of extraction via LEM. LEM extraction is a process of mass transfer accompanied by chemical reaction. Doraiswamy and Sharma¹⁷ have presented a comprehensive account of the theoretical aspects of mass transfer with chemical reactions. The reactions involved at the interfaces in this process are expected to be instantaneous, and the overall rates of the reaction components are to be controlled by the diffusion of reaction components to the reaction plane in the aqueous phase,⁶ as depicted in Figure 11.

The following assumptions were made:

1. Completely mixed batch reactor under isothermal operation.
2. Diluent and carrier are insoluble in aqueous phase.
3. Constant carrier concentration (D2EHPA acts as a shuttle to transport Cd(II)).
4. The emulsion globules are uniform and have no internal circulation. The internal droplets are evenly distributed in the globules.
5. No coalescence of the emulsion globules.
6. Emulsion breakage and swelling are neglected.
7. The complexation reaction of Cd^{2+} is deemed to be an instantaneous reaction at the interface.

The following equations will hold, for



where A = Cd(II) ion, B = D2EHPA, Z = stoichiometric coefficient, and C = Cd–D2EHPA complex. Mass transfer in bulk of aqueous stream

$$R_{A,a} = \frac{-d(A_0)}{dt} = k_{L,a}a((A_0) - (A_i)) \quad (6)$$

An instantaneous complexation reaction in the diffusion film

of the membrane phase

$$R_A \underline{a} = k_{LBA} \times (\bar{A}_i) \left(1 + \frac{(\bar{B}_0) \times \bar{D}_B}{Z \times (\bar{A}_i) \times \bar{D}_A} \right) \quad (7)$$

Solving eq 6 along with eq 7 gives the value of (\bar{A}_i) explicitly

$$(\bar{A}_i) = \left(\frac{k_{LA} \underline{a} \times (A_0) - k_{LBA} \frac{(\bar{B}_0) \times \bar{D}_B}{Z \times \bar{D}_A}}{k_{LA} \underline{a} + k_{LBA} \times K_D} \right) \quad (8)$$

Substituting eq 8 in eq 6 and solving further we get

$$-\frac{d(A_0)}{dt} = \left[\frac{\left((A_0) \times K_D + \frac{(\bar{B}_0) \times \bar{D}_B}{Z \times \bar{D}_A} \right)}{\left(\frac{K_D}{k_{LA} \underline{a}} + \frac{1}{k_{LBA} \underline{a}} \right)} \right] \quad (9)$$

Integrating eq 9, we get

$$\ln \left(\frac{\alpha_1}{\alpha_2} \right) = K_L \underline{a} (t_2 - t_1) \quad (10)$$

where

$$K_L \underline{a} \quad (11)$$

$$\frac{1}{K_L \underline{a}} = \frac{1}{k_{LA} \underline{a}} + \frac{1}{K_D \times k_{LBA} \underline{a}} \quad (12)$$

and

$$\alpha_1 = \left((A_{0,1}) \times K_D + \frac{(\bar{B}_0) \times \bar{D}_B}{Z \times \bar{D}_A} \right) \quad (13)$$

$$\alpha_2 = \left((A_{0,2}) \times K_D + \frac{(\bar{B}_0) \times \bar{D}_B}{Z \times \bar{D}_A} \right) \quad (14)$$

3.4.5. Estimation of the Model Parameters. The stoichiometric coefficient (Z) is 2, estimated from the equilibrium studies. The reported⁴ diffusivity of cadmium(II) in aqueous phase is $6.5 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$, and the diffusivity of the D2EHPA in organic phase estimated to be $6.19 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ using the Wilke–Chang correlation.¹⁸ We do not have knowledge of k_{LBA} . However, k_{LA} might be predicted from the published literature.^{19,20}

In our experiments, we have observed that overall mass transfer coefficient ($K_L \underline{a}$) is the function of the intensity of turbulence (speed of agitation) as shown in Table 5.

Thus, after knowing the value of the slope (mass transfer coefficient) for a particular batch of reactions, one can easily predict the performance of the LEM system for cadmium(II) extraction. Figure 12 shows a plot of experimental data directly compared to a plot of eq 10.

4.0. Conclusions

The stoichiometric coefficient (n) and equilibrium constant (K_{ex}) for the complexation of cadmium(II) with D2EHPA in n -dodecane diluent were 2 and 5.80×10^{-4} , respectively.

2^3 full factorial designs were carried out for the emulsion preparation studies to have a better understanding of the process. On the basis of that, statistical models were developed.

Methane sulfonic acid (MSA) as a strip phase can be advantageously used for the extraction and enrichment of cadmium(II) from MSA solution. The concentration of surfactant, quantity of extractant, and internal phase acid concentration

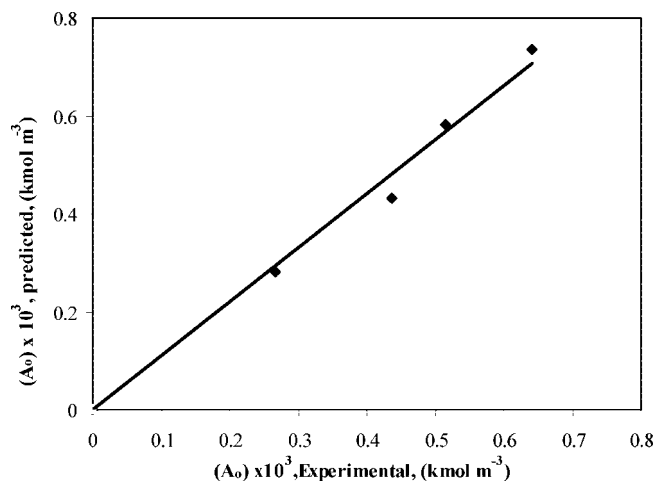


Figure 12. Plot of experimental data directly compared to a plot of eq 10.

were optimized in the present investigation to get maximum extraction and enrichment of cadmium(II).

It was found that an 85% extraction and 7 times enrichment of cadmium(II) was observed within 5 min of the residence time at 350 rpm and 1:10 treat ratio.

On the basis of these results, a simple realistic model has been developed which fits well with experimental findings to aid process design.

Acknowledgment

M.S.T. is thankful to the University Grants Commission, the Government of India, for awarding a Junior Research Fellowship during this investigation. The authors are grateful to Mohini Organics (P) Ltd., Mumbai, India, for the free sample of surfactant, Monemul-80.

Nomenclature

- $(A_{ex,0})$ = initial cadmium ion concentration in external feed phase ($\text{kmol} \cdot \text{m}^{-3}$)
- (A_0) = concentration of cadmium(II) ion in external feed phase at time t ($\text{kmol} \cdot \text{m}^{-3}$)
- $(A_i), (\bar{A}_i)$ = concentration of cadmium(II) ion in external feed phase and membrane phase interface ($\text{kmol} \cdot \text{m}^{-3}$)
- (\bar{B}_0) = carrier concentration in the organic phase ($\text{kmol} \cdot \text{m}^{-3}$)
- (C) = cyclohexanone concentration ($\text{kmol} \cdot \text{m}^{-3}$)
- (M) = concentration of MSA in internal phase ($\text{kmol} \cdot \text{m}^{-3}$)
- (S) = surfactant concentration ($\text{kmol} \cdot \text{m}^{-3}$)
- \bar{D}_A, \bar{D}_B = diffusivity of cadmium(II) ion and D2EHPA in organic phase ($\text{m}^2 \cdot \text{s}^{-1}$)
- En = enrichment
- Ex = fractional extraction
- T = temperature (K)
- $\Delta_r H^\circ$ = heat of reaction ($\text{kJ} \cdot \text{mol}^{-1}$)
- $\Delta_r S^\circ$ = entropy of reaction ($\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
- k_{LA}, k_{LB} = individual mass transfer coefficient (s^{-1})
- $K_L \underline{a}$ = overall mass transfer coefficient (s^{-1})
- K_{ex} = equilibrium constant in eq 2 unit, depends upon “ n ”
- K_D = distribution coefficient
- over bar = organic phase
- $R_A \underline{a}$ = volumetric rate of extraction of cadmium(II) ($\text{kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$)
- R = universal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
- Sw = swelling (%)
- $y_{\%Ex}, y_{\%En}, y_{\%SW}$ = the response; % extraction, enrichment, and %

swelling, respectively

χ_1, χ_2, χ_3 = coded variables (surfactant, carrier, and strip phase concentration) from +1 to -1

$\chi_{12}, \chi_{13}, \chi_{23}, \chi_{123}$ = coded variables of the interaction parameters from +1 to -1

b_0, b_1, b_2 , etc. = coefficients of equation

TR = treat ratio

V_i = volume of internal phase (m^3)

V_f = volume of feed phase (m^3)

V_e = Volume of emulsion phase (m^3)

Z = Stoichiometric constant

δ = film thickness (m)

λ = reaction plane

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Received for review April 24, 2007

Revised manuscript received March 12, 2008

Accepted March 31, 2008

IE0705711