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An experimental study on removal cadmium from wastewater by emulsion liquid membrane

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AN EXPERIMENTAL STUDY ON REMOVAL CADMIUM FROM WASTEWATER BY EMULSION LIQUID MEMBRANE

by
Jing-Chi Shiu

Research was conducted on cadmium, a heavy metal pollutant, extraction out of wastewater by means of an emulsion liquid membrane system. The emulsion liquid membrane was made of a carrier (di(2-ethylhexyl) phosphoric acid), a surfactant (ECA 4360J), and a stripping agent (sulfuric acid). The effects of using the following parameters on the membrane to optimize the operating conditions were investigated: type of buffer solutions, initial external phase pH, initial cadmium concentration, internal sulfuric acid concentration, impeller stirring speed, carrier concentration, surfactant concentration, and selectivity between cadmium and sodium ion.

The best performance for the system presented in this thesis was:

The buffer solution is sodium phosphate with citric acid. The pH in the external phase should be maintained between 4-5. Those concentrations in the membrane should be: 3 wt % carrier and 3 wt % surfactant. The internal stripping agent is 6M sulfuric acid and the impeller stirring rate is 300 rpm. The ratio of the membrane phase to the internal phase is 82:18. Under these conditions, a single stage extraction performance of 98% is obtained within thirty minutes.

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by
Jing-Chi Shiu

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APPROVAL PAGE

AN EXPERIMENTAL STUDY ON REMOVAL CADMIUM FROM WASTEWATER BY EMULSION LIQUID MEMBRANE

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This Thesis is dedicated to my devoted parents,
my family members, good friends, and my lovely Demi

ACKNOWLEDGMENT

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

LIST OF TABLE

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

Cadmium, atomic weight 112.411, is a soft-white metal that is usually found in combination with other elements. The major uses of cadmium and its compounds are primarily for metal plating, coating operations, machinery, baking enamels, photography, and television phosphors, nickel-cadmium solar batteries and pigments [1].

Acute (short-term) inhalation exposure to high levels of cadmium in humans may result in negative effects on the lungs, such as bronchial and pulmonary irritation. A single acute exposure to high levels of cadmium can result in long-lasting impairment of lung function. Chronic (long-term) inhalation and oral exposure to cadmium affects the kidneys, with proteinuria, a decrease in glomerular filtration rate and an increased frequency of kidney stone formation [1-3]. The drinking water standard of cadmium is 0.005 mg/dm^3 (5 ppm) (From Technical Factsheet on Cadmium in the National Primary Drinking Water Regulations).

The emulsion liquid membrane (ELM) separation method was first invented by Dr. Norman N. Li in 1968 [4]. The emulsion liquid membranes (ELMs) are usually prepared by forming an emulsion between two immiscible phases, and then dispersing the emulsion in a third phase by agitation for extraction. Figure 1-1 shows the schematic of the emulsion liquid membrane system used in this research. The wastewater feed containing cadmium sulfate solution is the external phase. The encapsulated droplets with H$_2$SO$_4$ solution are the internal phase.

1
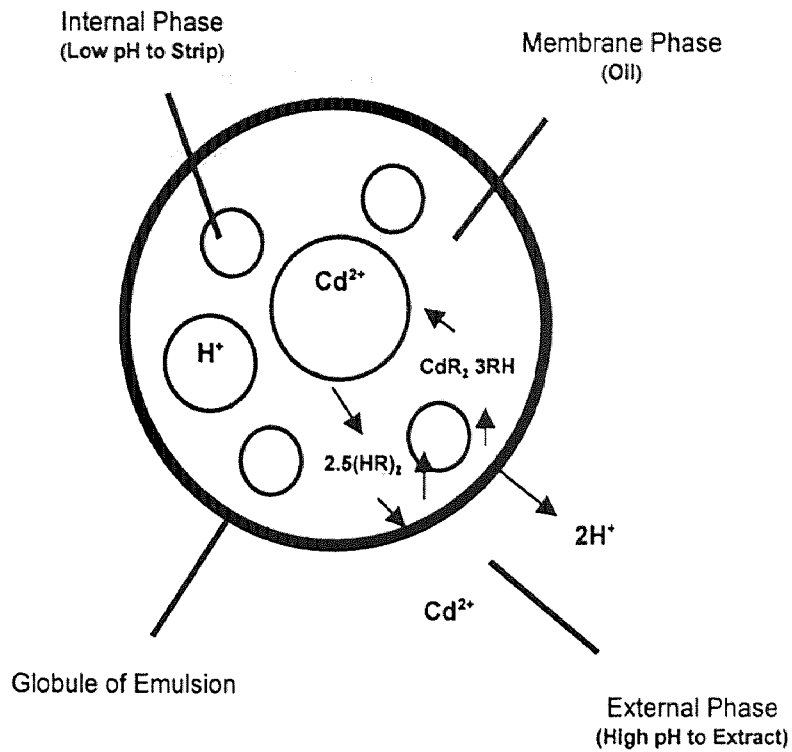
Figure 1-1 Schematic of an Emulsion Liquid Membrane System

The phase between external and internal phases is the membrane phase containing the extractant and the surfactant which are dissolved in an oil solvent. The separation of mixtures can be achieved by selective diffusion of one component through the membrane phase into the receiving phase of lower equivalent concentration. A component can be trapped and concentrated in the internal phase for the next treatment or recovery [5]. The extractant is used to extract metal ions from the external aqueous phase to the membrane phase, and also unload the extracted metal ions into the internal phase. The solvents used

phase, and also unload the extracted metal ions into the internal phase. The solvents used

in the membrane are organic solvents. The function of the surfactants is to maintain the

surface tension of the membrane and to protect it from being broken while processing.

In this study, di(2-ethylhexyl) phosphoric acid (D2EHPA, Figure 1-2, Sigma

Scientific) was used as the extractant and ECA 4360J (Figure 1-3, Exxon Chemical Co.)

as the surfactant. The diluent solvent was Exxsol D 80 (Exxon Chemical Co.), and

sulfuric acid (Sigma Scientific) was used as the internal phase stripping reagent. The

effects and factors of extracting cadmium from wastewater were tested on different buffer

solutions, initial external phase pH value, extractant and surfactant concentration, internal

phase acidities, and stirring rate of the contactor impeller.

$$RO\diagdown \overset{O}{\underset{OH}{P}}\diagup RO \qquad where \qquad R = CH_3-(CH_2)_3-\underset{\underset{CH_3}{|}}{\overset{}{\underset{CH_2}{|}}}CH-CH_2-$$
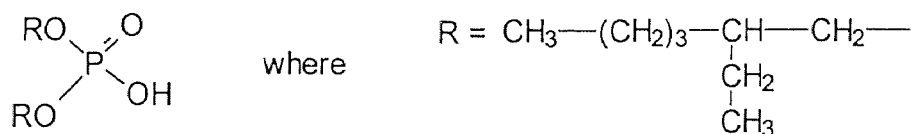
Figure 1-2   Chemical Structure of D2EHPA
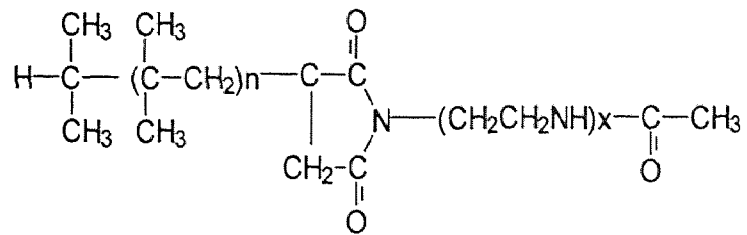
Figure 1-3 Chemical Structure of ECA 4360J

CHAPTER 2

LITERATURE REVIEW

Methods of cadmium removal include coagulation and filtration, ion exchange, lime softening, reverse osmosis, and membrane separation. Grimm and Kolarik [6] reported equilibrium data for cadmium extraction with D2EHPA dissolved in n-dodecane from an aqueous phase containing 1M sodium nitrate and nitric acid as a buffer. McDonald and Moore [7] reported liquid-liquid extraction of cadmium with high-molecular-weight amines (Aliquate 336) from iodide solutions and use 10M NH$_4$OH or 5% ethylenediamine. In Kitagawa's report [8], cadmium was tightly bound to a cyanide complex in the effluent from metal plating baths. This complex, Cd(CN)$_4^{2-}$, is readily extracted from aqueous solutions by Aliquate 336. However, stripping (unloading the solute from the extractant carried with from the external phase) was quite difficult because of the great stability of the Cd(CN)$_4^{2-}$ complex under basic conditions (K$_{sp}$= 10^{19}) [9]. Ethylenediaminetetraacetic acid (EDTA) is known to chelate strongly with the cadmium complex [10], and EDTA was successfully used to remove cadmium from Aliquate 336 with regeneration of the ion carrier. This process was possible so long as the pH of the external phase was maintained in the range of 4-6. The concentration of cadmium was reduced to 1% within ten minutes. Izzat, et al. [11] have studied the extraction of cadmium by various macrocycle ligand carriers in emulsion liquid membranes. Marr, Bart, and Draxler [12] removed heavy metals from wastewater in metallurgical and incineration plants. Saito [13] used a bathocuproine solution in dibenzyl ether as a carrier to lower the cadmium to half of the initial concentration within 2 hours.

5

Binary equilibrium data for lead and cadmium with D2EHPA and predictive models that incoporathe aqueous phase nonidealities and aqueous phase ionic reactions have been developed by Raguraman, et al [14]. Li, et al. [15] used a tri-n-octylamine (TOA)-sorbital monooleate (Span 80)-oxylene membrane to separate cadmium in a potassium iodide solution. Sodium hydroxide was used as the stripping reagent in their study. They found that cadmium could be completely separated from Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+}, and Mn^{2+}. Deorkar, et al.[16] separated cadmium with an inorganic solid-phase extractant (ISPE-302), which was prepared by attachment of bis(2,4,4-trimethyl) monothiophosphonic acid (Cyanex-302) on a functionalized silica surface. The maximum extraction efficiency of the cadmium removal achieved was 89% of the theoretical capacity. This performance could not, however, be sustained because of the loss of extractant.

CHAPTER 3

MECHANISM AND MODELS OF MASS TRANSFER IN THE ELM SYSTEM

3.1. Mechanism

As shown in Figure 3-1, the mechanism of a cadmium ion diffusing across the membrane can be represented as follows:

3.1.1. Extraction

The cadmium ion in the external phase diffuses and is carried across the membrane phase by a "carrier" (D2EHPA) in the membrane phase. This is called Type-II facilitation [17-19]. The reaction forms the Cd-extractant complex [6,14] in the membrane phase and releases hydrogen ions to the external aqueous phase.

$$Cd^{2+} \quad + \quad 2.5\,(HR)_2 \quad \rightarrow \quad CdR_2 \bullet 3RH \quad + \quad 2H^+ \tag{1}$$

external phase	interface (ext./memb.)	interface (ext./memb.)	external phase
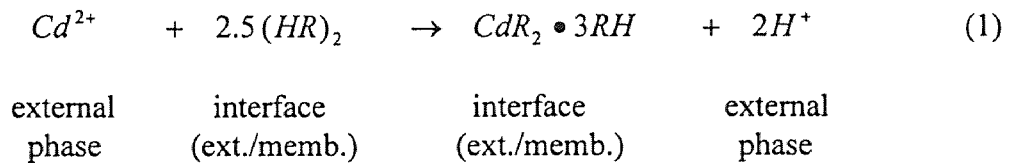
where $CdR_2 \bullet 3RH$ is the metal-extractant complex in the membrane phase.
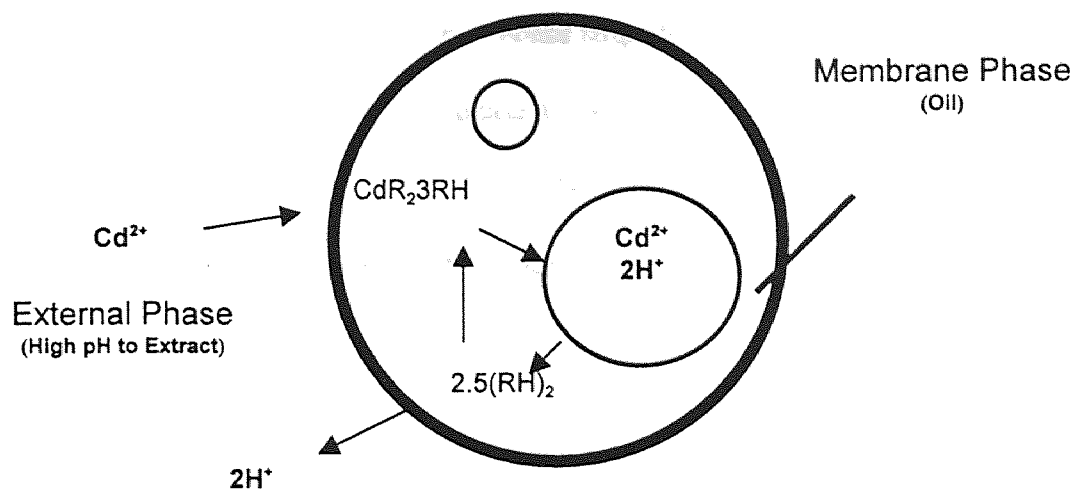
Figure 3-1 Extraction Reaction of Cadmium at
the External-Membrane Interface

3.1.2. Mass Transfer between Membrane Interfaces

The cadmium complex, $CdR_2 \bullet 3RH$, diffuses across the membrane phase to the interface

of membrane and the internal phase containing the concentrated H_2SO_4.

$$CdR_2 \bullet 3RH \quad \leftrightarrow \quad CdR_2 \bullet 3RH \tag{2}$$

$$\text{interface} \qquad\qquad \text{interface}$$
$$\text{(ext./memb.)} \qquad\qquad \text{(memb./int.)}$$
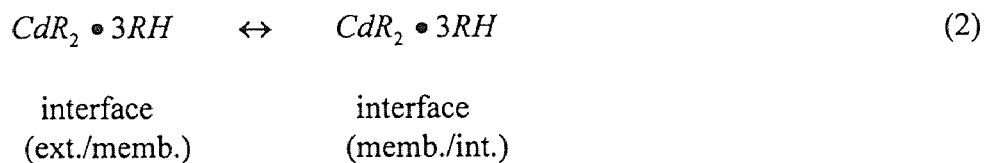
3.1.3. Stripping

The concentrated H_2SO_4 in the internal phase strips the metal-extractant complex from the membrane phase into the internal phase to become the cadmium ion and releases the carrier back to the membrane phase. It also donates protons to the extractant in the membrane phase. These mass transfer processes were shown in Figure 3-2.

$$2H^+ \quad + \quad CdR_2 \bullet 3RH \quad \rightarrow \quad 2.5\,(HR)_2 \quad + \quad Cd^{2+} \qquad (3)$$

internal	interface	interface	internal
phase	(memb./int.)	(memb./int.)	phase
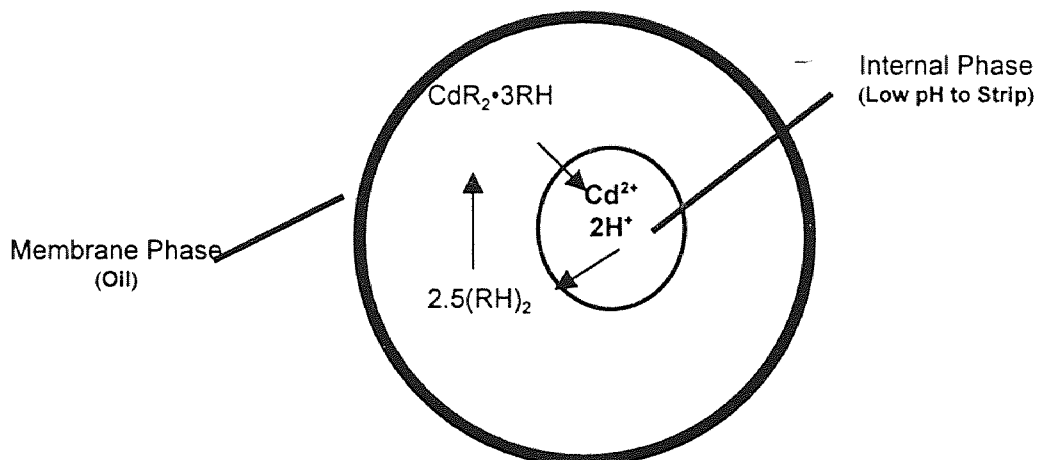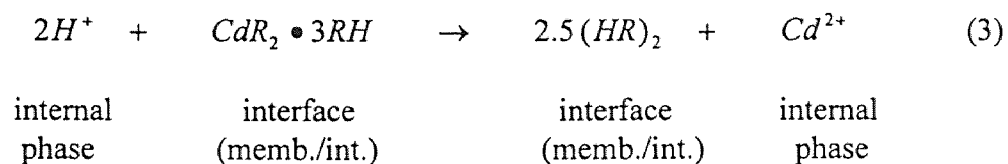
Figure 3-2 Stripping Reaction of Cadmium at the Membrane-Internal Interface

3.2. Mass Transfer Model of ELM

According to Huang, et al. [20], the mathematical equations governing the ELM system are as follows:

3.2.1. Mass Transfer between External-Membrane Interface

$$Ve\ \frac{dCe}{dt} = -N(4\pi R^2)\ K\ (Ce - Ce^*)$$

(4)

where:

Ve	=	volume of the external phase, dm³
N	=	total number of globules, dimensionless
R	=	radius of globules, m
K	=	external mass transfer coefficient, m/s
Ce(t)	=	concentration of M^{2+} in the external phase, moles/dm³
Ce*(t)	=	concentration of M^{2+} in the external phase at the external-membrane interface, moles/dm³

K (Ce-Ce*) = the flux for mass transfer across the external resistance film, moles/dm² s

3.2.2. Mass Fluxes at the External-Membrane Interface

$$N\,(4\pi R^2)\,K\,(Ce - Ce^*) = N\,(4\pi R^2)\,De\,(\frac{\partial Cm}{\partial r})_{r=R} \tag{5}$$

where:

Cm = concentration of metal-extractant complex in the membrane

phase, moles/dm^3

De = effective diffusivity of the metal-extractant complex in the

globule, m^2/s

$De(\frac{\partial Cm}{\partial r})_{r=R}$ = the flux for mass diffusion in the globules

3.2.3. Equilibrium at the External-Membrane Interface

At the external-membrane interface, there will be a chemical equilibrium. Thus,

$$Cme^* = p\;Ce^*\;(\text{a large p means better performance}) \tag{6}$$

where:

p = the extraction partition function at the external-

membrane interface, dimensionless

Cme*   =   concentration of the metal-extractant complex in the

membrane phase at the external-membrane interface

(or at r =R), moles/dm^3

3.2.4. Mass Transfer inside a Droplet of the Membrane Phase

A spherical shell material balance is taken inside the globule membrane assuming that

there is no internal mass transfer film being considered.

$$Vm \frac{\partial Cm}{\partial t} = (Vm + Vi) \, De \, \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial Cm}{\partial r}) - Vi \, \frac{\partial Ci}{\partial t} \qquad (7)$$

where:

Vi   =   volume of the membrane phase, dm^3

Vm   =   volume of the internal phase, dm^3

Ci (r ,t) =   concentration of metal ion in the

internal phase of a droplet, moles/dm^3

$\frac{\partial Ci}{\partial t}$ = the rate of release of the metal into the internal phase from the

membrane - internal interface.

3.2.5. Equilibrium at the Membrane-Internal Interface

At the membrane-external interface, there will be a chemical equilibrium. Thus,

$$Ci^* = Ci = q \, Cmi^* = q \, Cm \text{ (a large q means better performance)} \tag{9}$$

where:

Ci^* = concentration of metal ion at the membrane-internal

interface, moles/dm^3

q = the stripping partition function at the membrane-

internal interface, dimensionless

Cmi^* = concentration of metal-carrier complex at the

membrane-internal interface, moles/dm^3

3.3. Prediction of the Equilibrium Constrains p and q Theoretically

3.3.1. Find P from Equation (6)

We have

$$Cm^* = p\ Ce^*$$

From Raghuraman, et al., [14], cadmium was extracted by D2EHPA, and the equilibrium reaction at the internal-membrane interface was shown as Equation (1).

$$Cd^{2+} \quad + \quad 2.5\,(HR)_2 \quad \rightarrow \quad CdR_2 \bullet 3RH \quad + \quad 2H^+$$
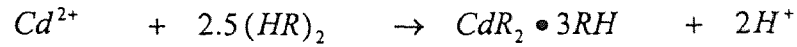
$$K = \frac{[CdR_2 \bullet 3RH]_m\ [H^+]_e^2}{[Cd^{2+}]_e\ [(RH)_2]_m^{2.5}} \tag{10}$$

$$[Cd^{2+}]e = \frac{[H^+]_e^2\ [CdR_2 \bullet 3RH]_m}{K\ [(RH)_2]_m^{2.5}} \tag{11}$$

since

$$[Cd^{2+}]e = Ce^* \tag{12}$$

$$[CdR_2 \bullet 3RH]_m = Cm^* \tag{13}$$

we get

$$p = K\ \frac{[(RH)_2]_m^{2.5}}{[H^+]_e^2} \tag{14}$$

Equation (9) shows that a lower hydrogen ion concentration in the external phase and a higher carrier concentration in the membrane phase will increase p, and would have a better performance in extraction reaction. Wang's thesis [21] experimentally verified that for Cu^{2+}, high [RH]m will perform better. Zhou's thesis [22] showed experimentally that for Sr^{2+} (Strontium) extraction:

- The pH is reduced gradually in the external phase, or there is [H^+]released from the membrane phase to the external phase

- When [H^+] increases in the external phase, the value of p decreases. Thus, Cm* is smaller and the performance of the ELM operation shows poor results.

3.3.2. Find q from Equation (8)

We have

Ci* =Ci = q Cmi* = q Cm

From Raghuraman, et al., [14], cadmium was extracted by D2EHPA, and the equilibrium reaction at the membrane-internal interface was shown as Equation (3).

$$2H^+ \quad + \quad CdR_2 \bullet 3RH \quad \rightarrow \quad 2.5\,(HR)_2 \quad + \quad Cd^{2+}$$
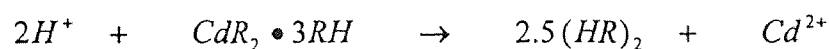
$$K_1 = \frac{[Cd^{2+}]_i \quad [(RH)_2]_m^{2.5}}{[H^+]_i^2 \quad [CdR_2 \bullet 3RH]_m} \tag{15}$$

$$Cd^{2+}{}_i \;+\; SO_4{}^{2-} \;\rightarrow\; CdSO_4{}_{\,i} \tag{16}$$

$$K_2 = \frac{[CdSO4]_i}{[Cd^{2+}]_i \quad [SO_4{}^{2-}]_i} \tag{17}$$

$$[Cd^{2+}]_i = \frac{K_1 \quad [CdR_2 \bullet 3RH]_m \; [H^+]}{[(RH)_2]_m^{2.5}} \tag{18}$$

Thus,

$$[CdSO_4]_i \;=\; K_2 \quad [Cd^{2+}]_i \quad [SO4^{2-}]_i \tag{19}$$

Since Ci* includes all forms of Cu in the internal phase,

$$Ci^* = [Cd^{2+}]i + [CdSO_4\,]i \tag{20}$$

$$= K_1 \{[CuR_2 \bullet 3RH]m / [(RH)2]^{2.5}{}_m \}[H^+]^2i +$$

$$K_2 K_1 \{[CuR2 \bullet 3RH]m /[(RH)2]^{2.5}{}_m\} \; [H^+]^2i \; [SO_4^{2-}]i$$

$$= \{ [CuR_2 \bullet 3RH]m /[(RH)2]^{2.5}{}_m \} \; [H^+]^2i \; \{K_1 + K_1 K_2 \, [SO_4^{2-}]i \tag{21}$$

Since,

$$Cm = [CuR_2 \bullet 3RH]m,$$

Plug into Equation (8), we get:

$$q = \frac{[H^+]_i^2}{[(RH)_2]_m^{2.5}} \{K_1 + K_1 K_2 [SO_4^{2-}]_i \}$$ (22)

Comments:

- Wang [21] indicated that if the internal phase nitric acid increases, it gives a higher q, therefore a better ELM performance could be achieved.

- From Equation (22), for a better performance, [RH]m should be small.

- From Equation (14), it presents that the [RH]m should be large in order to have higher p and would have a better extraction efficiency. It means, an important optimal value of [RH]m should be determined in the Cu^{2+} extraction by ELM.

3.4. Experimental Evaluation of p and q

3.4.1. Procedures for Experiments to Evaluate the Extraction Constant p

A one-stage equilibrium system was used. This involved putting equal volumes of the external and organic solvent with certain amount of the carrier into a closed vessel. The mixture was stirred. The efficiency was calculated by measuring the concentration of cadmium in both phases before and after the experiment.

3.4.2. Procedures for Experiments to Evaluate the Stripping Constant q

From Equation (8), $Ci^* = q\ Cm^*$, $Ci^* = Ci$ and $Cm^* = Cm$ in the system

A one-stage equilibrium system was used. This involved putting equal volumes of the internal and organic solvent with certain amount of the carrier into a closed vessel. The mixture was stirred. The efficiency was calculated by measuring the concentration of cadmium in both phases before and after the experiment. Thus, an stripping efficiency curve can be obtained.

3.4.3. Procedures to Find p and q

(1)   Read the value of Ce/Ce_0 from experimental curve when $t \rightarrow \infty$

(2)   From $Ce_\infty/Ce_0 = Ve/[Ve + p\ Vm]$, $Vm = q\ Vi$, we can have, $q = f(p)$

(3)   From analytical solution of Ce/Ce_0 vs t with p and q as parameter, find the best value of p and q that gives the best representation of experimental data. Analytical solution from Zhou [22] is:

$$Ce/Ce_0 = 3/B+3 + \Sigma \, 2B/ \, (3B+B2+ bn2 +G \, bn2 \, (Gbn2 -2B-1) \; e-bn2/\omega\tau$$

where B, G, bn, ω are defined in [22]; τ is the dimensionless time , $\tau= De \, t/R^2$

- Computer programs are available for regression analysis to find best values of the parameters.

(1) Pick a value of p

(2) Evaluate q from $Ce_\infty/Ce_0 = Ve/[Ve + p \, Vm]$.

(3) Entering data and equation

(4) Outcome is the best value of p

3.5. Theoretical Calculation to find p and q

(1)   Write the quilibrium reaction at the interfaces (external-membrane and

membrane-internal).

(2)   Find or decide what n should be?

(3)   Theoretical calculation of K from thermodynamics data: a semi-empirical

equations

CHAPTER 4

EXPERIMENTAL MATERIALS AND PROCEDURES

4.1. Preparation of ELM and Procedures

The cadmium solution was prepared by dissolving cadmium sulfate ($3CdSO_4$ $8H_2O$) in deionized water. The membrane phase was formed with Exxsol D 80, a diluent, di(2-ethylhexyl) phosphoric acid (D2EHPA) (Figure 1-2), a carrier, and ECA 4360J (Figure 1-3), a surfactant. The ELM was formulated by adding sulfuric acid to the membrane phase and then emulsified in a Warring blender for 30 minutes at 10,000 rpm. The ELM was cooled to ambient temperature for 30 minutes. Then, the prepared emulsion was dispersed in an agitated vessel with the cadmium solution in a volume ratio of 1/10. The agitation speed was monitored by a stroboscope (AMETEK 1723). Samples were collected periodically for separation in a centrifuge and the aqueous phase was removed for further measurement. The pH of a sample was measured by a pH meter (Atiorion Model 310). The cadmium concentration was measured by a flame atomic absorption spectrophotometer (Smith-Hieftje 12)

CHAPTER 5

RESULTS AND DISCUSSION

5.1. The Effect of Buffer Solution on Cd Removal via ELM

Results with no buffer, and the acetic acid/sodium peroxide, and sodium phosphate/citric acid buffer systems are shown in Figure 5-1. According to the models described in chapter 3, and data presented by Raghuraman, et al. [14], the extraction rate should drop sharply while the pH value of the external phase decreases. Thus, a buffer solution is needed to maintain the pH of the external phase around 4 during the operation for a better performance.

In Figure 5-2, the pH drops sharply in the external phase without a buffer solution, while the pH remains constant in the sodium hydroxide and acetic acid buffer solutions. After 30 minutes of operation, the extraction efficiency is 13 % in no buffer condition, 75 % in sodium and acetic acid solution, and up to 84% in sodium phosphate and citric acid buffer solution. Thus, the Na_2HPO_4 and citric acid buffer system was used in the later experiments.

It is also seen in Figure 5-3 that sodium hydroxide influences the membrane performance. As shown in Figure 5-3, when more sodium peroxide was added to the system, the extraction performance decreases. It is possible that sodium peroxide affects the stability of the membrane.
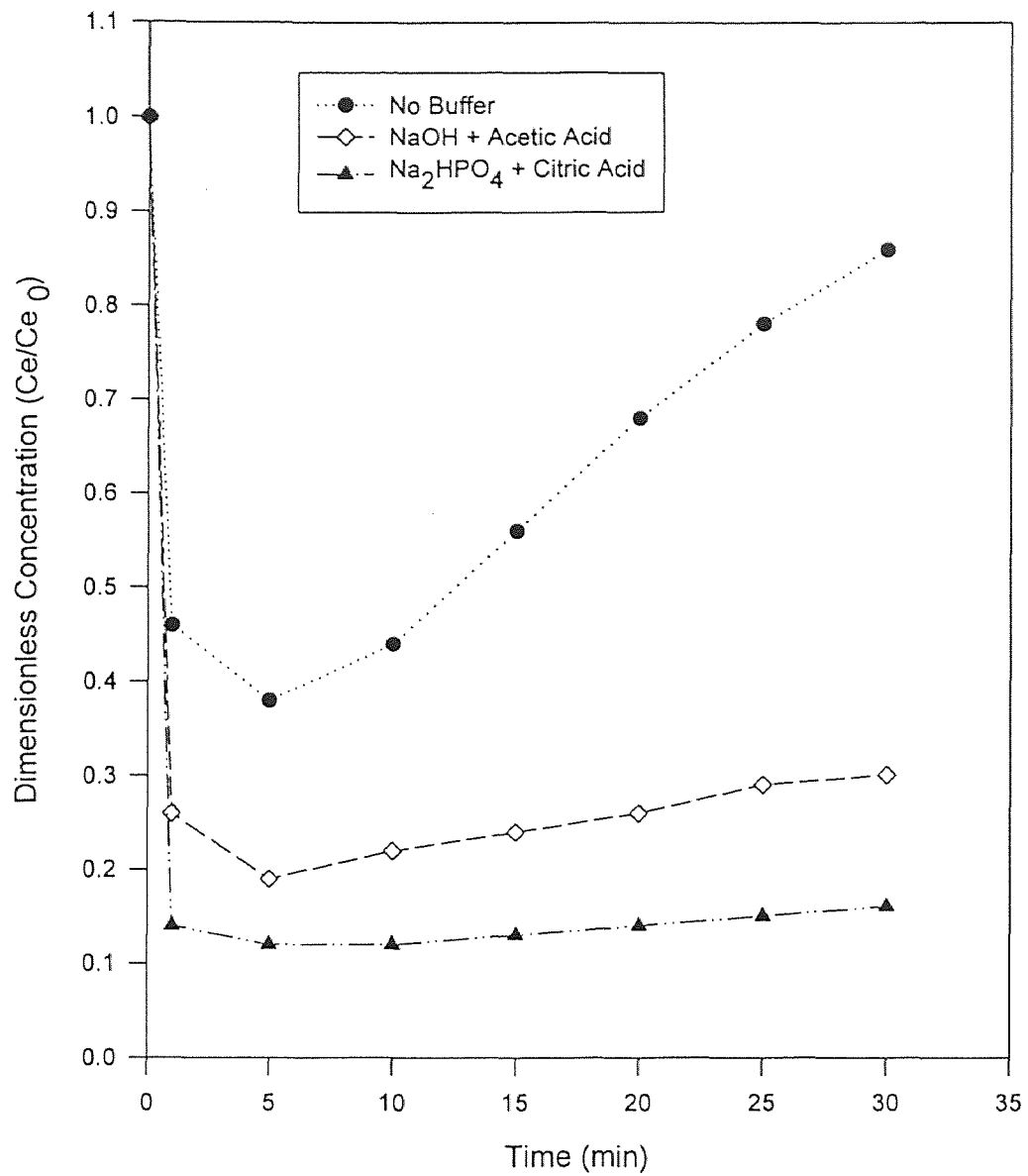
Figure 5-1   The Effect of the buffer Solutions in the ELM System

Membrane Phase 82 wt %: 5 wt % D2EHPA, 5 wt % ECA 4360J,
90 wt % Exxsol D 80
Internal Phase 18 wt %: 3M Sulfuric Acid
Impeller Stirring Speed: 300 rpm
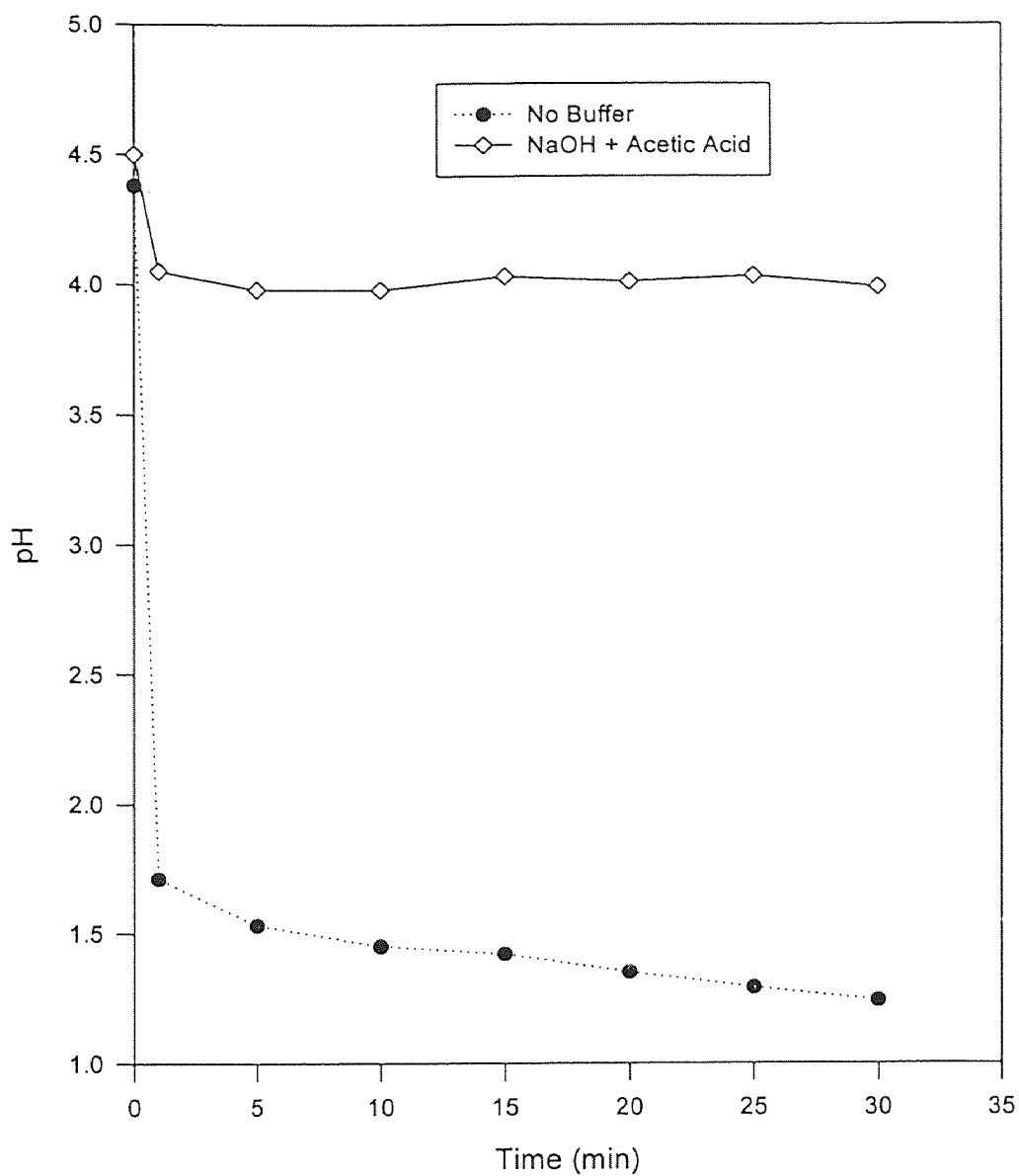
Figure 5-2 The pH of the External Phase with and without Buffer Solutions

Membrane Phase 82 wt %:5 wt % D2EHPA, 5 wt % ECA 4360J, 90 wt % Exxsol D 80
Internal Phase 18 wt %: 3 M Sulfuric Acid
Impeller Stirring Speed: 300 rpm
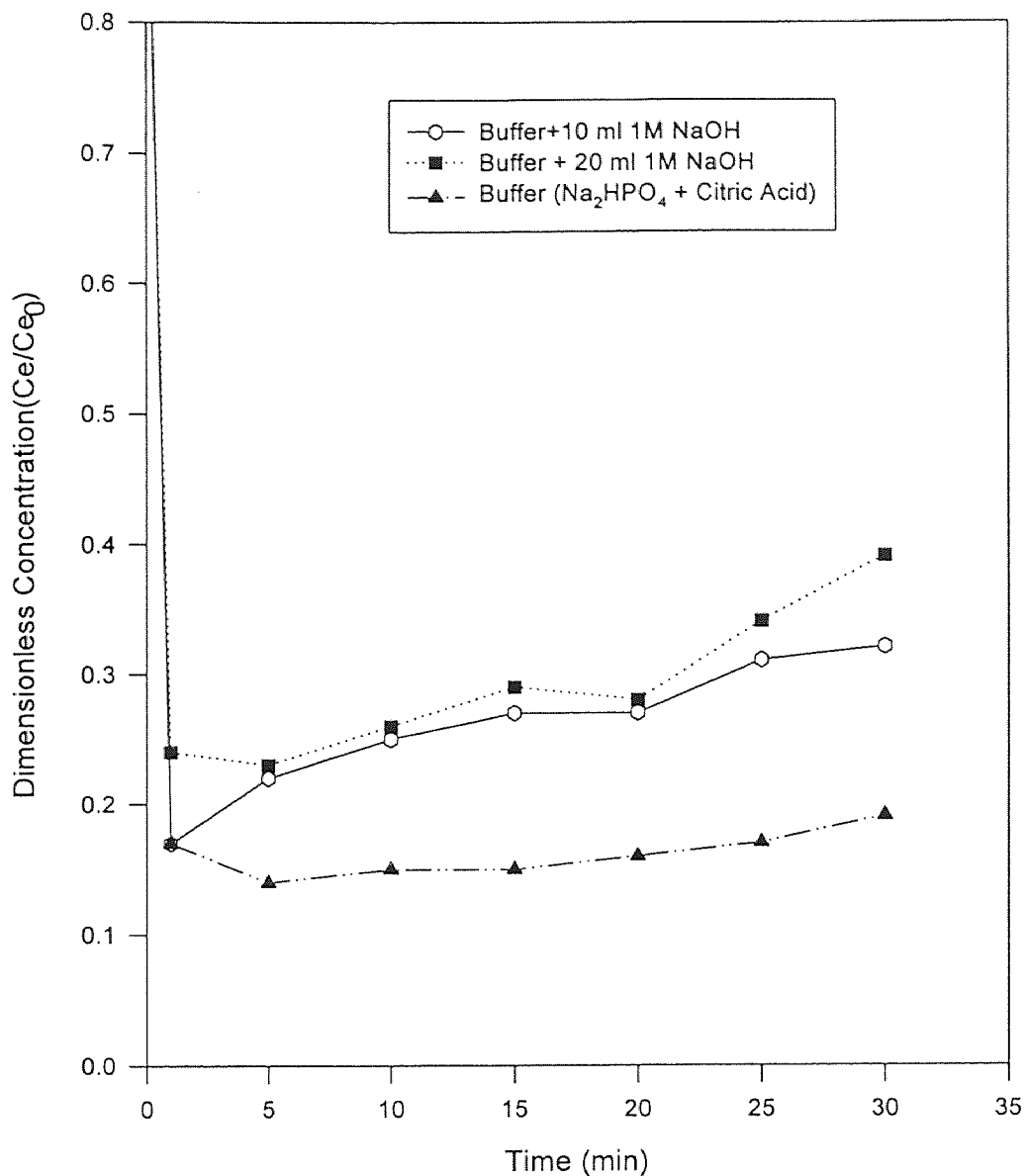
Figure 5-3   The Effect of Sodium hydroxide Concentration in the External Phase on the ELM Performance

Membrane Phase 82 wt %: 5 wt % D2EHPA, 5 wt % ECA 4360J, 90 wt % Exxsol D 80
Internal Phase 18 wt %: 3M Sulfuric Acid
Buffer Solution: 0.4M Sodium Phosphate + 0.2M Citric Acid
Impeller Stirring Speed: 300 rpm

5.2. The Effect of Internal Phase Concentration

Results of different acidity of the internal phase stripping agent are shown in Figure 5-4. The concentrations of sulfuric acid used were 1M, 3M, and 6M respectively while the other parameters were fixed. The best performance was obtained of 6M sulfuric acid in the internal phase. It could be explained that the more acidic the internal phase, the greater the driving force to strip cadmium ion from metal-extractant complex. The influence of the acidity in the internal phase on the ELM performance was also presented in Equation (22). This fact was also observed by Wang [21]. He found q (the stripping partition function at membrane-internal interface) to increase with increasing internal phase HNO_3 concentration. Thus, acidity improves membrane performance.

It was also found that 6M sulfuric acid was most viscous, and therefore resulted in a more stable emulsion liquid membrane system. The membrane with 1M sulfuric acid as stripping phase had the weakest membrane. It generally broke down after 10 minutes operation leaking the metal out to the external phase. Thus, its efficiency plummeted from 55% to 30 %, while the efficiency could be maintained at 92% in the 6M condition for a period 30 of minutes.

Figure 5-4   The Effect of the Internal Phase Stripping Agent
Concentration on the ELM Performance

Membrane Phase 82 wt %: 5 wt % D2EHPA, 7 wt % ECA 4360J,
88 wt % Exxsol D 80
Internal Phase 18 wt %: 3 M Sulfuric Acid
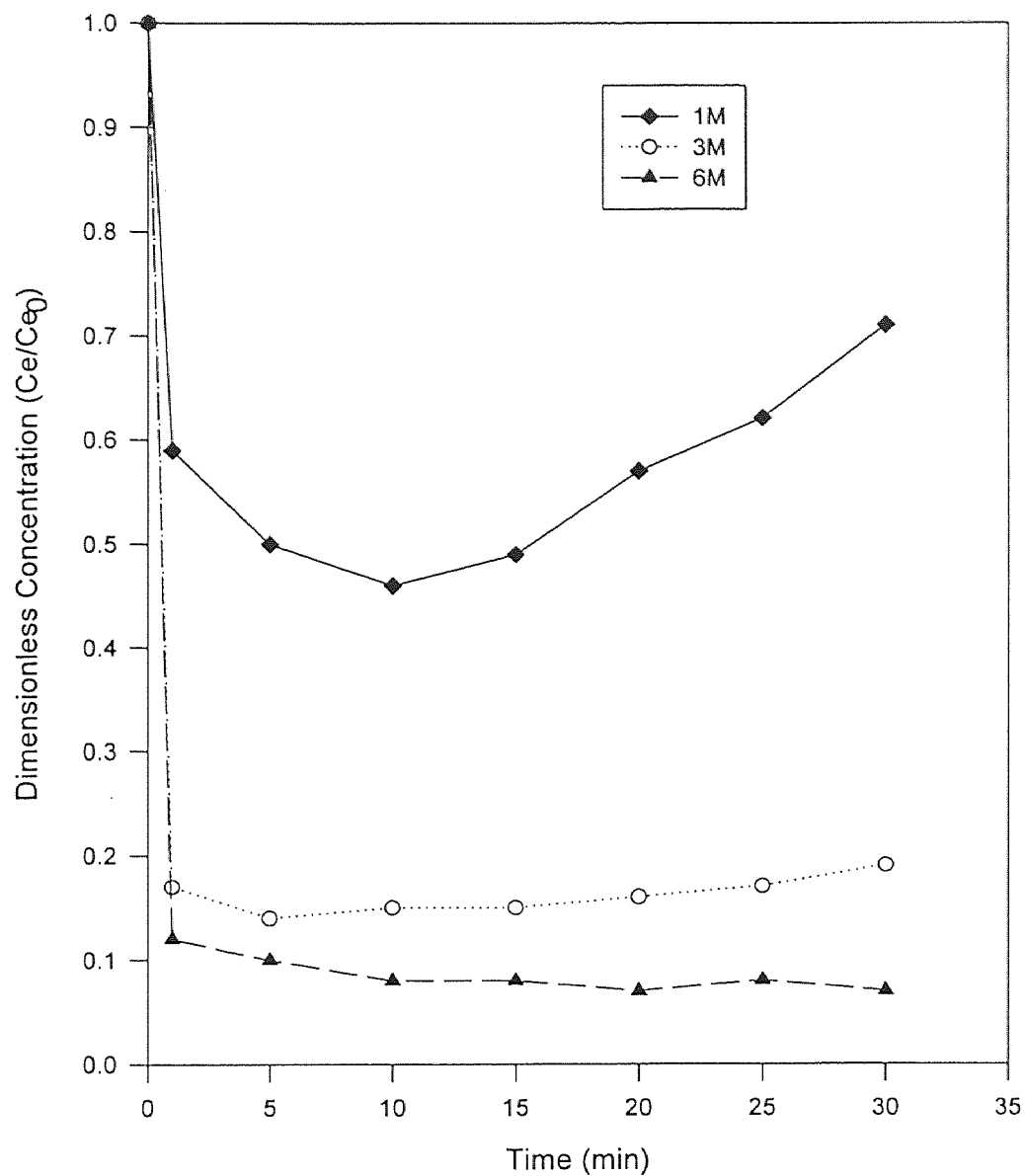Buffer Solution: 0.4M Sodium Phosphate + 0.2M Citric Acid
Impeller Stirring Speed: 300 rpm

5.3. The Effect of Initial External Phase pH

Results with different initial pH of the external phase are shown in Figure 5-5.The higher pH of the external phase results in a faster extraction rate during the first minute of these operations. The faster extraction rate could be because the driving force of the external phase is higher when the initial pH of the external phase is higher, compared with the sulfuric acid in the stripping phase. According to chapter 3, the more protons in the external phase, the less p (the extraction partition function at the external-membrane interface) will be. Therefore, it will perform less efficiently in the theoretical extraction function.

After 30 minutes of operation, the efficiency reaches 92% when the initial pH is higher than 5.0. It only can approach 85%, while the initial external phase is lower than 4.3. It is also found that if the initial pH is higher than 6.0, the cadmium in the external solution precipitates and affects the experiment performance.

Figure 5-5   The Effect of the Initial pH in the External
Phase of the ELM System

Membrane Phase 82 wt %: 5 wt % D2EHPA, 7 wt % ECA 4360J,
88 wt % Exxsol D 80
Internal Phase 18 wt %: 6 M Sulfuric Acid
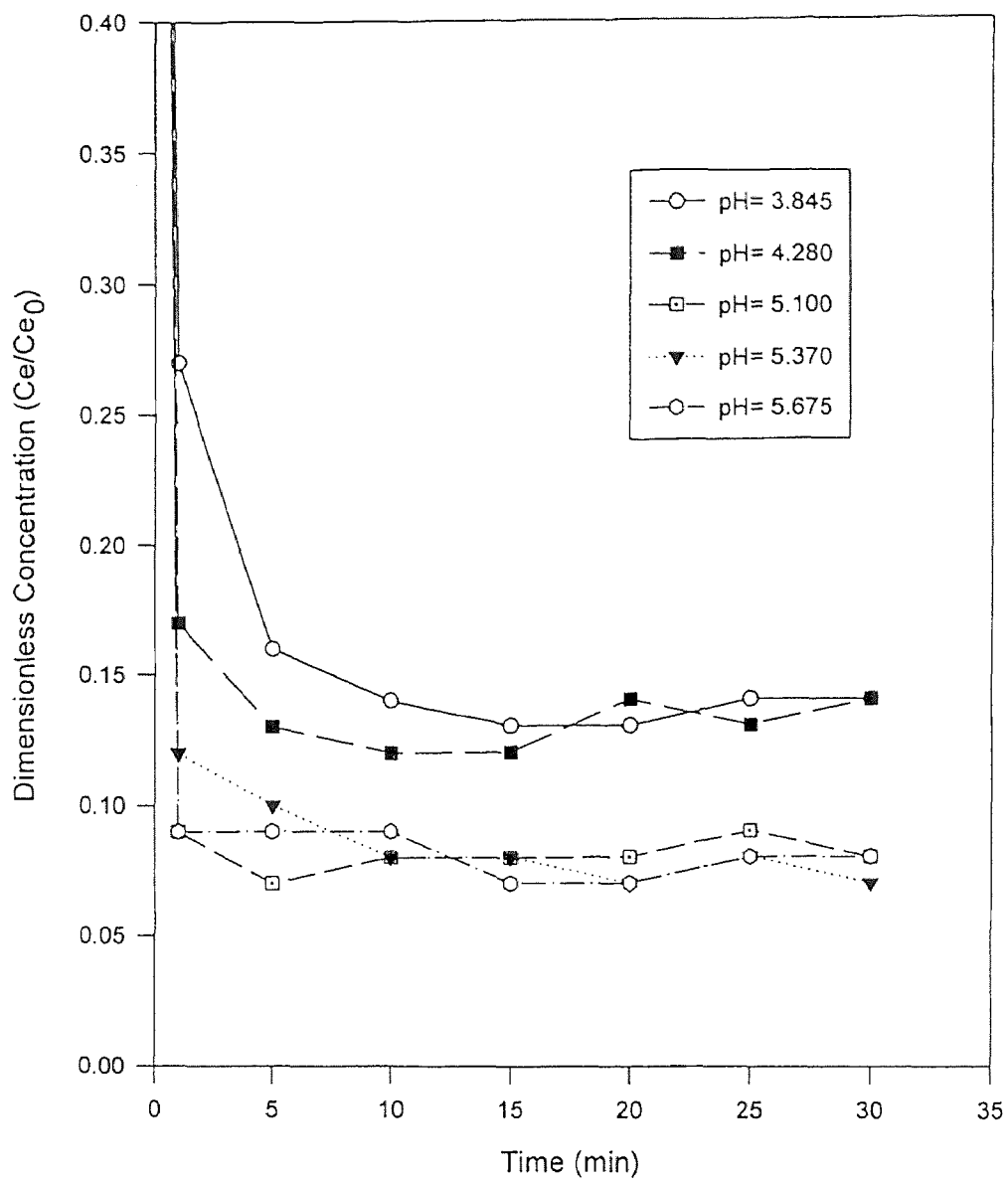Buffer Solution:0.4M Sodium Phosphate + 0.2M Citric Acid
Impeller Stirring Speed: 300 rpm

5.4. The Effect of Initial External Phase Concentration

Results of different initial cadmium concentrations in the external phase are shown in Figure 5-6. Although the 844 ppm (μg/dm^3) has a higher driving force than 360 ppm, the former had a lower pH drop in the operation than the latter.

From theory, the hydrogen ion concentration is a square function, however, the cadmium concentration in the equilibrium equation is linear. Possibly the driving force of the hydroxide ion is more important than the cadmium concentration. Ninety percent of the cadmium could be extracted in the 360 ppm case, and 87% at 844 ppm. This implies that the better results will be approached, if the pH can be controlled. The second stage of operation will also have the efficiency of the first at the same pH conditions, and it can be used in series operation.
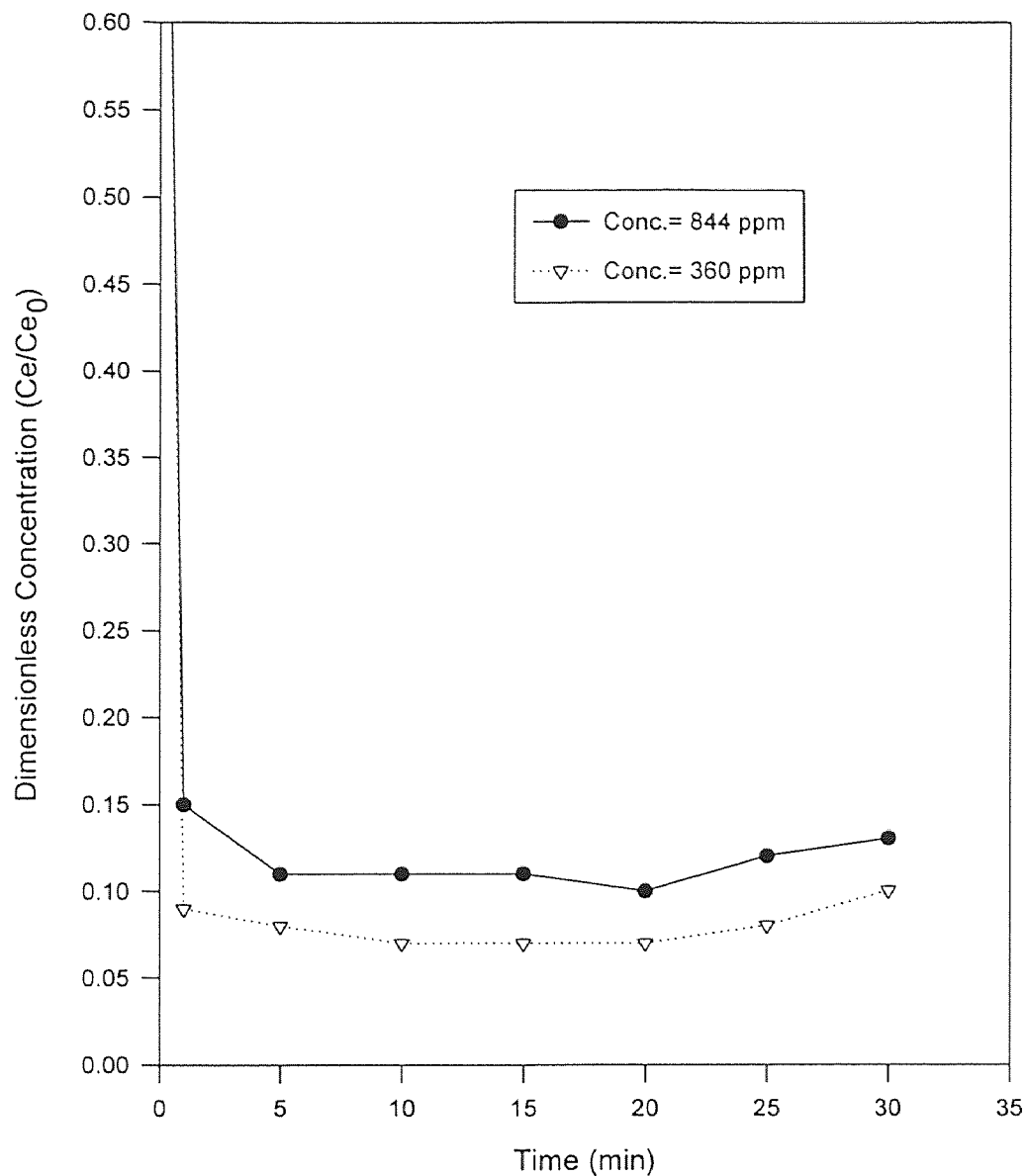
Figure 5-6   The Effect of the Initial Cadmium Concentration on the Extraction Efficiency in the ELM System

Membrane Phase 82 wt %: D2EHPA, 7 wt % ECA 4360J, rest: Exxsol D 80
Internal Phase 18 wt %: 6 M Sulfuric Acid
Buffer Solution:0.4M Sodium Phosphate + 0.2M Citric Acid
Impeller Stirring Speed: 300 rpm

5.5. The Effect of Extractant (D2EHPA) Concentration

Results of seven different concentrations of D2EHPA from 0.1% to 20% are displayed in Figure 5-7. It verifies that it is not true that better results are obtained by adding more extractant to the ELM. The cadmium in the external phase decreases sharply in short time, while the D2EHPA is 20%, but rises again after 5 minutes. It may be explained that the cadmium formed a metal-D2EHPA complex quickly when the extractant concentration was higher. It provided more chances to form a metal-extracant complex but much more protons are produced in a short time and diffused out of the membrane. The protons will lower the pH of the external phase and slow down the mass transfer rate. Also, there could be a problem of less surfactant to stabilize the membrane and the ELM of 20% D2EHPA would break during the operation.

Figure 5-7   The Carrier Concentration Effect on the Cadmium
Extraction Efficiency in the ELM System

Membrane Phase 82 wt %: D2EHPA, 7% wt ECA 4360J,
rest Exxsol D 80
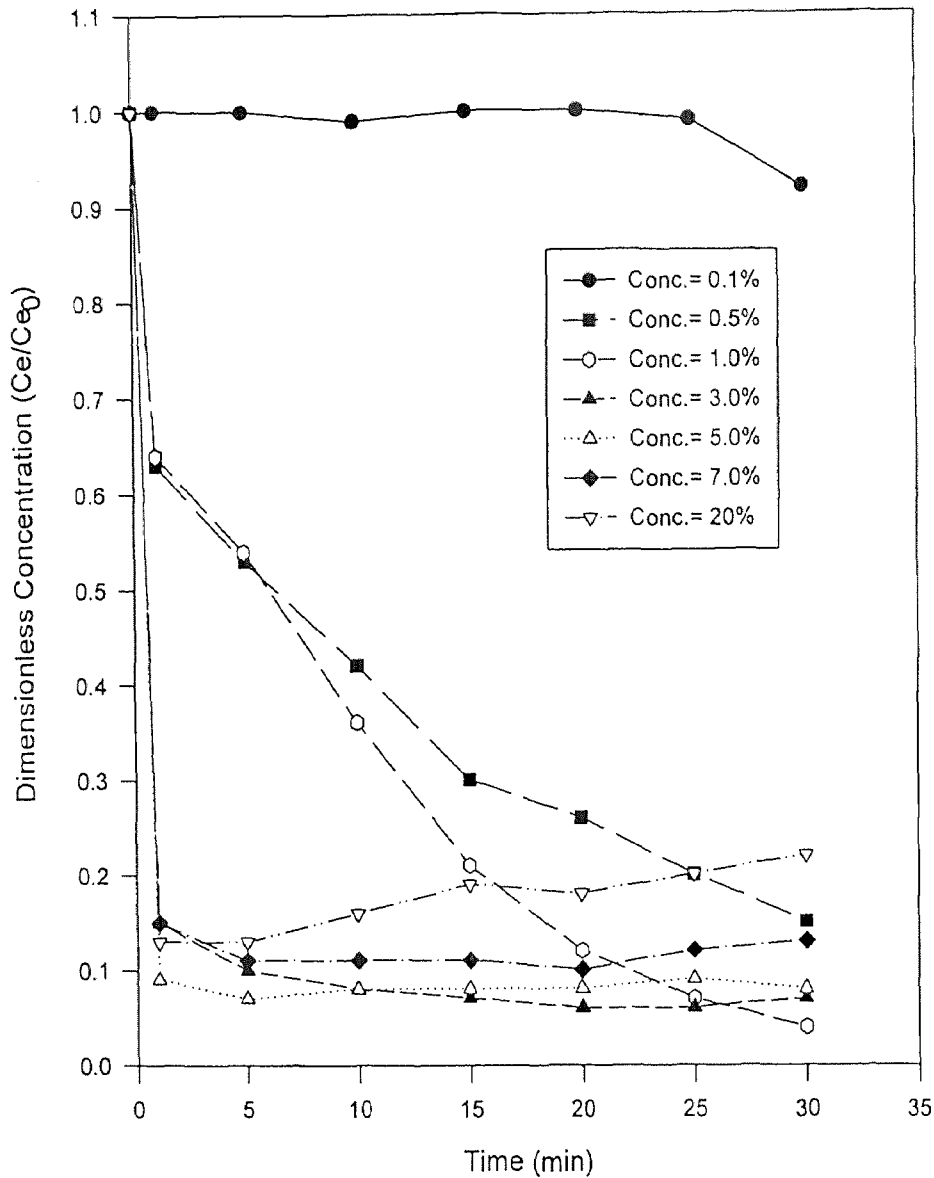Internal Phase 18 wt %: 6M Sulfuric Acid
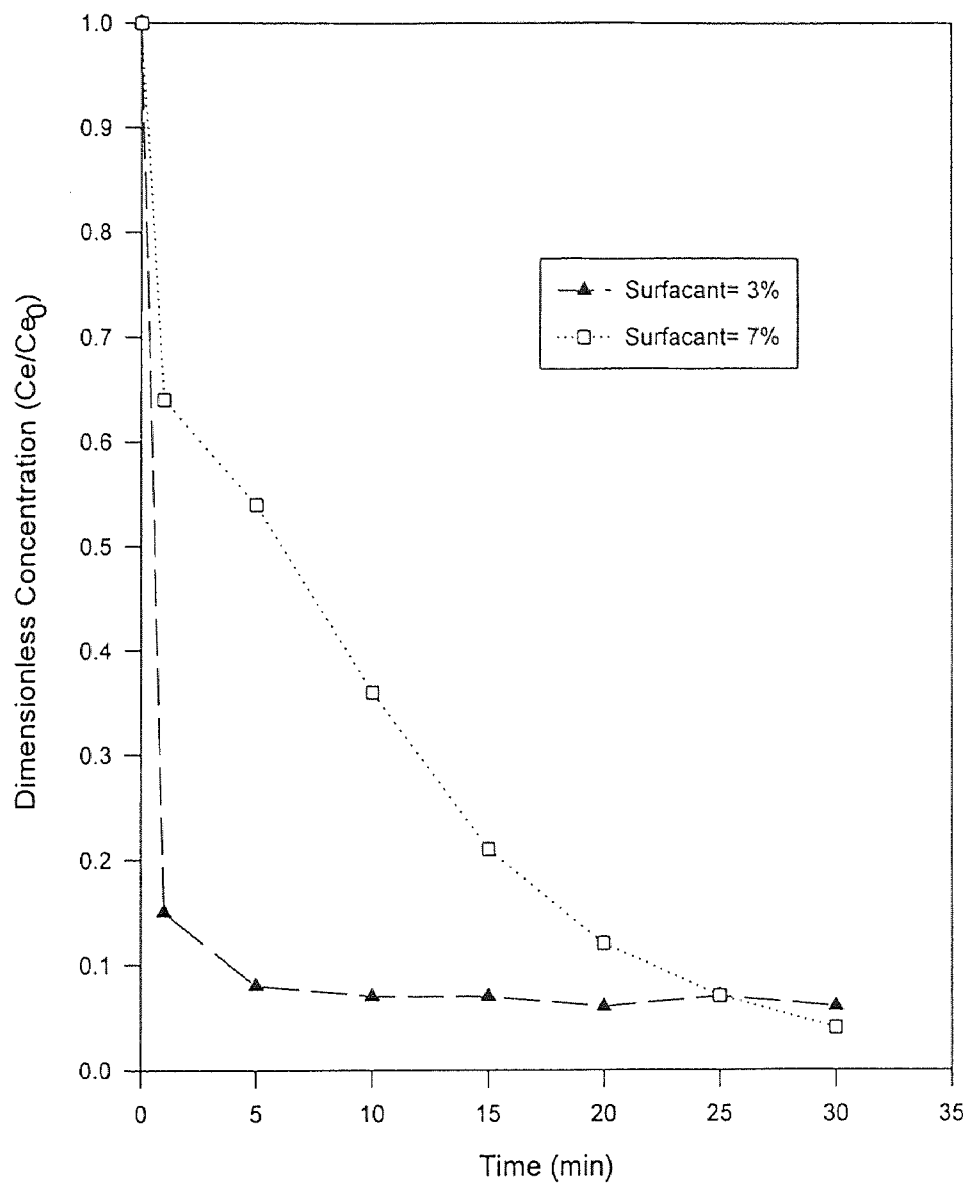Buffer Solution:0.4M Sodium Phosphate + 0.2M Citric Acid
Impeller Stirring Speed: 300 rpm

5.6. The Effect of Surfactant (ECA 4360J) Concentration at Different RPM

Results of a 3 wt % and a 7 wt % of ECA 4360J in the membrane at a 300 rpm stirring rate are shown in figure 5-8. The extraction rate in the 3% surfactant membrane system is faster than in the 7% system at a 300 rpm stirring rate. The equilibrium is reached within five minutes in the 3% ELM system, while equilibrium was not attained after thirty minutes in the 7% system. After 25 minutes, both systems show the same extraction efficiency. The 7% ELM system, has a little better performance than in the 3% one after thirty minutes of operation.

Results of the 3% and 7% ELM system at 350 rpm are shown in Figure 5-9. The 3% system has a faster mass transfer rate than the 7% one in the first five minutes at 350 rpm. However, the 7% ELM system presents better overall performance after ten minutes.

The 3% ELM system shows no difference in the first minute extraction at 300 rpm and 350 rpm, but it reaches a balanced status after five minutes at 300 rpm. At 350 rpm, the 3% ELM system continues to reduce cadmium from the external phase. Thus, adding more surfactant stablizes the membrane and enables high agitation rate which in turn results in a better extraction.

Figure 5-8   The Surfactant Concentration Effect on the Cadmium
Extraction Efficiency in the ELM System at 300 RPM

Membrane Phase 82 wt %:1 wt % D2EHPA, ECA 4360J,
rest Exxsol D 80
Internal Phase 18 wt %:   6M Sulfuric Acid
Buffer Solution: 0.4M Sodium Phosphate + 0.2M Citric Acid
Impeller Stirring Speed: 300 rpm
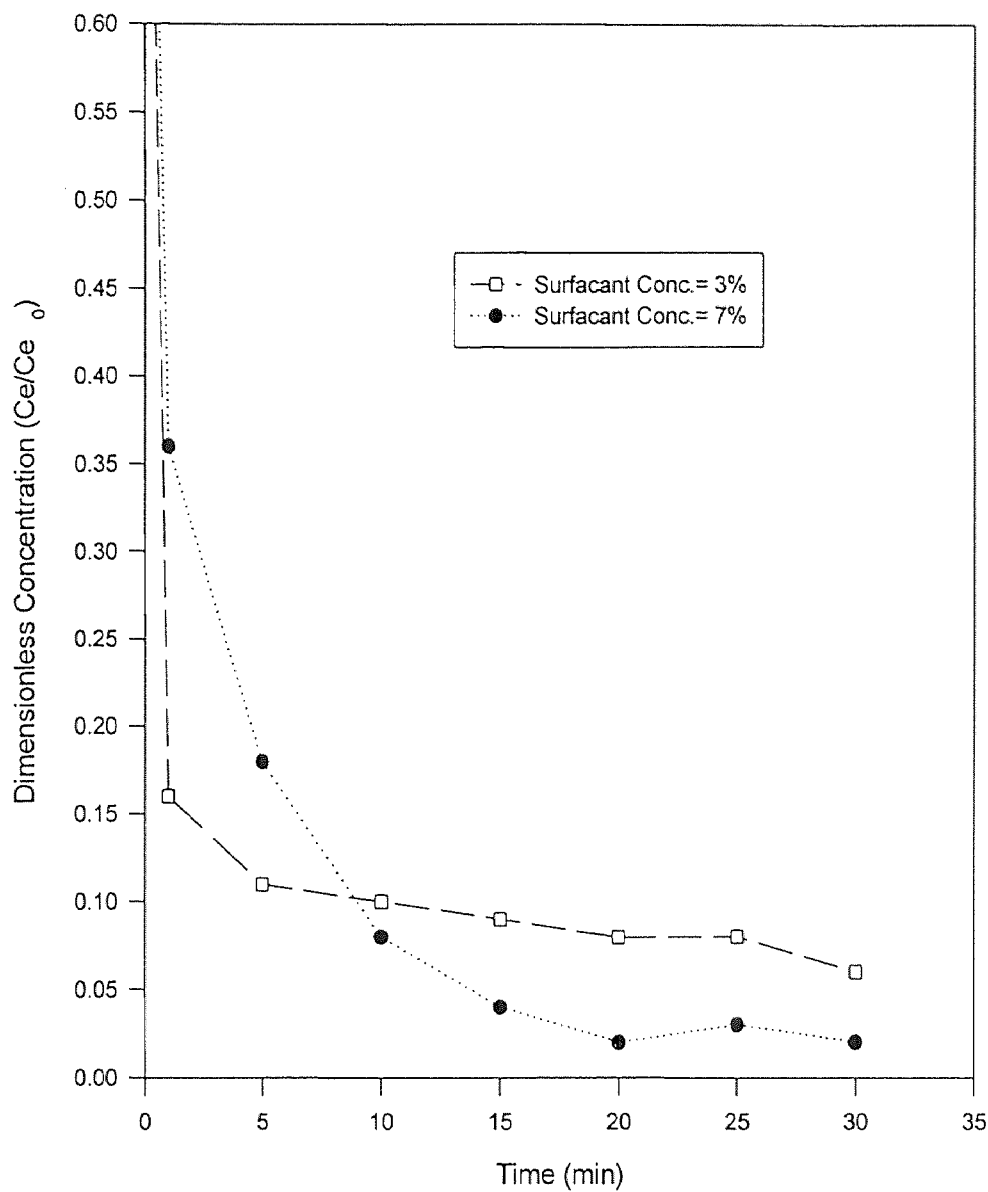
Figure 5-9   The Surfactant Concentration Effect on the Cadmium
Extraction Efficiency in the ELM System at 350 RPM

Membrane Phase 82 wt %:1 wt % D2EHPA, ECA 4360J,
rest Exxsol D 80
Internal Phase 18 wt %: 6M Sulfuric Acid
Buffer Solution: 0.4M Sodium Phosphate + 0.2MCitric Acid
Impeller Stirring Speed: 350 rpm

5.7. Selectivity of Cadmium and Sodium

Results of selectivity between cadmium and sodium in the external phase are presented in Figure 5-10. The sodium phosphate/citric acid buffer solution has a lot of sodium in it. This experiment was designed to identify the selectivity of the membrane towards the sodium ions on the cadmium ions during mass transfer process. It was found that 85% of the cadmium was extracted within the first minute and 97% was extracted after thirty minutes. Thus, it can be seen that most of the extraction occurs at the beginning of the process. However, only 1% of the sodium was removed after the experiment. It could be explained that the extractant (D2EHPA) does not react with an alkali metal, such as sodium, but can form a complex with cadmium (23).

Figure 5-10   The Selectivity of Cadmium and Sodium
Extraction in the ELM System

Membrane Phase 82 wt %:1 wt % D2EHPA, 3% ECA 4360J,
96% Exxsol D 80
Internal Phase 18 wt %: 6M Sulfuric Acid
Buffer Solution: 0.4M Sodium Phosphate + 0.2M Citric Acid
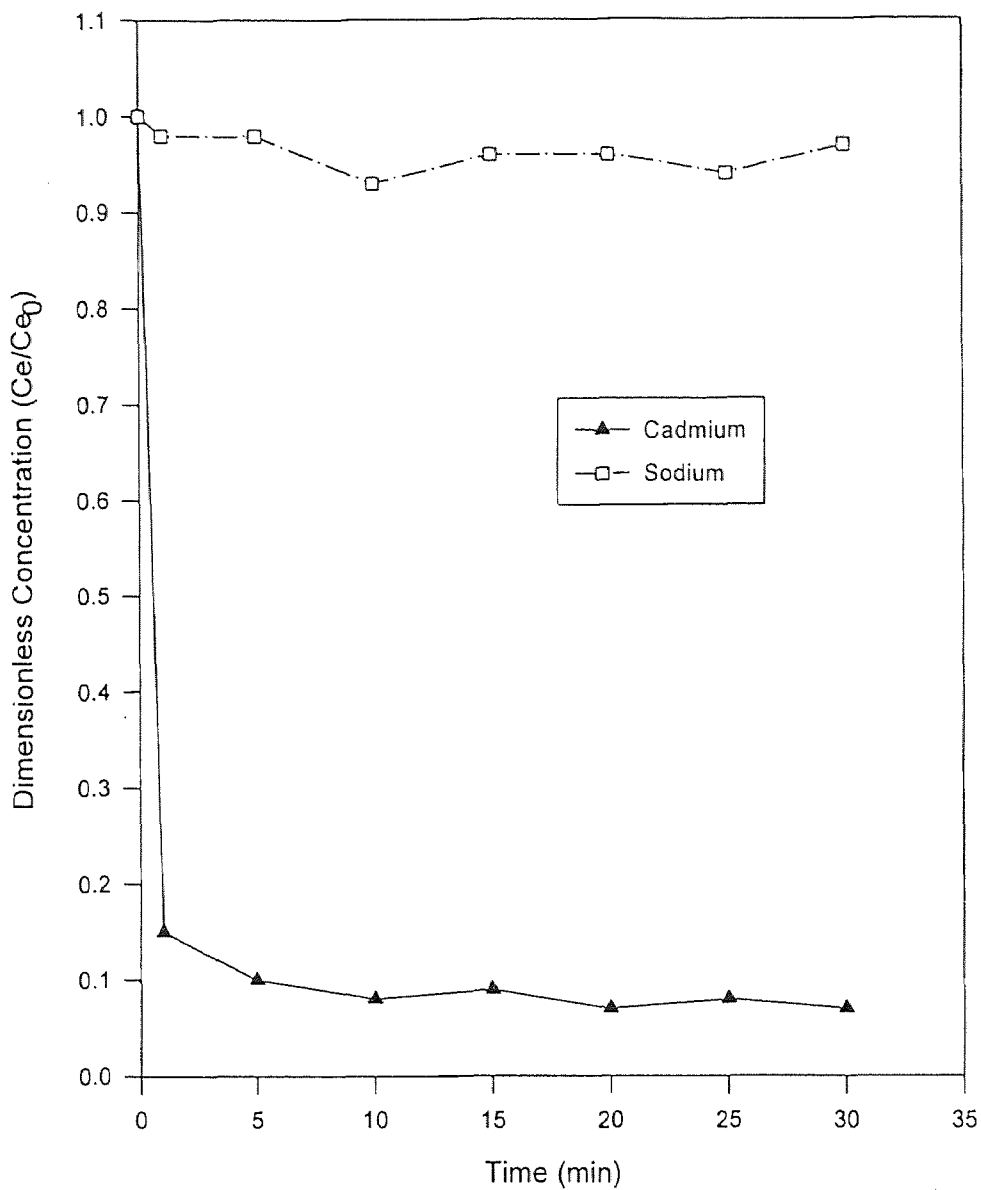Impeller Stirring Speed: 350 rpm

5.8. The Optimal Operating Conditions for Cadmium Removal by ELM

The optimal operating conditions in extracting cadmium out of wastewater by a ELM

system is displayed in Table 5-1.

Table 5-1   The Optimal Operating Conditions for the Cadmium
Extraction Out of the Wastewater by a ELM System

Initial cadmium concentration	1000 ppm (Approx.)
Volume ratio of the two phases	Ve: Vm = 10 : 1
Buffer solution and external phase pH	(Sodium phosphate, citric acid), pH= 5.0
Internal phase stripping agent	6M H_2SO_4
Agitating speed	300 RPM
Membrane phase composition (Membrane phase : Internal phase)	3 wt % D2EHPA, 3 wt % ECA 4360 J, 96 wt % Exxsol D 80 (82 wt % : 18 wt %)

CHAPTER 6

CONCLUSIONS

An experimental study on the removal of cadmium from wastewater by emulsion liquid membrane was conducted successfully in this work. At optimal conditions, as low as 3 wt % of carrier in the membrane phase can extract 98 % of cadmium out of the feed stream within thirty minutes. An increase of the surfactant from 3 wt % to 7 wt % in the membrane phase could help prevent the membrane from breaking and leaking when the impeller stirring speed is increased from 300 to 350 rpm. Although reduced amounts of carrier and surfactant in the ELM system would result in using more organic solvent, the low cost of the solvent makes this matter economically feasible.

In this study, most of the operations have 90 % efficiency by extracting in one-stage for five minutes. Under these conditions, equilibria can be shown in the operations, and they have a fast kinetic phenomena, which is suitable for continuous operation. It was found that the more acidic the internal phase, the better the performance. The viscosity of the membrane could be an index to whether the ELM would be stable or not because of the stripping reagent. The increase of the carrier concentration to 20 % will not help extraction performance in opposition to the performance of Equation (14), where higher wt % of the carrier should have given a better performance.

A model that describes the extraction process was described been put forward. It has, however, not been used to verify the experimental data at this time. This is a suggested for further research.

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