J. Applied Membrane Science & Technology, Vol.15, June 2012, 21-29

Separation and Recovery of Cadmium(II) from Wastewater of Zinc Mining by Using Hollow Fiber Supported Liquid Membrane

S. Treephaiboon[1*], U. Pancharoena[2] & A. W. Lothongkumb[3]

[1-2]Department of Chemical Engineering, Chulalongkorn University, 10330, Thailand

[3]Department of Chemical Engineering, King Mongkut's Institute of Technology Ladkrabang, 10520, Thailand

ABSTRACT

The extraction and recovery of cadmium(II) via a hollow fiber supported liquid membrane (HFSLM) containing D2EHPA as a carrier dissolved in kerosene. The various effects on extraction and recovery cadmium were studied pH of feed phase, concentration of extractant and pH of stripping phase. The extraction and recovery of cadmium by using the hollow fiber supported liquid membrane method were 97% and 57%, respectively. The transport of cadmium ions was achieved by driving force of the concentration gradient. The behavior of extraction and/or recovery in HFSLM could be demonstrated in mass-transfer coefficient among feed phase, membrane phase and stripping phase. Determining the limiting step controlling the mass transfer of cadmium ion used the permeability coefficient.

Keywords: Hollow fiber supported liquid membrane, cadmium; separation, recovery, sulphate media

1.0 INTRODUCTION

The cadmium was used many industries [1] such as metallurgy, electroplating, pigmenting, nuclear industry and in the fabrication of Ni-Cd batteries. The poisons and many utilities of cadmium have been well recognized about the negative effect on the environment it accumulated in living systems. The health effects are well documented and reported such as renal disturbances, lung insufficiency, bone lesions and cancer in humans, causing nausea, salivation, diarrhea and muscular cramps [2, 3]. Due to many health effects of cadmium, WHO recommended guideline concentration in drinking water for 0.005 mg Cd/L [3] and water reuse for 0.01 mg Cd/L [4].

The pollution of cadmium came mainly from industry. This work concerned to determine the factors affecting the extraction and recovery of cadmium ions by using cadmium sulphate of wastewater from zinc mining. General in sulphate solutions, the zinc contains cadmium 0.5 to 1.5 percent [5]; therefore, the amount of cadmium is concerned by zinc. For this reason, the work chose the wastewater from the zinc mining, which used sulfuric acid to dissolve the zinc ions. Hence, the mixed cadmium is formed in cadmium sulphate solution.

It is challenging to extraction and recovery metal ions from wastewater because the ions can be treated and reused simultaneously. It is found from many previous literatures that extraction and/or recovery of cadmium ions are almost the basic of research such as the solvent extraction and absorption [6, 7]. These

* *Corresponding to:* S. Treephaiboon (email: pappap_song@hotmail.com)

methods have many limitations. The selective and the extraction rate of solvent extraction are very low, so the extractant and the reaction area are much needed for the solvent extraction. Moreover, the operating cost for absorption is very high because of the high price of absorbent and the need of changing or regenerating when it is deteriorated. There is abundant demand of reusing cadmium because of its many utilities but these methods cannot recovery cadmium ions. Membrane is an alternative method for simultaneous extraction and recovery of cadmium ions. Moreover, the operating cost is cheaper and the amount of extractant used is less than other methods because of its high selectivity and mass-transfer area [8, 9]. Another advantage of membrane is that it can extract metal ions at low concentration, i.e. from ppb to ppt [10], is easy to scale up [11] and apply for using in industrial [12].

This work focuses to study the separation and recovery of cadmium(II) in sulphate media from wastewater through the hollow fiber supported liquid membrane using di-2-ethylhexyl phosphoric acid (D2EHPA) as a carrier and kerosene as a solvent. The mathematical models of HFSLM for each reaction step show the description, the extraction equilibrium, the mass-transfer and permeability coefficients. Many parameters affecting the extraction and recovery are, for example, pH's of feed phase, concentrations of extractant and stripping phase. The mass-transfer coefficient of cadmium ions was determined by using the permeability coefficient.

2.0 THEORY

The membrane system is composed of three important phases: feed, membrane, and stippping phases. The first, feed phase, brings the extract ions from feed to the feed-membrane interface. The next phase is the membrane phase which is in the middle of feed and stripping phases. The complex ions between the extractant and the ions occur at the feed-membrane interface. The complex ions then diffuse into the membrane phase. The last phase, stripping phase, receives the metal ions which have reacted in the membrane phase by reacting, at the membrane-stripping interface, with the complex species which diffuse to this interface by the concentration gradient between feed and stripping phases.

The cadmium ions in feed phase appear as cation (Cd^{2+}) in sulphate media, and the feed solution is prepared from synthetic $3CdSO_4.8H_2O$. The organophosphorus extractant is a good choice for extraction due to the basic properties of the oxygen atom [6]. This extractant has been widely used for separation and/or recovery of Cd(II) from sulphate solutions [6, 7].

The method of cadmium ion complex occurs between cadmium ion and extractant. The monomer is occurred metal ions and organic at interface, method of cadmium complex showed below:

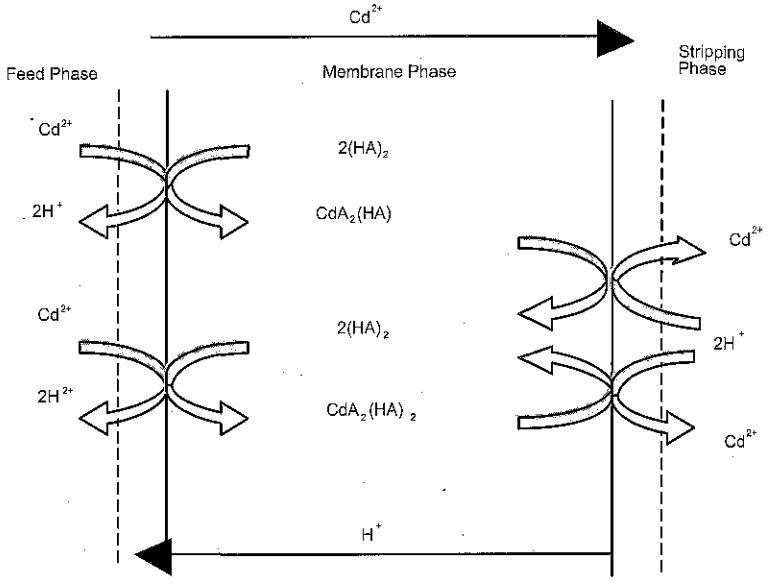

Figure 1 The mechanism transport of cadmium ions

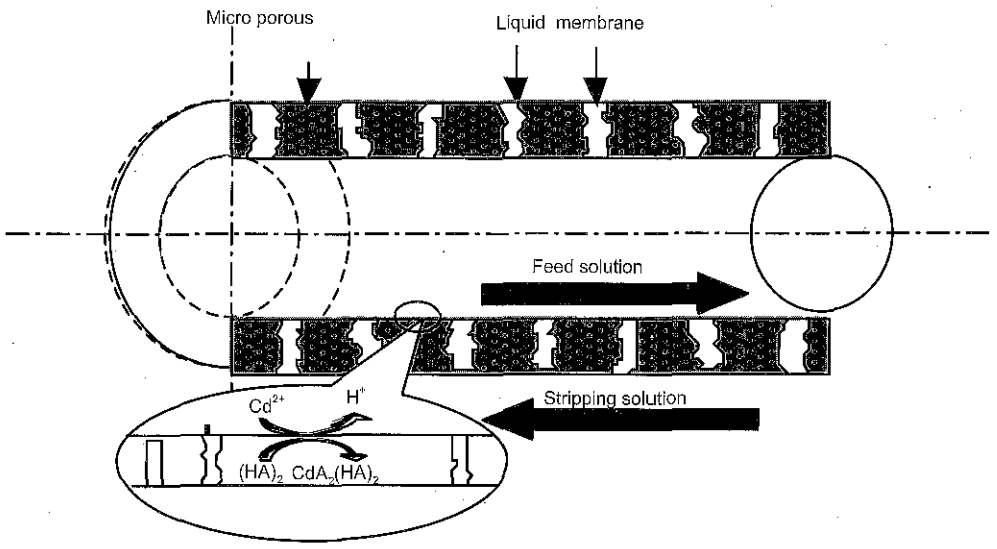

Figure 2 Flow pattern in the hollow fiber supported liquid membrane module

$$(HA)_{2\,Org.} \leftrightarrow 2(HA)_{Org.} \quad (1)$$

$$2(HA)_{Org.} \leftrightarrow 2(HA) \quad (2)$$

$$2(HA) \leftrightarrow HA_2^- + H^+ \quad (3)$$

$$Cd^{2+} + HA_2^- \leftrightarrow CdHA_2^+ \quad (4)$$

$$CdHA_2^+ + 2(HA)_{Org} \leftrightarrow CdA_2(HA)_{2Org.} + H^+ \quad (5)$$

HA is the extractant. The overall extraction process is governed by [7]:

$$Cd_{aq}^{2+} + 2(HA)_{2org} \leftrightarrow CdA_2(HA)_{2Org}^{+2} + H_{Aq}^+ \quad (6)$$

The percentage of extraction and recovery was determined as:

$$\%\ \text{Extraction} = \frac{[C]_{f,in} - [C]_{f,out}}{[C]_{f,in}} \times 100 \quad (7)$$

$$\%\ \text{Recovery} = \frac{[C]_{s,out}}{[C]_{s,in}} \times 100 \quad (8)$$

3.0 EXPERIMENTAL

3.1 Apparatus

The experiments were carried out in a hollow-fiber module (Liqui-Cel@ Extra-Flow module) purchased from CELGARD LLC (Charlotte, NC; formerly Hoechst Celanese), Cat# 5PCM-106 model. The module is composed of Celgard@ microporus polyethylene fiber woven into fabric and wrapped around the central tube feeder. The properties of hollow fiber are shown in Table 1 [8], and the appearance is shown in Fig. 2. The flow rate was controlled by using two pumps for feed and stripping phase, respectively.

Table 1 Properties of hollow fiber module

Property	Description
Material	Polypropylene
Number of hollow fibers(N)	10,000
Inside diameter of hollow fiber (μm)	240
Outside diameter of hollow fiber (μm)	300
Pore size (μm)	0.05
Porosity (%)	30 %
Effective surface area (m^2)	1.4
Area per unit volume (m^2/m^3)	29.3
Module dimension (diameter (cm) × length (cm))	6.3 × 20.3
Maximum pressure (kg/cm^2)	4.2
Temperature rang (°C)	1 – 60
Tortuosity factor	2.6

3.2 Chemicals and Reagents

The synthetic cadmium sulphate ($3CdSO_4 \cdot 8H_2O$), used as the feed solution, was AR grade from Loba chemie Co., Ltd.; India. The pH was adjusted by adding sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH), which were AR grade from Merck Ltd. The extractants are D2EHPA and Cyanex 923, AR grade from Merck Ltd. The kerosene was used for dissolved carrier. The D2EHPA is phosphine oxide, average molecular weight is 322 g/mol. The diluent is kerosene. The stripping solution is sulfuric acid.

Table 2 The concentration waste water of zinc mining.

Composition	Concentration (ppm)
Cd	43
Zn	323
Mn	339
Mg	1,853

3.3 Procedures

Continuous system operation using series module is showed in Fig. 5. The membrane phase was prepared by dissolving D2EHPA dissolved in kerosene. Feed phase solution is prepared by synthesis $3CdSO_4.8H_2O$ and the concentration of cadmium was controlled at about 50 ppm. The stripping phase solution is sulfuric acid solution. Firstly, the hollow fiber in membrane phase is prepared by circulation in the tube side and shall side 40 min [8] for assuring the membrane phase was trapped in the porous hollow fiber. The experimental was started by pumping the feed and stripping solutions into the module simultaneously. The flowing feed and stripping are counter current in one through. The operating for 1 experimental 100 ml/min time was 50 min and kept sample about 10 cm^3 each experimental. The concentration of cadmium ions was determined by using Atomic Absorption Spectroscopy (AAS) model valence 280FS AA.

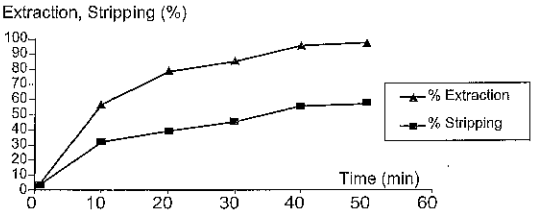

Figure 4 The percentage of extraction and stripping cadmium ions in HFSLM; Feed phase – 50 ppm of synthetic $3CdSO_4.8H_2O$; Membrane phase – D2EHPA dissolved in kerosene 0.12 molar; Stripping phase – sulfuric acid with pH4

4.0 RESULTS AND DISCUSSION

4.1 The Effects of Sulfuric Acid Concentration in Feed Phase

The influence of H_2SO_4 concentrations in the feed phase solutions on the percentage of extraction cadmium was studied in the pH range of 1.5 to 7 for each extractant. The results were shown in Fig. 8. The extractant, D2EHPA, can extract cadmium ions better than Cyanex 923 in this pH range, because availability of more and more extractant in dissociated form to form the neutral complex and also in agreement with the complexing ability of the extractants with Cd [9]. The highest extraction of cadmium ions at pH 5.5 by using

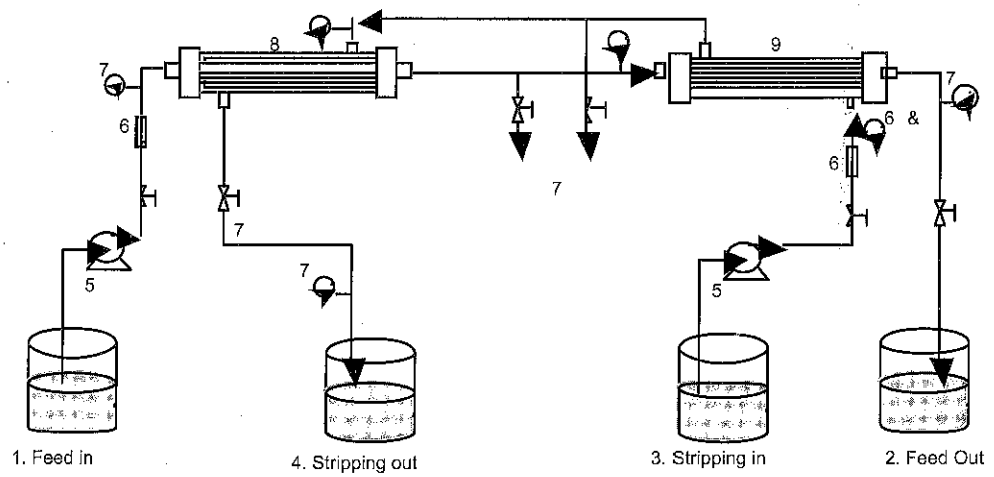

Figure 3 Schematic counter-current flow diagram for series module and continue system in the HFSLM: (1) Feed flow through in module 1; (2) Feed flow out from module 2; (3) Stripping flow through in module 2; (4) Stripping flow out from module 1; (5) gear pump; (6) flow rate meter; (7) pressure gauge; (8) hollow fiber module 1; (9) hollow fiber module 2

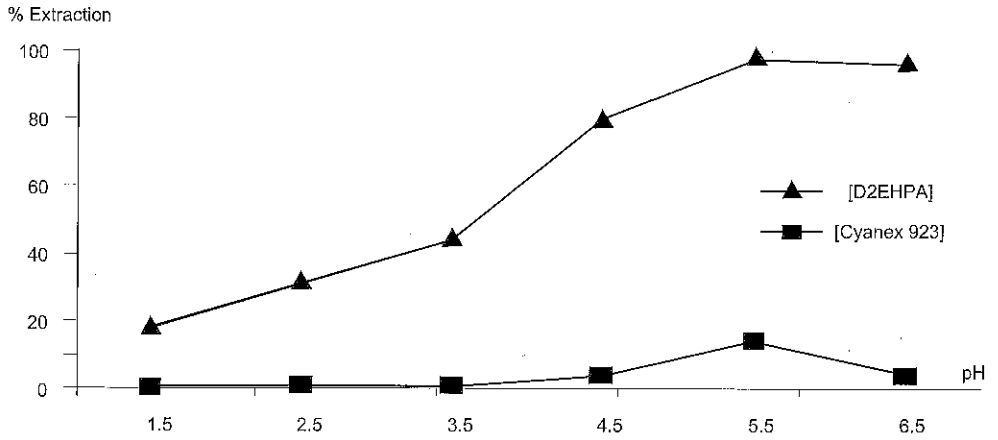

Figure 5 The percentage of extraction cadmium ions agents pH of feed phase; Feed phase – 50 ppm of synthetic $3CdSO_4.8H_2O$; Extractant – 0.12 molar of D2EHPA in kerosene; Stripping phase – sulfuric acid with pH4

D2EHPA and Cyanex 932 were 98.57% and 14.35%, respectively. It was observed the pH in feed phase had the strong effects on extraction cadmium ions. Thus, the appropriate pH of peed phase is necessary for forming of an anionic complex of cadmium. The extraction reaction of cadmium ions is showed in Eq. (6).

4.2 The Effects of Carrier Concentration in Membrane Phase

The effects of carrier concentration on the percentage of extraction were observed. The extraction of cadmium ion was formed with difference D2EHPA concentration, the concentration ranges from 0.005 to 0.22 molar in the membrane phase. The results were shown in Fig. 9. The concentration of D2EHPA was important in the extraction percentage of cadmium ions in the feed phase. Increasing the concentration of carrier from 0.005 to 0.12 molar enhances the percentage of extraction cadmium ions immediately according to Le Chatelaine's principle. The optimum concentration for extracting cadmium ion was about 97%. When the concentration was over 0.12 molar, the percentage of extraction decreased. With highly increasing in the concentration of carrier, the percentage of extraction was low because of the increasing viscosity of membrane phase. The viscosity and diffusivity were reversely correlated as shown in Eq. (13). The diffusion coefficients in water were estimated by using the Wilke-Chang method [10] as shown in Table 3. The viscosity of D2EHPA in kerosene can be estimated by using Kendel and Monroe equation [11]. The excellent representations for the estimation of mixture viscosity were shown in Table 3.

Table 3 The distribution coefficient (D) of cadmium and the viscosity of D2EHPA in kerosene at the range of 0.05 to 0.22 molars

D2EHPA(molar)	D_m(cm²/s)	h(mPa × s)
0.05	7.48×10^{-5}	1.210
0.07	5.74×10^{-5}	1.289
0.10	4.34×10^{-5}	1.376
0.12	3.64×10^{-5}	1.472
0.17	2.57×10^{-5}	1.692
0.22	1.90×10^{-5}	1.961

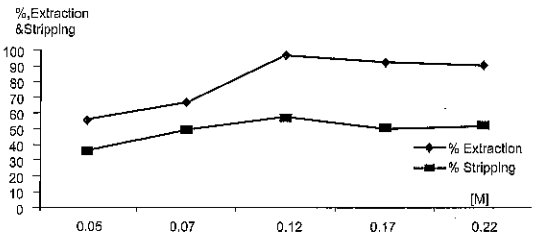

Figure 6 The percentage of extraction against the D2EHPA concentration in membrane phase: Feed phase – 50 ppm of synthetic $3CdSO_4.8H_2O$, pH 5.5; Membrane phase –D2EHPA in kerosene; Stripping phase – sulfuric acid with pH_4

$$D_m = \frac{7.4\times10^{-8}(M)^{0.5}\cdot T}{\eta\cdot V_A^{0.6}} \quad (13)$$

where D_m is the diffusion coefficient at membrane phase (cm^2/s), M is the molecular weight, T is the absolute temperature (K), η is the viscosity of water (cP), and V_A is the molar volume of contaminant (cm^3/molar).

4.3 Effect of Stripping Phase Concentration

The concentration of sulfuric acid (H_2SO_4) was studied. The concentrations were varied from pH 6 to 1 as shown in Fig. 10. The percentages of cadmium stripping decreased from pH 3 to pH 6, and the other percentages of recovery were essentially constant. The highest recovery was 57% at pH3. The transport of cadmium ions in couple-facilitated counter-transport was due to the driving force of the concentration gradient of H^+ [12]. The initial H+ of feed phase was nil, it was observed from pH 3 of H_2SO_4 which was enough for the stripping reaction of cadmium ions.

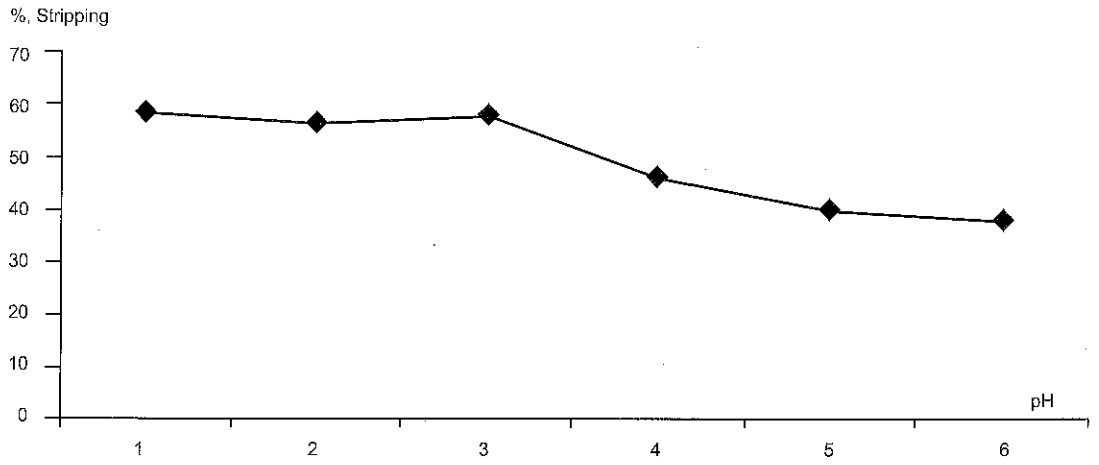

Figure 7 The percentage of recovery cadmium ions against the pH of stripping phase: Feed phase – 50 ppm of synthetic $3CdSO_4.8H_2O$, pH 5.5; Membrane phase – 0.12 molar of D2EHPA in kerosene; Stripping phase – sulfuric acid

4.4 The Extraction Equilibrium Constant and The Distribution Coefficients

The estimation of extraction equilibrium constants (K_{ex}) of cadmium ions extracted by D2EHPA can be described by Eq (14), and from the plot of $[CdA_2(HA)_{2org}][H+]^2$ vs $[Cd^{2+}][(HA)_{2org}]^2$ at equilibrium, the slope shown in Fig. 11 determined K_{ex} as 2.18×10^{-3}.

$$K_{ex} \frac{[CdA_2(HA)_2]_{Org}[H^+]^2_{Aq}}{[Cd^{2+}]_{Aq}[(HA)_2]^2_{Org}} \quad (14)$$

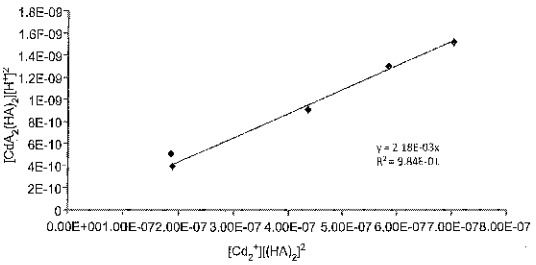

Figure 8 The plot of $[CdA_2(HA)_{2org}][H^+]^2$ vs $[Cd^{2+}][(HA)_{2org}]^2$ at equilibrium for the equilibrium constant of cadmium extraction

4.5 The Estimation of Mass-Transfer Coefficient

The mass-transfer-controlling step through a hollow fiber supported liquid membrane is the diffusion. The three mass-transfer coefficients are: k_f for cadmium ions diffusing through the feed phase to membrane phase, k_m for cadmium complexes diffusing through the membrane phase, and k_s for cadmium ions diffusing through the stripping phase. The mass-transfer coefficients in the membrane and the stripping phases are much lower than that in feed phase to membrane phase. Therefore, the distribution of the stripping phase can be neglected [13], and Eq. (15) is obtained:

$$\frac{1}{P}=\frac{1}{k_i}+\frac{r_i}{r_{lm}}\frac{1}{P_m} \quad (15)$$

where P is the permeability coefficient (cm/s), k_i is the mass-transfer coefficient of feed phase, r_i is the inner radius of hollow fiber (cm), r_{lm} is the log-mean radius of hollow fiber, and P_m is the membrane permeability coefficient.

The permeability coefficient (P) was determined by Denesi [14]:

$$-V_f \ln(\frac{C_f}{C_{f,0}}) = AP\frac{\beta}{\beta+1}t \quad (16)$$

$$\beta=\frac{Q_f}{PL\varepsilon\pi Nr_i} \quad (17)$$

where V_f is the volume of the feed (cm^3), C_{f0} is the cadmium concentration at time 0 (mol/L), C_f is the cadmium concentration at time t (mol/L), A is the effective area of the hollow-fiber module (cm^2), t is the time (min), Q_f is the volumetric flow rate of feed solution (cm^3/s), L is the length of the hollow fiber (cm), ε is the porosity of the hollow fiber (%), N is the number of hollow fiber in the module. r_i is the internal radius of the hollow fiber (cm), and N is molar volume of contaminant (cm^3/molar).

The relation between P_m and the distribution ratio (D) is demonstrated as follow:

$$P_m = Dk_m \quad (18)$$

The distribution ratio for cadmium was given by:

$$D=\frac{[CdA_2(HA)_2]_{Org}}{[Cd^{2+}]_{Aq}}=K_{ex}\frac{[(HA)_2]^2_{Org}}{[H^+]^2_{Aq}} \quad (19)$$

Combining Eqs.(18) and (19), thus

$$P_m = K_{ex}K_m\frac{[(HA)_2]^2_{Org}}{[H^+]^2_{Aq}} \quad (20)$$

where K_m is the mass-transfer coefficient of the membrane.

Therefore, the mass-transfer rates through a hollow fiber supported liquid membrane can be arranged as:

$$\frac{1}{P}=\frac{1}{k_i}+\frac{r_i}{r_{lm}}\frac{[H^+]^2_{Aq}}{K_{ex}K_m[(HA)_2]^2_{Org}} \quad (21)$$

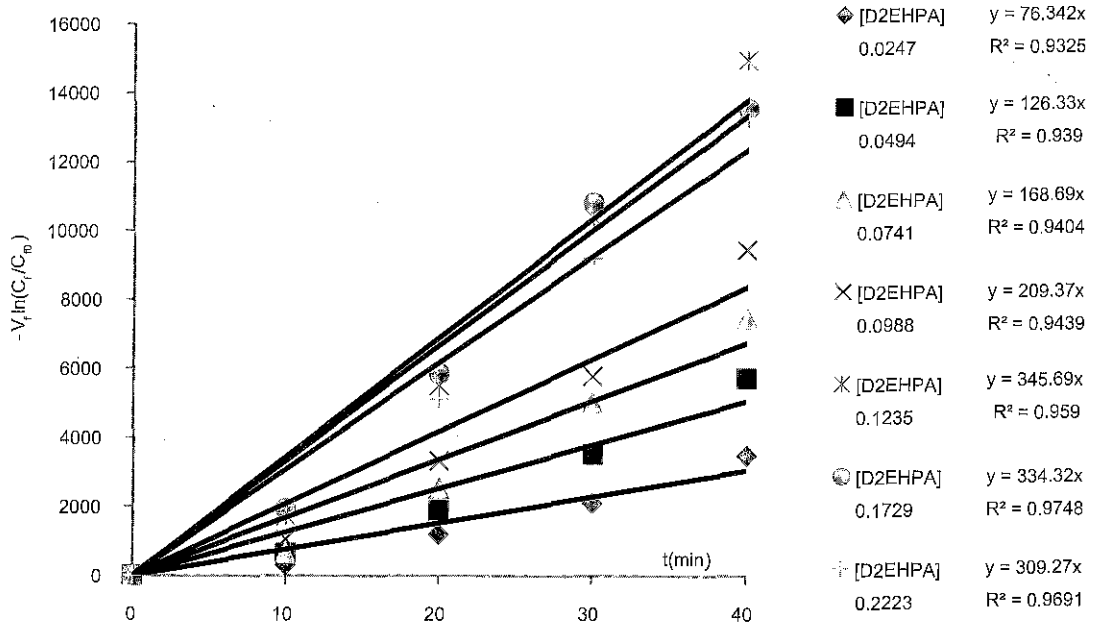

Figure 9 The plot of $-V_f \ln(C_f/C_{f0})$ of cadmium ions in the feed phase against time, with different concentrations of D2EHPA

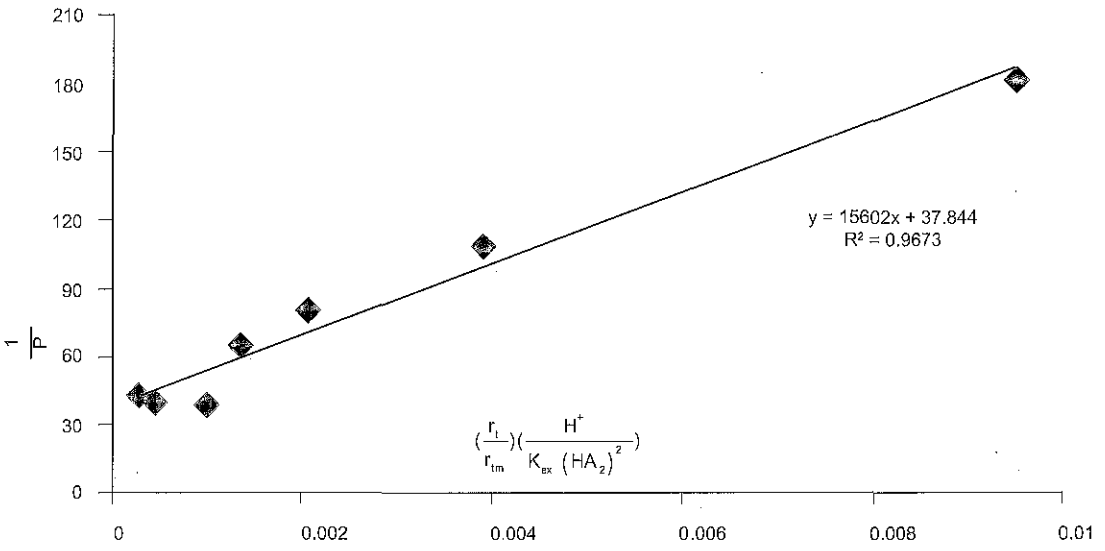

Figure 10 The plot of $1/P$ against $(r_f/r_{fm})(([H^+]/(K_{ex}[(HA_2)^2])$

The mass-transfer coefficient of cadmium ions through the feed diffusion layer (K_f) is 2.64×10^{-2} cm/s and the mass-transfer coefficient of cadmium complexes through the membrane phase (K_m) is 6.41×10^{-5} cm/s.

5.0 CONCLUSION

The best condition for extracting cadmium ions were as follows: D2EHPA was used as a carrier, the pH of feed phase was 5.5, the concentration of extractant was 0.12 molar, and the pH of stripping phase was 3. The maximum extraction and recovery of cadmium ions were 97% and 57%, respectively. The mass-transfer coefficients of feed phase (K_f) and membrane phase (K_m) were 2.64×10^{-2} and 6.41×10^{-5} cm/s, respectively. The mass-transfer-controlling step was, therefore, the diffusion of cadmium ions through the membrane phase.

REFERENCE

[1] N. S. Rathore *et al.* 2009. Extraction and permeation studies of Cd(II) in acidic and neutral chloride media using Cyanex 923 on supported liquid membrane. *Hydrometallurgy.* 96 : 81–87.

[2] Benguella, B. *et al.* 2002. Cadmium removal from aqueous solution by chitin kinetic and equilibrium studies. *Waterres.* 36 : 2463-74.

[3] Mohan, D. *et al.* 2002. Single and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse-an agricultural waste. *Carbon.* 3 : 2304-18.

[4] World Health Organization. 2006. A compendium of standards for wastewater reuse in the Eastern Mediterranean Region. *CEHA.*

[5] M. S. Safarzadeh *et al.* 2007. A review on hydrometallurgical extraction and recovery of cadmium from various resources. *Minerals Engineering.* 20 : 211–220.

[6] A. Mellah, *et al.* 2006. The solvent extraction of zinc and cadmium from phosphoric acid solution by di-2-ethylhexyl phosphoric acid in kerosene diluent. *Chemical Engineering and Processing.* 45 : 684-690.

[7] Yan-Hui Li, *et al.* 2003. Adsorption of cadmium (II) from aqueous solution by surface oxidized carbon nanotubes. *Carbon.* 41 : 1057-1062.

[8] Pancharoen, U. *et al.* 2005. Purely extraction and separation of mixture of cerium(IV) and lanthanum (III) via hollow fiber supported liquid membrane. *Journal of Industrial and Engineering Chemistry.* 11 : 926-931.

[9] Prakorn, R. *et al.* 2007. Separation of radioactive metal ions by hollow fiber-supported liquid membrane and permeability analysis. *Journal of the Chinese Institute of Chemical Engineers.* 38.

[10] Kislik, *et al.* 2010. Liquid membrane. Principles and applications in chemical separations and wastewater treatment. *Edition first.*

[11] Leon, R. *et al.* 2005. Determination of viscosity and density of Di-(2-ethylhexyl) phosphoric acid + aliphatic kerosene. *J. Chem. Eng.* 50 : 587-590.

[12] Hamid, R. *et al.* 2009. Study on removal of cadmium from wastewater by emulsion liquid membrane. *Journal of Hazardous Materials.* 165 : 630-636.

[13] Zhang, W. *et al.* 2010. Transport study of cu(II) through hollow fiber supported liquid membrane. *Chinese Journal of Chemical Engineering.* 18(1) : 48-54.

[14] Danesi, P. R. A. 1984. Simplified model for the coupled transport of metal ions through hollow fiber supported liquid membranes. *J. Membr. Sci.* 20 : 231.