



Study on removal of cadmium from wastewater by emulsion liquid membrane

Hamid R. Mortaheb^{a,*}, Hitoshi Kosuge^b, Babak Mokhtarani^a, Mohammad H. Amini^a,
Hamid R. Banihashemi^a

^a Chemistry and Chemical Engineering Research Center of Iran, Tehran, P.O. Box 14335-186, Iran

^b Chemical Engineering Department, Tokyo Institute of Technology, Tokyo, 152-8552, Japan

ARTICLE INFO

Article history:

Received 12 July 2008

Received in revised form 7 October 2008

Accepted 7 October 2008

Available online 19 October 2008

Keywords:

Liquid membrane

Emulsion

Cadmium

Surfactant

Removal efficiency

ABSTRACT

Removal of cadmium from wastewater using emulsion liquid membrane (ELM) is studied in the present study. A polyamine-type surfactant was used for stabilizing the emulsion phase. Tri-iso-octyl amine (TIOA) has been used as a carrier for transferring of cadmium through the membrane. The results show good performance in the separation process. To determine the optimum operation conditions, the effect of several parameters such as surfactant concentration, carrier concentration, pH of external and internal phases, oil to internal phase volume ratio, emulsion to external phase volume ratio, solvent type, solute concentration, presence of iodide and chloride in external phase, and mixing conditions have been investigated.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Cadmium as a toxic heavy metal, which is found in industrial discharges of different industries such as manufacturing of cadmium–nickel batteries, phosphate fertilizers, pigments, stabilizers, alloys, and electroplating industries, has very harmful environmental impacts [1,2]. In addition, cadmium exists naturally as a minor constituent of base metal ores and coal deposits. As a result, it exists in effluent of related industries, e.g. zinc hydrometallurgical processes.

Various methods have been applied for treatment of wastewaters containing cadmium. Precipitation of the metal hydroxide and filtration is mainly used when higher concentrations are treated [3,4]. In contrary to its simplicity, it needs adjusting of pH to alkaline conditions while most of these wastewaters have an acidic nature. Also, disposal of produced sludge is considered as another problem in this process. Ion exchange operation by ionic resins [5], clays [6] or zeolites [7] is considered as an alternative method. However, exhausted ion exchange materials must be regenerated by adding chemical reagents, and this causes a serious secondary pollution. Adsorption of cadmium on the surface of materials such as carbon [8] or alumina [9] gives good results but those methods are expensive when pure sorbents are employed. Another alternative is to apply a biofiltration process by using microalgal [10] or bacteria

[11]. However, the process needs a constant source of nutrients and strict control of treatment conditions for its consistent and effectiveness operation [12].

Liquid–liquid extraction from aqueous media by using specific extractants is also applied for separation of cadmium [13–17]. The disadvantage of this method is that the large amount of solvent of the extracted phase should be refreshed in a costly stripping step.

On the other hand, removal of heavy metals from wastewater using membrane in the processes such as ultrafiltration and reverse osmosis has been attempted. However, those methods are subjected to the drawback of membrane fouling [18]. Alternatively, separation can be made in an emulsion liquid membrane (ELM) process with significant advantages such as its very high driving force and selectivity, where the separation performance is enhanced by combination of extraction and stripping processes in one step [19–22]. The stability of emulsion is a major problem in industrial application of this process while the emulsions made by commercial emulsifiers show weak performances. In order to overcome this deficiency, a new polyamine-type surfactant, which was previously designed and synthesized in our lab [23], was applied and the performance of the process in removal of cadmium from wastewater is studied in the present research.

2. Basic concept

Liquid membrane process incorporates a dispersed emulsion including organic membrane and aqueous internal phase in a continuous external phase (W/O/W). The solute in the external phase

* Corresponding author. Tel.: +98 21 44580751; fax: +98 21 44580762.
E-mail address: mortaheb@ccerci.ac.ir (H.R. Mortaheb).

Nomenclature

C	concentration of cadmium in external phase at time t [ppm]
C_0	primary concentration of cadmium in external phase [ppm]
C_{acid}	concentration of acid in external phase [M]
C_{aq}	concentration of cadmium in aqueous phase at time t [ppm]
C_{aq}^0	initial concentration of cadmium in aqueous phase [ppm]
$C_{carrier}$	concentration of carrier in organic phase [M]
C_{KI}	concentration of KI in external phase [M]
C_{org}	concentration of cadmium in organic phase [ppm]
C_s	concentration of surfactant in membrane phase [M]
$C_{stripper}$	concentration of stripper agent in internal phase [M]
d_{32}	Sauter mean diameter = $\frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2}$
d_i	globule diameter [m]
d_i	impeller diameter [m]
k_{ext}	mass transfer coefficient in continuous phase [m/s]
K_1, K_2, K_3, K_4	stepwise complex formation constants
K_D	distribution coefficient of cadmium in extraction tests = C_{org}/C_{aq}
n_i	number of globules
N	impeller speed [rpm]
pH_e	pH of external phase at time t
pH_e^0	initial pH of external phase
pH_i^0	initial pH of internal phase
P/V	power consumed by the propeller per unit volume of reaction mixture [W/m^3]
R_{ew}^0	initial volume ratio of emulsion to external phase = V_{em}/V_e
R_{oi}^0	initial volume ratio of oil phase to internal phase = V_o/V_i
t	mixing time [min]
V_{aq}	volume of aqueous phase in extraction tests [cm^3]
V_e	volume of external phase [cm^3]
V_{em}	volume of emulsion phase (= $V_i + V_o$) [cm^3]
V_i	volume of internal phase [cm^3]
V_o	volume of organic phase [cm^3]
We	Weber number = $d_i^3 N^2 \rho_c / \sigma$
<i>Greek letters</i>	
β_n	overall complex formation constant
ρ_c	density of external phase [kg/m^3]
σ	interfacial tension [N/m]

penetrates through the membrane phase, in which carrier is added to solubilize otherwise insoluble solute in the membrane phase. The transferred solute by the carrier reacts with a stripping agent at the interface of the membrane and internal phases and will be trapped in internal phase. The emulsion phase is then broken in a demulsifier and the oil phase is recycled for reusing in the emulsification process.

In the present research, tri-iso-octyl amine (TIOA) is used as the carrier in the membrane phase. Although TIOA and tri-*n*-octyl amine are structural isomers, TIOA was preferred due to its lower price.

The mechanism can be explained as follows:

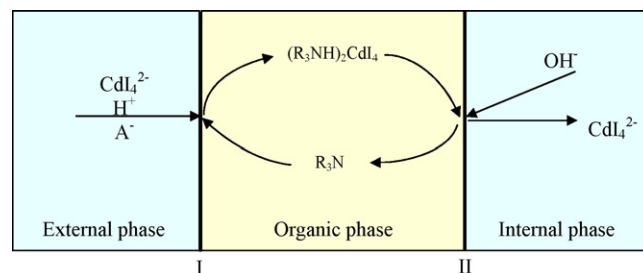
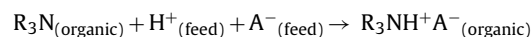
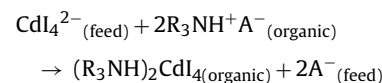


Fig. 1. Co-transport of CdI_4^{2-} and H^+ with TIOA as the carrier.

1. TIOA (shown as R_3N) in the organic phase reacts with H^+ of the external phase at the external-membrane interface to form $R_3NH^+A^-$, where A^- is a counter ion



2. At the external-membrane interface, A^- is replaced by CdI_4^{2-} of $R_3NH^+A^-$



3. NaOH in the stripping solution reacts with the transferred $(R_3NH)_2CdI_4$ at the membrane-internal interface to transfer cadmium into the internal phase

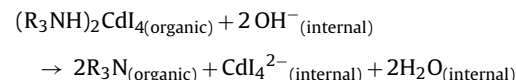


Fig. 1 shows a schematic of the transportation mechanism.

3. Experimental

As described in our earlier research [23], several evidences of emulsion breakage were observed for the emulsions prepared by commercial surfactants. On the other hand, it was found that presence of carrier in the membrane phase may aggravate the instability problems of emulsions [24]. Based on these experiences and in order to increase the stability of liquid membrane, a new polyamine-type surfactant was designed and synthesized in our lab. The synthesis of the new surfactant consists of the following steps:

- (1) thermal degradation of butyl rubber;
- (2) adding a hydrocarbon solvent;
- (3) reaction with maleic anhydride;
- (4) reaction with polyethylene polyamine with low molecular weight.

The characteristics of synthesized surfactant were brought elsewhere [23]. Emulsion breakage could be done by adding about 15% (v/v) petroleum sulphate as demulsifier.

The emulsion is prepared by mixing of the synthesized surfactant, the carrier, an organic solvent, and NaOH solution in a homogenizer (Phycotron, Niton-i Co.) for 15 min with high rotational speed. The emulsion is then gradually added to the external phase, i.e. the feed phase, in a glass cell equipped with a variable-speed propeller. For proper mixing, the cell is equipped with four baffles with 10 cm height, 1 cm width, supported by top and bottom o-rings. 5 ml of mixture is taken from the extraction cell in certain intervals by using a micropipette. The sample, which contains

the emulsion and external phase, is then separated in a decanter. The concentration of cadmium in the samples was measured by atomic absorption spectroscopy (SAS7500A, SII, Seiko Instruments Inc.). Potentiometry titration method was applied for measuring the amount of iodide ion in extraction experiments.

The removal efficiency of cadmium is then calculated by using the following equation:

$$\text{Removal of cadmium} = \left[\frac{C_0 - C}{C_0} \right]. \quad (1)$$

4. Results and discussion

4.1. Effect of surfactant concentration

In our experiments, it was observed that while other conditions are kept constant, increasing concentration of surfactant results in smaller globules. Such a behavior is in accordance with the experimental correlation [25], in which $d_{32} \propto We^{-0.6}$. Since the Weber number is increased by decreasing interfacial tension, it is expected that Sauter mean diameter, d_{32} , will be decreased by increasing interfacial tension due to adding more surfactant. Therefore, increasing surfactant concentration results in higher contact area between the donor and receiving phases, and it may increase the removal efficiency. On the other hand, excessive amount of surfactant may inversely decrease the removal efficiency. As shown in Fig. 2, by increasing of surfactant concentration from 1 to 4%, removal efficiency is increased steadily. However, the increment in efficiency is not significant when the concentration of surfactant is increased from 3 to 4 wt%. Therefore, the optimum concentration of surfactant is determined about 3 wt% of the membrane phase.

4.2. Effect of carrier concentration

The effect of carrier concentration in the oil phase on mass transfer was investigated by batch-wise extraction experiments. Since a wide range of concentration has been reported for cadmium in the wastewater of different industries (10–240 ppm) [26,27], the aqueous phase with an arbitrary concentration of about 117 ppm was mixed with an equal volume of organic phase including solvent (toluene) and carrier with different concentrations. The phases were then separated at the equilibrium conditions. The concentrations of other chemicals in the aqueous phase were selected same as those in the ELM experiments. Fig. 3 shows the distribution coefficient of cadmium between the two phases, $K_D = C_{org}/C_{aq}$,

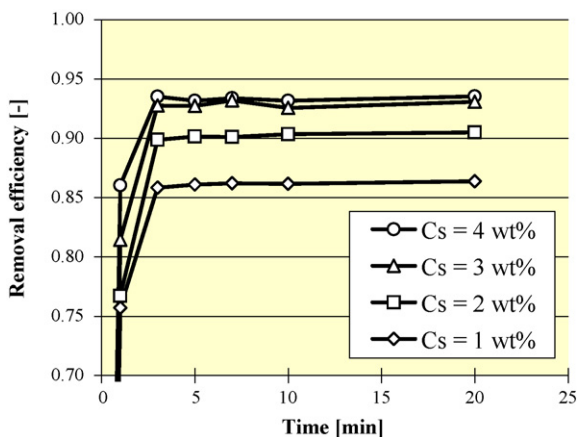


Fig. 2. Effect of surfactant concentration on removal efficiency. $C_0 = 33$ ppm, $R_{oi}^0 = 1$, $R_{ew}^0 = 0.1$, $C_{carrier} = 0.02$ M, $C_{acid} = 0.025$ M, $C_{stripper} = 0.05$ M, and $C_{KI} = 0.01$ M.

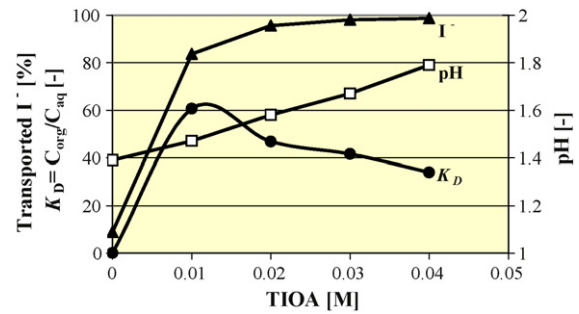


Fig. 3. Effect of carrier concentration on distribution coefficient, transported iodide and pH of the aqueous phase. $C_{aq}^0 = 117$ ppm, $V_o/V_{aq} = 1$, $C_{acid} = 0.025$ M, and $C_{KI} = 0.01$ M.

transported iodide into the organic phase, and pH of the aqueous phase in these experiments. The figure shows that maximum concentration of cadmium in the organic phase is attained where 0.01 M carrier is used and it decreases when more TIOA is added to the organic phase. On the other hand, the pH of aqueous phase and transported iodide into organic phase steadily increase with increasing carrier concentration. Such a behavior can be interpreted as follows.

As the amount of TIOA (shown as R_3N) in the organic phase is increased, the protonation reaction (reaction of mechanism 1) tends to the right hand side and more H^+ will be consumed. This causes increase in pH of the aqueous phase. Also, as the concentration of R_3N increases, anions such as I^- and I_3^- (produced from the reaction of $I^- + I_2 \rightarrow I_3^-$) can compete with CdI_4^{2-} to conjugate with R_3NH^+ . Therefore, although the amount of transported cadmium might be slightly decreased, the transported iodide shows a steady increasing trend.

The effect of carrier concentration on removal efficiency in the ELM experiments is shown in Fig. 4. The figure shows that the removal efficiency increases as the concentration of carrier is increased. However, lower increment is observed as the concentration is increased from 0.02 to 0.04 M. As a result, 0.04 M might be considered as the optimum value of carrier concentration in the organic phase. Higher amounts of carrier may even interfere in the emulsion stability as a demulsifier. It is noticeable that, even in the absence of carrier, cadmium is removed by a slower rate up to about 30%. This might be due to structural similarity of the carrier and surfactant. The structure of the synthesized surfactant includes a number of secondary amines in the polymeric chain and an additional tertiary amine conjugated with two carbonyl groups. Those functional groups have enough basicity to produce the ammonium cation in order to subsequently act as the counter ion for CdI_4^{2-} species to help partial removal of cadmium when no carrier is used in the experiment.

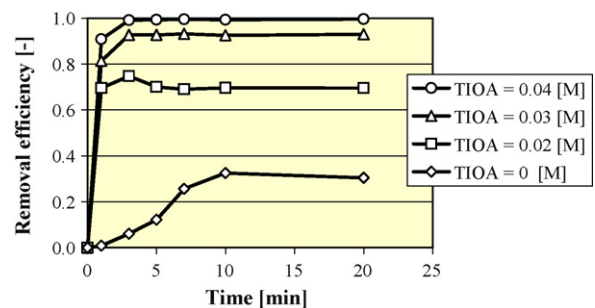


Fig. 4. Effect of carrier concentration on removal efficiency. $C_0 = 33$ ppm, $R_{oi}^0 = 1$, $R_{ew}^0 = 0.1$, $C_s = 3$ wt%, $C_{acid} = 0.025$ M, $C_{stripper} = 0.05$ M, and $C_{KI} = 0.01$ M.

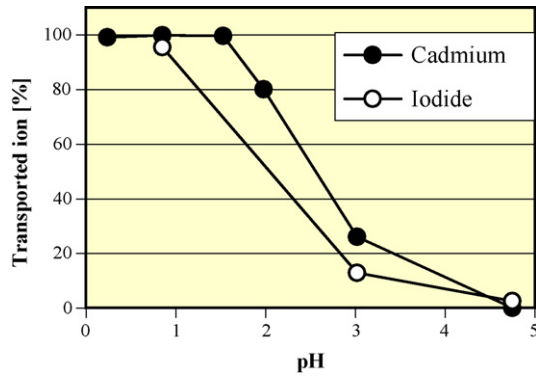


Fig. 5. Effect of pH of external phase on transported cadmium into organic phase. $C_{aq}^0 = 50$ ppm, $V_o/V_{aq} = 1$, and $C_{Kl} = 0.01$ M.

4.3. Effect of pH of external phase

Since H^+ is absorbed by carrier at the external-organic interface to produce R_3NH^+ , the effect of pH of external phase, i.e. availability of H^+ at the interface, on transported cadmium was studied in extraction experiments. The procedure of experiments was the same as described in the previous section. Fig. 5 shows that $pH < 1.5$ is the most appropriate pH of aqueous phase for transferring of solute. It is then decreased by increasing pH. This result is confirmed by ELM experiments as shown in Fig. 6. Among the experiments made by using hydrochloric acid 36% with pHs of 1.6, 2.4, and 3.2, the best removal efficiencies are obtained when pH_e^0 is 1.6 but very close to those when pH_e^0 is 2.4. The dotted lines in the figure also show the variation of pH of external phase with time. As seen, for the external phase with pH_e^0 1.6, the pH remains close to its initial value through the experiment while for the other two experiments with pH_e^0 2.4 and 3.2, pH increases sharply in the earlier times due to consuming of H^+ in the experiment.

4.4. Effect of the type of acid

Experiments were also made to study the effect of type of acid in the external phase. As seen in Fig. 7, when three different acids acetic acid, nitric acid, and hydrochloric acid with the same pH_e^0 of 2.4 is used in the external phase, the removal efficiencies show the following tendency: $CH_3COOH > HNO_3 > HCl$. The trend can be explained by considering the dotted pH_e curves in the figure: Among these acids, pH_e only for the weak acid CH_3COOH does not

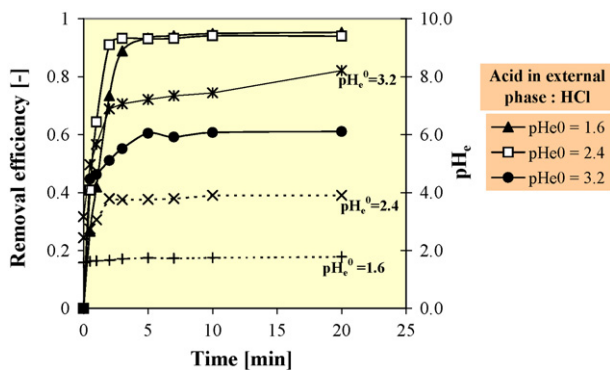


Fig. 6. Effect of pH_e^0 on removal efficiencies (solid lines), and pH_e (dotted lines). $C_0 = 33$ ppm, $R_{oi}^0 = 1$, $R_{ew}^0 = 0.1$, $C_{carrier} = 0.02$ M, $C_{stripper} = 0.05$ M, and $C_{Kl} = 0.01$ M.

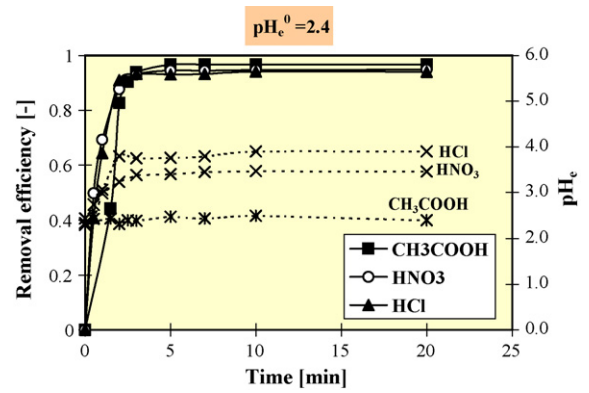


Fig. 7. Effect of acid on removal efficiencies (solid lines), and pH_e (dotted lines). $C_0 = 33$ ppm, $R_{oi}^0 = 1$, $R_{ew}^0 = 0.1$, $C_{carrier} = 0.02$ M, $C_{stripper} = 0.05$ M, and $C_{Kl} = 0.01$ M.

change through the experiment. This is because of higher concentration of acetic acid, which was used to obtain the same pHs for all of the experiments. The available H^+ , which is obtained by gradual dissociation of acetic acid, facilitates the transferring of cadmium. It can be concluded that removal efficiency is rather associated to the availability of H^+ in the external phase than to the acidity of the applied acid.

4.5. Effect of pH of internal phase

The effect of pH of internal phase was investigated by experiments with different pHs of internal phase using NaOH as the stripping agent. The results are shown in Fig. 8. As seen in the figure, the removal efficiencies increase slightly as the pH of internal phase is increased. Although the best results were obtained when pH_i^0 is 13.6 but the pH of external phase in that experiment was increased from initial value of 1.7 to 11.5 while in all of the other experiments it varied in the range of 1.6–1.8. This shows an adverse diffusion of OH^- from internal to external phase when pH_i^0 is 13.6 that may aggravate the emulsion stability and possible precipitation of cadmium hydroxide in the external phase. Therefore, the pH of about 12.3 might be considered as the desired pH for the internal phase.

4.6. Effect of volume ratio of oil phase to internal phase

As volume ratio of the oil phase to internal phase (R_{oi}^0) increases, the strength of emulsion wall and its resistance against breakage increase. Therefore, it is expected to have more stable emulsion by

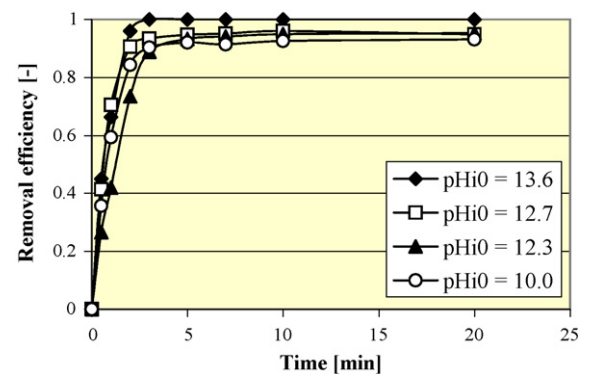


Fig. 8. Effect of pH_i^0 on removal efficiencies. $C_0 = 33$ ppm, $R_{oi}^0 = 1$, $R_{ew}^0 = 0.1$, $C_{carrier} = 0.02$ M, $C_{acid} = 0.025$ M, and $C_{Kl} = 0.01$ M.

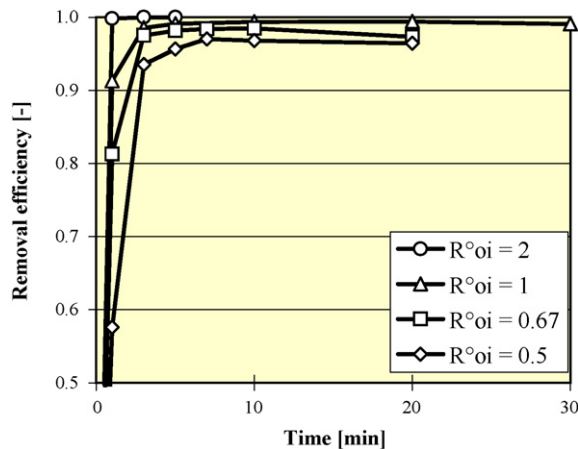


Fig. 9. Effect of oil to internal phases ratio on removal efficiency. $C_0 = 33$ ppm, $R_{ew}^0 = 0.2$, $C_s = 3$ wt%, $m_{carrier} = 0.09$ gr, $C_{acid} = 0.025$ M, $C_{stripper} = 0.05$ M, and $C_{kl} = 0.01$ M.

increasing this ratio. Fig. 9 confirms this concept. The figure shows that for four different R_{oi}^0 ratios of 0.5, 0.67, 1, and 2, the removal efficiency of the system with $R_{oi}^0 = 2$ at $t = 20$ min is 3% higher than that for the system with $R_{oi}^0 = 0.5$. Therefore, the larger value of 2 is selected as the optimum value of R_{oi}^0 since it minimizes the waste aqueous effluent, which is produced by breaking of emulsion in the demulsifier.

4.7. Effect of the type of solvent

The effect of solvent type on removal efficiency was examined by using three solvents including toluene, cyclohexane, and kerosene. It is expected that a non-polar solvent can transfer solute more efficiently through the membrane phase because of less hindrance against transportation. However, experimental results show only a marginal difference of 2–3% in removal efficiency in earlier mixing times and even lower differences of <1% in longer mixing times. As expected, cyclohexane has the highest cadmium removal but close to that by toluene. In addition, the removal efficiencies using kerosene are slightly less than those by the other two solvents. In the experiments made in this research, toluene was used as the solvent. However, since a less volatile solvent is preferred because of environmental issues and since the results show minor effect of solvent on extraction efficiency, toluene can be replaced by kerosene in real applications with similar expected results.

4.8. Effect of emulsion to external ratio

As the amount of emulsion in the external phase is increased, the number of available globules and interfacial surface area per unit volume of external phase is increased and thus the flux of transferred cadmium from external feed to emulsion, and removal efficiency is increased. It is noticeable that according to literature [28], increasing R_{ew}^0 may slightly increase the size of globules ($d_{32} \propto (1 + 1/R_{ew}^0)^{-0.1}$), which causes inversely a reduction in interfacial surface area. However, the effect of increment in the size of globule is suppressed by that of increment in the number of globules [28]. Fig. 10 shows that the removal efficiency is increased by increasing the emulsion to feed ratio from 0.05 to 0.2. However, total removal capacity, which is calculated from $[(C_0 - C)/R_{ew}^0] \times 10^{-3}$, remains in a constant range of 0.20–0.25 mg Cd/ml emulsion in all of the experiments.

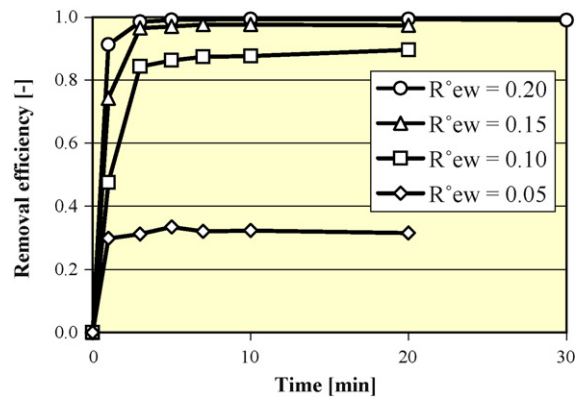


Fig. 10. Effect of emulsion to external ratio on removal efficiency. $C_0 = 33$ ppm, $R_{oi}^0 = 1$, $C_s = 3$ wt%, $C_{carrier} = 0.02$ M, $C_{acid} = 0.025$ M, $C_{stripper} = 0.05$ M, and $C_{kl} = 0.01$ M.

4.9. Effect of solute concentration in external phase

Changing the solute concentration affects concentration driving force and possibly mass transfer rate. Removal capacity is defined as the total amount of removed cadmium per unit volume of the emulsion as mentioned above. Therefore, at the same mixing conditions (the same size and distribution of globules in the external phase) and at a specified time, the removal capacity can be applied as an index of mass transfer rate. Fig. 11 compares the total removal capacities in the systems with three different solute concentrations of 33, 66 and 99 ppm. As seen in the figure, the removal capacities in the system with lower solute concentration of 33 ppm are always lower than those in the two other systems due to the smaller concentration driving force. The figure also shows that between $t = 1$ and 3 min, the removal capacities for the system with the highest solute concentration of 99 ppm is higher than those in the system with the solute concentration of 66 ppm. However, the capacity for the former system will decrease as the experiment proceeds. Its decrement might be attributed to the possible swelling of emulsion due to difference in ion strength and thus difference in osmotic pressure between the two phases [29] that partly hinders against solute transferring. Ultimately the removal capacities in the two systems with higher feed concentrations show the same value of about 0.44 mg Cd/ml emulsion while the capacity for the system with lower feed concentration of 33 ppm is 0.27 mg Cd/ml emulsion.

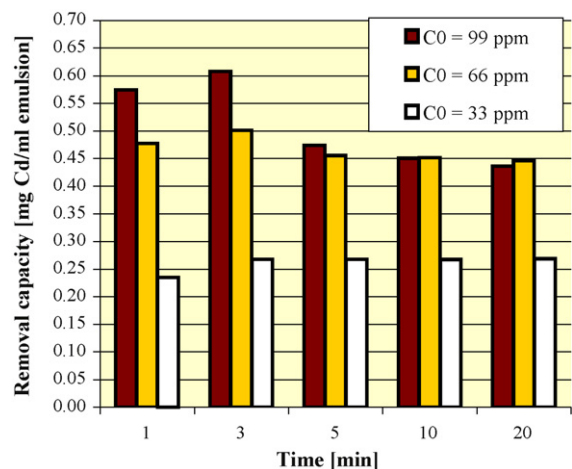


Fig. 11. Effect of solute concentration on removal capacity. $R_{oi}^0 = 1$, $R_{ew}^0 = 0.1$, $C_s = 3$ wt%, and $C_{carrier} = 0.02$ M.

Table 1
Complex formation constants for some ligands with cadmium.

Cation	Ligand	K_1	K_2	K_3	K_4	$\log(\beta_n)$
Cd ²⁺	Cl ⁻	85.11	2.69	0.54	4×10^{-4}	-1.28
	SO ₄ ²⁻	199.53				2.3
	I ⁻	251.19	39.81	10.00	12.59	6.1
	CH ₃ COO ⁻	85.11	16.60	0.13		2.26

4.10. Effect of iodide in external phase

Since cadmium is transferred through the membrane in the form of complex with iodide (CdI₄²⁻), the role of presence of iodide in the transportation phenomena was examined by experiments with and without adding KI to the external phase with the same other parameters as those in Fig. 10. Only negligible removal of less than 5% has been observed when no KI is added to the external phase while the transportation is done well in the presence of iodide, as observed also in the previous sections. This behavior can be explained by considering the fact that in competition with small size ions such as I⁻ and Cl⁻, CdI₄²⁻ can be selectively coupled with R₃NH⁺ to facilitate the transportation through the organic phase. This may be attributed to the lower hydration enthalpy of large-size anions such as CdI₄²⁻ in comparison to that of the small size ions, which make them better candidates to form zwitterions with R₃NH⁺ at the interface. On the other hand, as shown in Table 1, the overall complex formation constant (β_4) of Cd²⁺ with I⁻ as CdI₄²⁻ is much higher than those with the other present anions, e.g. Cl⁻, SO₄²⁻ in the external phase [30–32]. Therefore, CdI₄²⁻ is the only stable anion in the external phase, which can be coupled with R₃NH⁺. It is noticeable that when iodide is present in the solution, I⁻ may be oxidized to I₂, which introduces a yellowish color. However, this phenomenon was observed only in very low-pH conditions where sulphuric acid has been used in the feed phase and for long exposure time of 1 day or more. In all other conditions both phases in the experiments were colorless.

4.11. Effect of chloride in external phase

Since chloride is found in wastewater of some industries which contain cadmium [33], it might be helpful to study its effect on removal efficiency. Fig. 12 shows the effect of chloride with different concentrations in the external phase on removal efficiencies. As shown in the figure, the removal efficiencies at a specified mixing time are decreased steadily as the concentration of chloride is increased. For example, at $t = 20$ min, the removal efficiency of about

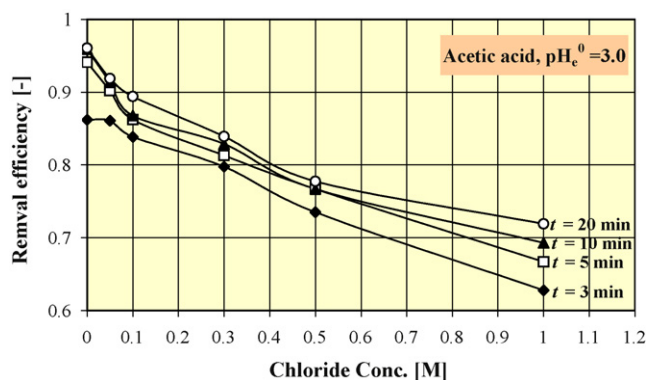


Fig. 12. Effect of chloride in the external phase on removal efficiency. $C_0 = 33$ ppm, $R_{oi}^0 = 1$, $R_{ew}^0 = 0.1$, $C_s = 3$ wt%, $C_{carrier} = 0.02$ M, $C_{acid} = 0.025$ M, $C_{stripper} = 0.05$ M, and $C_{KI} = 0.01$ M.

0.96 for the system without Cl⁻ is reduced to 0.71 for the system with Cl⁻ = 1 M. The hindering effect of chloride against transport of cadmium can be interpreted by the considering the data in Table 1. As seen in the table, cadmium can make complexes with Cl⁻ to produce CdCl₄²⁻ via four consecutive steps. The formation constant for the first step to produce CdCl⁺ is much higher than of the next steps, which represents its more stability compared to the consequent complexes. Since CdCl⁺ has been repelled by R₃NH⁺, it has no role in transferring of cadmium through the membrane phase. On the other hand, when the concentration of chloride is significant comparing to the concentration of iodide, it may block a part of cadmium in the external phase in the form of CdCl⁺ (or even CdCl₂), and therefore prevent cadmium to be transferred by iodide ions.

4.12. Effect of mixing conditions

Fig. 13 shows that by increasing the rotational speed of propeller in the extraction cell from 150 to 280 rpm, the cadmium in the external phase is removed more rapidly. This might be due to reducing of boundary layer thickness for mass transfer at the outer interface by increasing of mixing intensity ($k_{ext} \propto (P/V)^{0.25}$) [28]. However, assuming a first-order kinetics equation for cadmium transferring reveals that when the propeller speed in the extraction cell is increased from 150 to 280 rpm, increase in overall mass transfer rate is much higher than increasing of the mixing intensity. It can be related more to increase in mass transfer contact area due to reduction in the size of globules ($d_{32} \propto N^{-1.4}$) [28]. However, the emulsion might be broken under higher mixing intensities. Such a tendency is observed in the figure by increasing the impeller speed from 280 to 400 rpm, where lower removal efficiency is observed for higher speed of 400 rpm.

Comparing the results using extraction cells with or without baffles also shows about 5% increase in removal efficiencies when baffles were used due to improvement in mixing pattern.

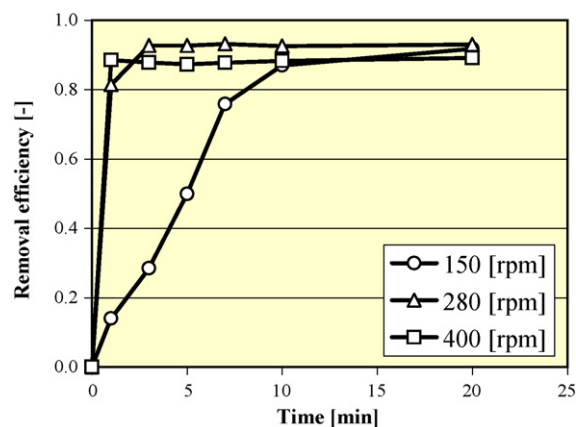


Fig. 13. Effect of mixing intensity on removal efficiency. $C_0 = 33$ ppm, $R_{oi}^0 = 1$, $R_{ew}^0 = 0.1$, $C_s = 3$ wt%, $C_{carrier} = 0.02$ M, $C_{acid} = 0.025$ M, $C_{stripper} = 0.05$ M, and $C_{KI} = 0.01$ M.

5. Conclusion

Removal of cadmium from aqueous phase by emulsion liquid membrane was studied. A synthesized polyamine type surfactant was used for stabilizing of the emulsion.

- (1) Removal efficiency increases by increasing of surfactant up to a certain concentration, and then levels off due to counter effect of surfactant on mass transfer rate.
- (2) Mass transfer is facilitated as carrier concentration in the organic phase is increased. The optimum concentration of carrier in the organic phase was found to be about 0.04 M.
- (3) Removal efficiency of cadmium depends on the availability of H^+ in the external phase. It also increases slightly as the pH of internal phase is increased.
- (4) The removal efficiency of cadmium is increased as the ratio of organic phase to internal phase is increased. $R_{oi}^0 = 2$ was found as the optimum value for this ratio.
- (5) Although non-polar solvents are better candidates for mass transfer, the solvent type has insignificant effect on removal efficiency.
- (6) Removal capacity of the systems with higher solute concentrations is higher than that in the system with lower solute concentrations due to the larger concentration driving force.
- (7) Chloride was found to have a hindering effect against transport of cadmium as a blocking agent for cadmium in the external phase.

Acknowledgements

The authors are grateful to Japan Student Services Organization (JASSO) for the awarded fellowship to the corresponding author. The authors also thank Mr. Akira Narita from Tokyo Tech High School of Science and Technology for his kind help in analyzing the samples.

References

- [1] L.J.J. Janssen, L. Koene, The role of electrochemistry and electrochemical technology in environmental protection, *Chem. Eng. J.* 85 (2002) 137–146.
- [2] K. Jüttner, U. Galla, H. Schmieder, Electrochemical approaches to environmental problems in the process industry, *Electrochim. Acta* 45 (2000) 2575–2594.
- [3] H.A. Aziz, N. Otham, M.S. Yusuff, D.R.H. Basri, F.A.H. Ashaari, M.N. Adlan, F. Otham, M. Johari, M. Perwira, Removal of copper from water using limestone filtration technique—determination of mechanism of removal, *Environ. Int.* 26 (2001) 395–399.
- [4] C. Kim, Q.H. Zhou, B.L. Deng, E.C. Thornton, H.F. Xu, Cr^{6+} reduction by hydrogen sulfide in aqueous media: stoichiometry and kinetics, *Environ. Sci. Technol.* 35 (2001) 2219–2225.
- [5] S. Yalcin, R. Apak, J. Hizal, H. Afsar, Recovery of Cu^{2+} and $Cr^{3+/6+}$ from electroplating-industry wastewater by ion exchange, *Sep. Sci. Technol.* 36 (2001) 2181–2196.
- [6] K.R. Reddy, S. Chinthamreddy, Sequentially enhanced electrokinetic remediation of heavy metals in low buffering clayey soils, *J. Geotech. Geoenviron. Eng.* 129 (2003) 263–277.
- [7] M.J. Zamow, J.E. Murphy, Removal of metal-cations from water using zeolites, *Sep. Sci. Technol.* 27 (1992) 1969–1984.
- [8] K. Kadirvelu, C. Faur-Brasquet, P. Le Cloirec, Removal of Cu^{2+} , Pb^{2+} , and Ni^{2+} by adsorption onto activated carbon cloths, *Langmuir* 16 (2000) 8404–8409.
- [9] M.L. Cervera, M.C. Arnal, M. Guardia, Removal of heavy metals by using adsorption on alumina or chitosan, *Anal. Bioanal. Chem.* 375 (2003) 820–825.
- [10] A.M.Y. Chong, Y.S. Wong, N.F.Y. Tam, Performance of different microalgal species in removing nickel and zinc from industrial wastewater, *Chemosphere* 41 (2000) 251–257.
- [11] M. Vainshtein, P. Kuschik, J. Mattusch, A. Vatsourina, A. Wiessner, Model experiments on the microbial removal of chromium from contaminated groundwater, *Water Res.* 37 (2003) 1401–1405.
- [12] N.K. Srivastava, C.B. Majumder, Novel biofiltration methods for the treatment of heavy metals from industrial wastewater, *J. Hazard. Mater.* 151 (2008) 1–8.
- [13] C.A. Nogueira, F. Delmas, New flowsheet for the recovery of cadmium, cobalt, and nickel from spent Ni–Co batteries by solvent extraction, *Hydrometallurgy* 52 (1999) 267–287.
- [14] B. Gupta, A. Deep, P. Malik, Extraction and recovery of cadmium using Cyanex 923, *Hydrometallurgy* 61 (2001) 65–71.
- [15] K. Takeshita, K. Watanabe, Y. Nakano, M. Watanabe, Solvent extraction separation of Cd(II) and Zn(II) with the organophosphorus extractant D2EHPA and the aqueous nitrogen-donor ligand TPEN, *Hydrometallurgy* 70 (2003) 63–71.
- [16] K. Takeshita, K. Watanabe, Y. Nakano, M. Watanabe, Extraction separation of Cd(II) and Zn(II) with Cyanex 301 and aqueous nitrogen-donor ligand TPEN, *Solvent Extr. Ion Exc.* 22 (2004) 203–218.
- [17] Q. Jia, C.H. Zhan, D.Q. Li, C.J. Niu, Extraction of zinc (II) and cadmium(II) by using mixtures of primary amine N1293 and organophosphorus acids, *Sep. Sci. Technol.* 39 (2004) 1111–1123.
- [18] G. Srisuwan, P. Thongchai, Removal of heavy metals from electroplating wastewater by membrane, *Songklanakarin J. Sci. Technol.* 24 (Suppl.) (2002) 965–976.
- [19] R.P. Cahn, N.N. Li, Separation of phenol from wastewater by liquid membrane technique, *Sep. Sci. Technol.* 9 (1974) 505–519.
- [20] M. Ruppert, J. Draxler, R. Marr, Liquid-membrane permeation and its experiences in pilot-plant and industrial scale, *Sep. Sci. Technol.* 23 (1988) 1659–1666.
- [21] J. Draxler, W. Furst, R. Marr, Separation of metal species by emulsion liquid membranes, *J. Membr. Sci.* 38 (1988) 281–293.
- [22] A. Nemeš, A.P. Van Peteghem, Extraction of multicomponent system metals from simulated and industrial effluents by liquid surfactant membranes, *Hydrometallurgy* 31 (1992) 149–159.
- [23] H.R. Mortaheb, M.H. Amini, F. Sadeghian, B. Mokhtarani, H. Daneshyar, Study on a new surfactant for removal of phenol from wastewater by emulsion liquid membrane, *J. Hazard. Mater.* 160 (2008) 582–588.
- [24] A.H.P. Skelland, X. Meng, Non-Newtonian conversion solves problems of stability, permeability, and swelling in emulsion liquid membranes, *J. Membr. Sci.* 158 (1999) 1–15.
- [25] T. Gallego-Lizon, E.S. Pérez de Ortiz, Drop sizes in liquid membrane dispersions, *Ind. Eng. Chem. Res.* 39 (2000) 5020–5028.
- [26] N.L. Nemerow, *Industrial Water Pollution Origins, Characteristics, and Treatment*, Addison-Wesely Publishing Company, Massachusetts, 1978.
- [27] P. Venkateswaran, S. Vellaichamy, K. Palanivelu, Speciation of heavy metals in electroplating industry sludge and wastewater residue using inductively coupled plasma, *Int. J. Environ. Sci. Technol.* 4 (2007) 497–504.
- [28] S. Datta, P.K. Bhattacharya, N. Verma, Removal of aniline from aqueous solution in a mixed flow reactor using emulsion liquid membrane, *J. Membr. Sci.* 226 (2003) 185–201.
- [29] W. Li, Y. Shi, Water permeation swelling of emulsion liquid membrane, *Sep. Sci. Technol.* 28 (1993) 241–254.
- [30] S. Stenström, Extraction of cadmium from phosphoric acid solutions with amines. Part III. A thermodynamic extraction model, *Hydrometallurgy* 18 (1987) 1–20.
- [31] D.A. Skoog, D.M. West, F.J. Holler, *Fundamentals of Analytical Chemistry*, seventh ed., Saunders College Publishing, USA, 1996.
- [32] D. Harvey, *Modern Analytical Chemistry*, first ed., McGraw Hill, USA, 2000.
- [33] B.R. Reddy, D.N. Priya, S.V. Rao, P. Radhika, Solvent extraction and separation of Cd(II), Ni(II) and Co(II) from chloride leach liquors of spent Ni–Cd batteries using commercial organo-phosphorus extractants, *Hydrometallurgy* 77 (2005) 253–261.