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Emulsion liquid membranes for cadmium removal: Studies of extraction efficiency

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Abstract. Emulsion liquid membrane (ELM) process suffers from emulsion instability problem. So far, emulsion produced by mechanical methods such as stirrer and homogenizer has big size and high emulsion breakage. This paper discussed the application of emulsion produced by sonicator to extract cadmium in a batch ELM system. The emulsions consist of N,N-Dioctyl-1-octanamine (trioctylamine/TOA), nitrogen trihydride (ammonia/NH4OH), sorbitan monooleate (Span 80), and kerosene as carrier, stripping solution, emulsifying agent, and organic diluent, respectively. Effects of comprehensive parameters on extraction efficiency of Cd(II) such as emulsification time, extraction time, stirring speed, surfactant concentration, initial feed phase concentration, carrier concentration, volume ratio of the emulsion to feed phase, and pH of initial feed phase were evaluated. The results showed that extraction efficiencies of Cd(II) greater than 98% could be obtained under the following conditions: 15 minutes of emulsification time, 4 wt.% of Span 80 concentration, 4 wt.% of TOA concentration, 15 minutes of extraction time, 250 rpm of stirring speed, 100 ppm of initial feed concentration, volume ratio of emulsion to feed phase of 1:5, and initial feed pH of 1.53.

Keywords: emulsion liquid membrane; extraction efficiency; cadmium; ultrasonication

1. Introduction

Cadmium is a harmful heavy metal commonly found in processes involving metal alloys, ceramic materials, electronics, pigments, and textiles; therefore, wastewater from industries that employ these materials is a potential source of cadmium. In addition, cadmium naturally exists as a minor constituent of base metal ores and coal deposits (Mortaheb, Kosuge *et al*. 2009). However, approximately 95% of all cadmium species are byproducts of zinc hydrometallurgical processes (Kumbasar 2009). The removal of cadmium (II) from wastewater is of great importance, especially for the protection of human health. According to World Health Organization (WHO), the lower limit for concentration of cadmium in drinking water is 5 μg/L. Most of cadmium effluent from industrial wastewater can be quickly adsorbed by fine particles; therefore, sediment may be a significant sink for cadmium released into aquatic environments (Friberg, Elinder *et al*. 1992). Recent studies have shown that the cadmium concentration of sediments in lakes and water

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streams ranges from 0.2 to 0.9 ppm, which is greater than the level generally observed in fresh water (less than 0.1 ppm) (Cook and Morrow 1995). Although cadmium has negative environmental impacts as it is highly toxic, cadmium recovery has attracted a considerable amount of attention from researchers, due to its economic value.

In point of fact, the cadmium concentration in wastewater is very low therefore the recovery method must be efficient and highly selective. To date, cadmium has been removed via coagulation (Xu, Yang *et al*. 2010), activated carbon adsorption (Huang and Ostovic 1978, Ahn, Kim et al. 2009), liquid-liquid extraction (Parus, Wieszczycka *et al*. 2011), ion exchange (Bai and Bartkiewicz 2009), reverse osmosis (Soares, Bertrand et al. 2005), and electrochemical precipitation (Bazrafshan, Kord Mostafapoor *et al*. 2006). Chemical precipitation, ion exchange, and solvent extraction, however, are rather expensive, ineffective, and recovery is uneconomical (Soares, Bertrand *et al*. 2005, Xu, Yang *et al*. 2010). Activated carbon does not have sufficient functional groups to adsorb heavy metals in an economic manner (Ahn, Kim *et al*. 2009), and long contact times between the adsorbate and adsorbent are required to achieve equilibrium, which limits its practical application in wastewater treatment (Xu, Yang *et al*. 2010).

The extraction of various contaminants in liquid waste including heavy metals are favorable to be carried out using emulsion liquid membranes (ELM) due to its high interfacial mass transfer area of about 3000 m2/m3 (Cahn and Li 1974, Chakraborty, Bhattacharya *et al*. 2010). The required organic solvent is also relatively low thus making the process to extract the contaminants becomes feasible. Another advantage of ELM-based processes is the extraction and stripping processes take place simultaneously, which reduces the number and size of contacting equipment usually required in conventional liquid-liquid extraction processes (Cahn and Li 1974). Compared to conventional liquid-liquid extraction, the materials cost needed in the ELM process are about 40% lower (Chakraborty, Bhattacharya *et al*. 2010).

So far, emulsion formation was done using stirrer, homogenizer, and other mechanical methods. However, the produced emulsion suffered from instability due to the relatively big size. The most common emulsion instabilities in ELM process are membrane breakage and emulsion swelling. The big size gives a disadvantage in the low interfacial area therefore lowering extraction efficiency. Concerning about the emulsion instability, the use of ultrasound emulsification is promising due to the high mixing intensity results in high emulsion stability with small emulsion droplets (Ahmad, Kusumastuti *et al*. 2012). Therefore in this paper we demonstrate the performance of emulsion produced by sonicator for cadmium extraction. The extraction efficiency was studied under some parameters and operating conditions.

A number of works on cadmium recovery via emulsion liquid membranes have been published (Li, Liu *et al*. 1997, Basualto, Poblete *et al*. 2006, Kumbasar 2009, Mortaheb, Kosuge *et al*. 2009). The effects of independent variable such as initial pH of feed phase solution, time of emulsification and extraction, speed of extraction, concentration of initial Cd(II), surfactant, and carrier, and volume ratio of the membrane to the internal phase on the extraction efficiency of Cd(II) were investigated in the present study. The aforementioned operating conditions were evaluated in a system containing Trioctylamine (TOA) as a carrier, Span 80 as a surfactant, kerosene as a membrane phase, and ammonia (NH_4OH) as a stripping solution.

2. Materials and methods

2.1 Chemicals

Deionized water was used for all of the solutions preparation. The membrane phase consisted of kerosene (commercial grade), non-ionic surfactant (Span 80, Merck), and carrier (Trioctylamine, Merck). In standard condition, the membrane density and viscosity are 0.8162 g/cm^3 and 2.60776 cp, respectively. While the emulsion diameter ranging from 0.878 to 2.46 μm. Cadmium solution was prepared from cadmium chloride, supplied by Sigma Aldrich. Stripping solution was prepared from a 25% solution of ammonia, supplied by Merck. pH was adjusted using HCl and NaOH, supplied by Merck.

2.2 Analytical instruments

Cadmium concentration in the external feed phase was measured using an atomic absorption spectrophotometer (AA-6650 Shimadzu) at wavelength of 228.85 nm. pH of the solution was measured using a Fisher Scientific Accumet AB15 pH meter.

2.3 Procedure

2.3.1 Preparation of the emulsion

An ultrasonicator was used to prepare the emulsion. The emulsification setup consisted of a jacketed cylindrical glass reactor, allowing the emulsification cell to be cooled with water. Ultrasonic irradiation was performed at 22.5 kHz using a USG-150 commercial ultrasonicator equipped with a titanium horn mounted at the top of the cylindrical glass cell. A predetermined volume of Span 80 and TOA were dissolved in kerosene and stirred at 500 rpm for 5 min using magnetic stirrer to prepare the membrane phase. An adequate amount of 3 M ammonia as the internal aqueous phase was then added into the prepared membrane phase solution. The mixture was then homogenized using the ultrasonicator by immersing the probe at the interface of the membrane-internal phase. Coolant was circulated around the jacket to maintain the process temperature at 20°C. The water in oil (W/O) emulsion volume was set to 60 mL.

As shown in Table 1, various emulsification parameters, including time of emulsification, concentration of surfactant and carrier, and volume ratio of membrane to internal phase, were varied. In each step, a single parameter was changed while the other variables were held constant.

The optimal conditions were then employed in the subsequent experiments.

2.3.2 Extraction of cadmium

Extraction studies were carried out by dispersing the emulsion into the feed phase, of cadmium chloride in deionized water. The experiments were performed in a 500-mL glass vessel containing a magnetic stirrer. In this step, the extraction time, stirring speed, initial concentration of the feed phase, treatment ratio (volume ratio of feed to emulsion phase), and initial pH of the feed phase were varied (see Table 1) to determine the optimal extraction efficiency of Cd(II). Each experiment was performed in triplicate, and the mean values are presented.

At the end of extraction, the emulsion phase was separated from the feed phase using a separatory funnel, and 50-mL aliquots were collected to analyze the Cd(II) concentration. The extraction efficiency of cadmium was subsequently calculated using the following equation

$$\textit{Extraction efficiency}\ (\%) = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \tag{1}$$

where C_0 and C_t are the initial cadmium concentration of the feed solution and raffinate,

Table 1 Experimental condition for the ELM

External phase	
Volume (mL)	250
pH	0.39 – 2.6
Cd(II) Conc. (ppm)	10–150
Internal phase	
Volume (mL)	15
[NH_3] (M)	3
Organic solution	
Volume (mL)	45
Diluent	Kerosene
[TOA] (wt.-%)	2 – 8
Span 80 (wt.-%)	2 – 10
Emulsification time (min)	5 – 30
Extraction time (min)	10 – 25
Extraction speed (rpm)	200 – 350
Treat ratio (v_f/v_e)	3 – 10

respectively.

When TOA (R_3N) is used as a carrier, the solute ($CdCl_4^{2-}$) from the feed solution diffuses into the emulsion globule interface and reacts with the carrier

$$2H^+_{(aq)} + CdCl^{2-}_{4(aq)} + 2R_3N_{(org)} \leftrightarrow (R_3NH)_2CdCl_{4(org)} \quad (2)$$

The carrier–solute complex diffuses into the internal phase interface and reacts with the stripping reagent (NH_4OH). As a result, the solute and carrier are released

$$\left[(R_3NH)_2CdCl_4\right]_{(org)} + \left[2OH^-\right]_{(aq)} \leftrightarrow 2\left[R_3N\right]_{(org)} + \left[CdCl_4^{2-}\right]_{(aq)} + \left[2H_2O\right]_{(aq)} \quad (3)$$

where (*aq*) refers to the feed and stripping phase, and (org) refers to the membrane phase. The Cd(II) extraction mechanism of ELM is illustrated in Fig. 1. In an ELM, Cd(II) is extracted from an external feed phase to an internal stripping phase in W/O emulsions in accordance with the mechanism proposed in Fig.1 as adopted from Hasan *et al*. (Hasan, Selim *et al*. 2009). Specifically,

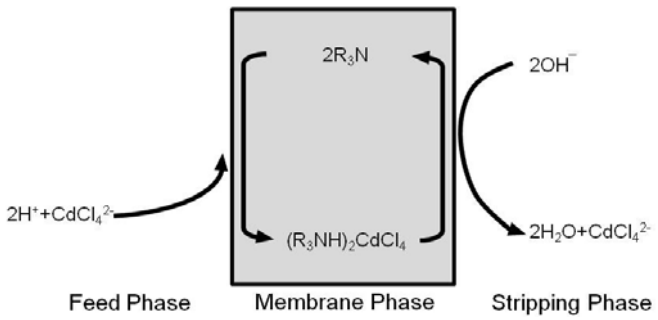

Fig. 1 Transport mechanism of Cd(II) through an emulsion liquid membrane

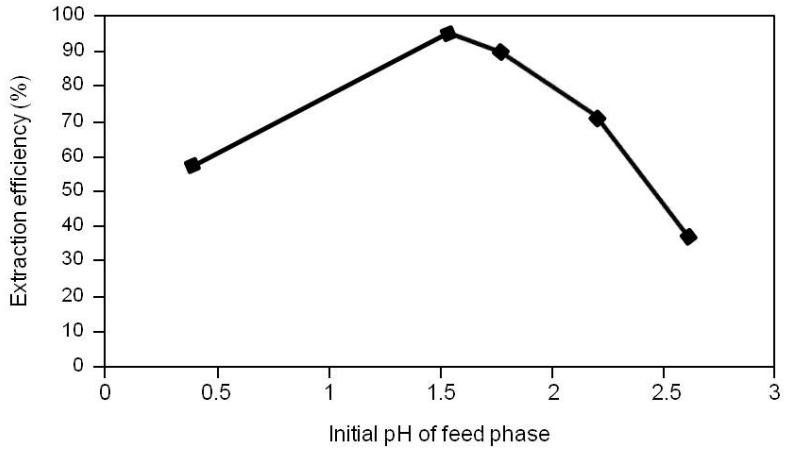

Fig. 2 Effect of the initial feed pH on the extraction efficiency of Cd(II). Span 80 = 4 wt.%; TOA = 4 wt.%; stripping solution (NH_4OH) = 3 M; ratio of membrane to internal phase = 3; emulsification time = 15 min; initial concentration of Cd(II) = 100 ppm; treatment ratio = 5; stirring speed = 250 rpm; extraction time = 15 min

the carrier (represented by R_3N in the organic membrane phase) reacts with the metal ion ($CdCl_4^{2-}$ at the interface of the aqueous feed phase and organic membrane phase) to form a metal-carrier complex ($[R_3NH]_2CdCl_4$). The diffusion of the complex is driven by the concentration gradient of the complex in the interface and in the internal phase. In the internal phase, metal will be released and stripped. Then the carrier diffuses back towards the organic membrane phase.

3. Results and discussion

3.1 Effects of initial feed pH

The pH of the feed phase plays an important role in the extraction efficiency of cadmium. The solute-carrier complex diffuses through the membrane phase, due to the presence of a pH gradient between the feed and internal phase. In the present study, the effect of the initial feed pH as the driving force for cadmium extraction was investigated at a pH of 0.39 to 2.6 while the internal phase pH was kept constant at 12. Fig. 2 describes the performance of cadmium extraction under the parameter of initial feed pH. The decrease of initial feed pH from 2.6 to 1.53 resulted in the gradually increase of the extraction efficiency. Further pH decrease up to 0.39 led to the reduction of the extraction efficiency.

The pH gradient between external and internal phase serves as driving force for the diffusion process. In this study, the pH gradient increase as the decrease of initial feed pH. Theoretically, higher pH gradient results in higher extraction efficiency. In this research, the highest extraction efficiency was obtained at initial feed pH of 1.53. The decrease in the pH gradient reduces the surfactant diffusivity and emulsion swelling as was also reported by Yan and Pal (2004). When swelling occurred, water was transported from the external phase to the internal phase, leading to

emulsion breakage (Wan and Zhang 2002). Therefore, the captured cadmium was released back into the external phase. As a result, the extraction efficiency was lower at lower pH values as a consequence of the high emulsion swelling at higher pH gradient, while an increase of the pH beyond 7.5 may cause metal precipitation (Basualto, Poblete *et al*. 2006).

3.2 Effects of the emulsification time

In order to study the effect of the emulsification time on the extraction efficiency, the emulsion was prepared at a predetermined time of 5-30 minutes as shown in Fig. 3. The extraction efficiency increased with an increase in the emulsification time but declined after 15 minutes. This was due to the smaller emulsion diameters and greater amounts of emulsion globules produced at longer emulsification times as reported in our previous paper (Ahmad, Kusumastuti *et al*. 2012). Tiny emulsions contributed to higher surface areas, which increase the extraction rate. At longer emulsification times, more stripping phase was encapsulated in the membrane phase, which improved cadmium extraction. In the present study, the greatest extraction efficiency of approximately 99% was achieved at an emulsification time of 15 minutes. Further increases in the emulsification time allowed to the coalescence phenomenon (Djenouhat, Hamdaoui *et al*. 2008) thus enlarging the emulsion diameter. The big emulsion diameter lowers the extraction efficiency. Therefore, subsequent studies were performed at an emulsification time of 15 minutes.

3.3 Effect of the surfactant concentration

The surfactant concentrations were varied at 2 wt.%, 4 wt.%, 6 wt.%, 8 wt.%, and 10 wt.%, to investigate its effect on the extraction efficiency and the resulting data is presented in Fig. 4. As shown in Fig. 4, increasing the surfactant concentration from 2 wt.% to 4 wt.% resulted in the increase of the extraction efficiency to 99% at 4 wt.% surfactant dosage. However, further increase in the surfactant concentration gradually decreased the extraction efficiency. This is due to the bigger emulsion droplets produced at higher surfactant concentration caused by the coalescence of the emulsion droplets or the micelle adsorption onto the emulsion surface (Ahmad, Kusumastuti *et*

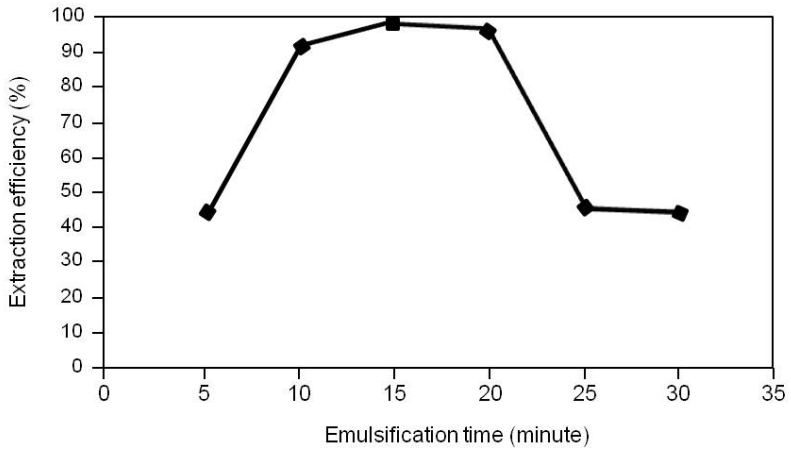

Fig. 3 Effect of emulsification time on the extraction efficiency of Cd(II). Span 80 = 4 *wt*.%; TOA = 4 wt.%; stripping solution (NH_4OH) = 3 M; ratio of membrane to internal phase = 3; initial concen-tration of Cd(II) = 100 ppm; treatment ratio = 5; initial pH of feed solution = 1.53; stirring speed = 250 rpm; extraction time = 15 min

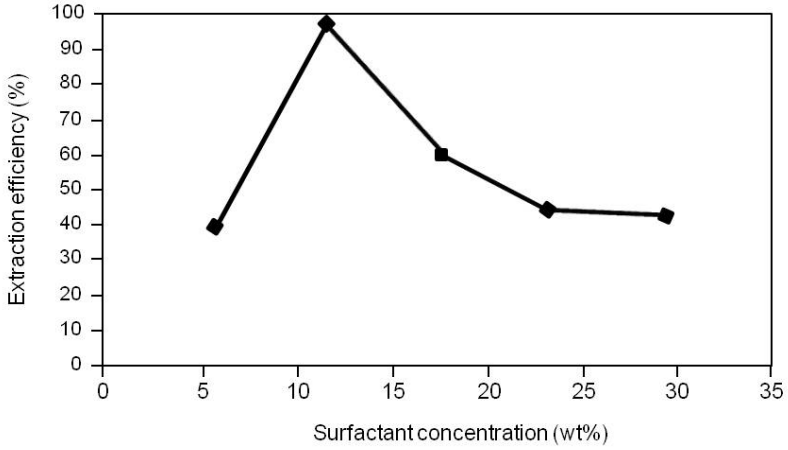

Fig. 4 Effect of the surfactant concentration on the extraction efficiency of Cd(II). TOA = 4 wt.%; stripping solution (NH_4OH) = 3 M; ratio of membrane to internal phase = 3; emulsification time = 15 min; initial concentration of Cd(II) = 100 ppm; treatment ratio = 5; initial pH of feed solution = 1.53; stirring speed = 250 rpm; extraction time = 15 min

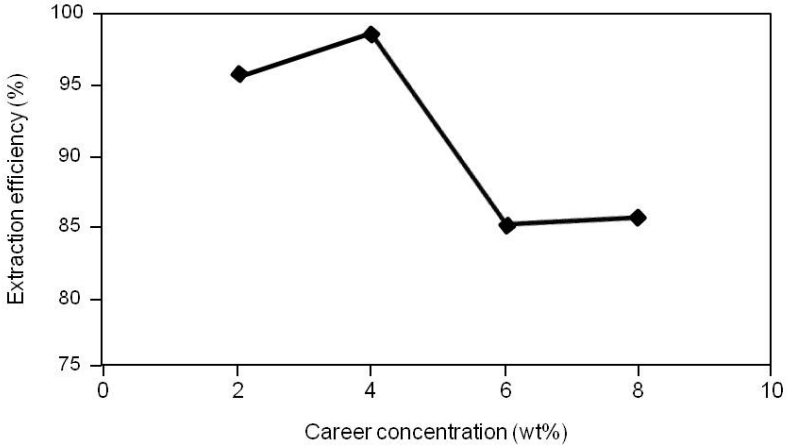

Fig. 5 Effect of the carrier concentration on the extraction efficiency of Cd(II). Span 80 = 4 wt.%; stripping solution (NH_4OH) = 3 M; ratio of membrane to internal phase = 3; emulsification time = 15 min; initial concentration of Cd(II) = 100 ppm; treatment ratio = 5; initial pH of feed solution = 1.53; stirring speed = 250 rpm; extraction time = 15 min.

al. 2012). Bigger emulsions droplet suffered from lower mass transfer area for extraction. Besides, high surfactant concentrations also prevent membrane leakage but enhance emulsion swelling due to the water transport of the reversed micelle (Gasser, El-Hefny *et al*. 2008, Jilska and Geoff 2008). The excess surfactant encouraged the entrainment of the external phase during the extraction process which also resulted in emulsion swelling (Jilska and Geoff 2008). At high concentrations,

the surfactant tends to form aggregates, which causes emulsions to swell (Ahmad, Kusumastuti *et al*. 2011). This phenomenon was evidenced by an increase in the emulsion volume after extraction. It is also important to note that, increasing the surfactant concentration does not beneficial for the extraction kinetics since at high viscosities the emulsion has high interface resistance that decrease the diffusivity and mass transfer coefficient (Li, Liu *et al*. 1997, Chakravarti, Chowdhury *et al*. 2000, Kargari, Kaghazchi *et al*. 2004, Kumbasar 2009).

3.4 Effect of the carrier concentration

The experiments were done at carrier concentration of 2 wt.%, 4 wt.%, 6 wt.%, and 8 wt.% in order to study its effect on the extraction efficiency. Fig.5 shows the extraction efficiency profile at different carrier concentrations. As shown in the figure, the increase of the carrier concentration from 2 wt.% to 4 wt.% enhanced the extraction efficiency. The highest extraction efficiency of approximately 99% was achieved at a carrier concentration of 4 wt.%. Increasing the carrier concentration beyond this optimal value provoked emulsion swelling, which diluted the concentrated solute in the internal phase and decreased the extraction efficiency (Gasser, El-Hefny *et al*. 2008). Membrane breakage also occurred at high carrier concentrations because complexes between the carrier and metal provoke the loss of internal aqueous solutions (Valenzuela, Fonseca *et al*. 2005). Furthermore, high carrier concentrations increase membrane viscosity, which lead to the formation of larger globules (Chiha, Samar *et al*. 2006; Gasser, El-Hefny *et al*. 2008; Ahmad, Kusumastuti *et al*. 2012) and reduce the interfacial area (Sengupta, Sengupta *et al*. 2006). Based on economic perspective, the use of minimum carrier is preferable because of the expensive cost of the chemical compared to others membrane phase reagents (Kulkarni and Mahajani 2002, Kulkarni, Mukhopadhyay *et al*. 2002).

3.5 Effect of the volume ratio of the membrane to the internal phase

The effect of the volume ratio of the membrane to the internal phase is described in Fig. 6. The phase ratios were varied at 2, 3, 4, and 5, and the total emulsion volume was held constant. As the phase ratio increased from 2 to 3, an increase in the extraction efficiency was observed. Specifically, at a ratio of 2, the membrane phase could not enclose all of the internal phase.

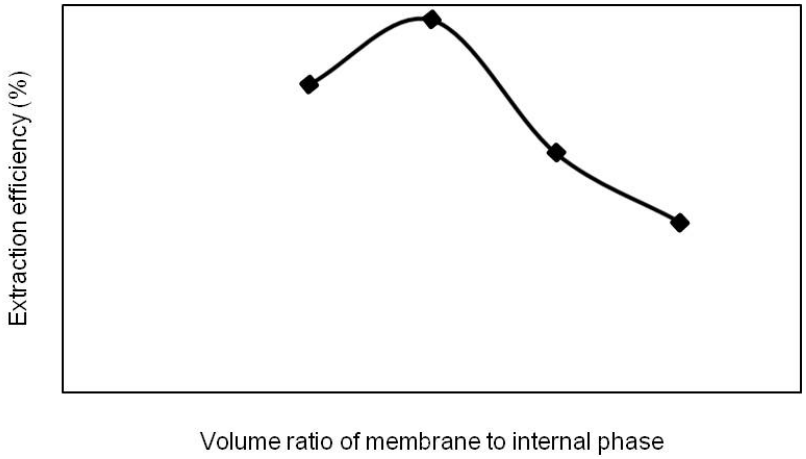

Fig. 6 Effect of the volume ratio of the membrane to the internal phase on the extraction efficiency of Cd(II). Span 80 = 4 wt.%; TOA = 4 wt.%; stripping solution (NH_4OH) = 3 M; emulsification time = 15 min; initial concentration of Cd(II) = 100 ppm; treatment ratio = 5; initial pH of feed solution = 1.53; stirring speed = 250 rpm; extraction time = 15 min

Therefore, larger emulsion droplets were produced at lower ratios (Ahmad, Kusumastuti *et al*. 2012). In addition, due to the lack of a membrane phase, thinner emulsion walls were produced, which facilitated internal phase leakage. In the present study, the highest extraction efficiency was achieved at a membrane to internal phase volume ratio of 3. At this ratio, a stable and fine emulsion was produced (Ahmad, Kusumastuti *et al*. 2012). However, increasing the volume ratio from 3 to 5 decreased the extraction efficiency, due to an increase in the emulsion size. Further increase of the phase ratio would not be effective to increase the efficiency. Excessive amounts of membrane solution produce thick emulsion walls and resulting in the difficult dispersion of the internal solution. The thickness of the emulsion membrane is not favorable for the extraction process. The thick emulsion wall lowered the solute transfer into the internal phase as stated by Kargari (Kargari, Kaghazchi *et al*. 2004) that an increase in oil phase volume resulted in the thickening of emulsion wall which in turn enlarging the diffusion path and lowering the mass transfer rate. Moreover, the interfacial resistance also increases with an increase in the volume ratio. In the proposed extraction system, high interfacial resistance was not valuable because they lowered the diffusion and mass transfer coefficient (Kargari, Kaghazchi *et al*. 2004).

3.6 Effect of the extraction time

The extraction time was varied at 10, 15, 20, and 25 minutes to study its effect on the extraction efficiency. As shown in Fig. 7, the extraction efficiency increased as the extraction time increased from 10 to 15 minutes. Longer contact times generally enhance the rate of water transport towards the inner stripping phase which promotes membrane swelling and emulsion breakdown (Ahmad, Kusumastuti *et al*. 2011). Therefore, the contact time must be precisely controlled to obtain an optimal extraction process. In the present study, the highest extraction efficiency was achieved at an extraction time of 15 minutes, and the corresponding efficiency was greater than 98%. At a contact time of 20 minutes, excessive swelling of the internal phase was observed, which induced emulsion breakage and the cadmium leakage from the inner stripping phase to the outer feed phase,

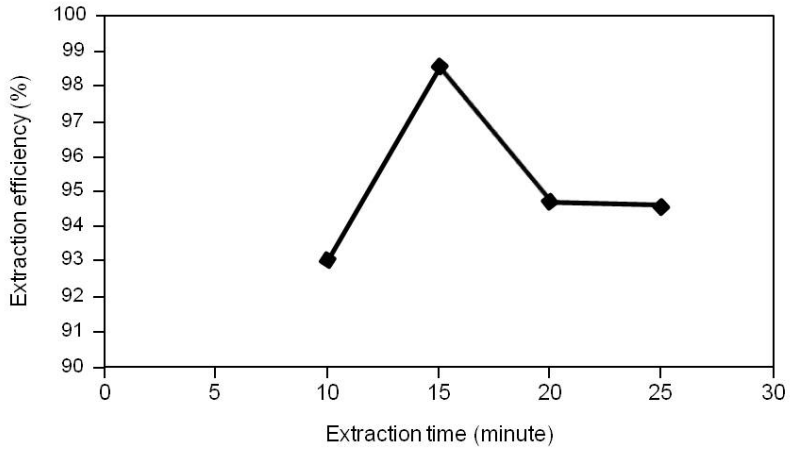

Fig. 7 Effect of the extraction time on the extraction efficiency of Cd(II). Span 80 = 4 wt.%; TOA = 4 wt.%; stripping solution (NH_4OH) = 3 M; ratio of membrane to internal phase = 3; emulsification time = 15 min; initial concentration of Cd(II) = 100 ppm; treatment ratio = 5; initial pH of feed solution = 1.53; stirring speed = 250 rpm

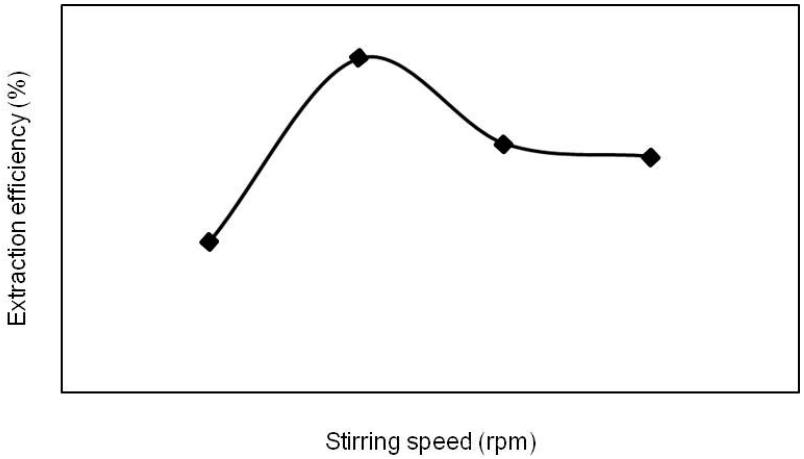

Fig. 8 Effect of the stirring speed on the extraction efficiency of Cd(II). Span 80 = 4 wt.%; TOA = 4 wt.%; stripping solution (NH_4OH) = 3 M; ratio of membrane to internal phase = 3; emulsification time = 15 min; initial concentration of Cd(II) = 100 ppm; treatment ratio = 5; initial pH of feed solution = 1.53; extraction time = 15 min

thereby reducing the extraction efficiency (Ahmad, Kusumastuti *et al*. 2012). The membrane swelling was indicated by the increase of the emulsion volume after the extraction process.

3.7 Effect of the stirring speed

An appropriate stirring speed must be selected to optimize emulsion liquid membrane performance. The effect of the stirring speed on the extraction efficiency was investigated at stirring speeds of 200 rpm, 250 rpm, 300 rpm, and 350 rpm. As shown in Fig. 8, the highest extraction efficiency was attained at a stirring speed of 250 rpm. Higher stirring speeds increased emulsion swelling and

globule rupture (Fouad 2008, Kumbasar and Şahin 2008) because the shearing force could destroys fragile emulsion droplets near the tip of the impeller (Kulkarni and Mahajani 2002) and cause enhancement of the water transport rate into the emulsion (Wan and Zhang 2002, Sengupta, Sengupta *et al*. 2006). Valenzuela *et al.* (Valenzuela, Fonseca *et al*. 2005, Valenzuela, Araneda *et al*. 2009) also found that an excessively high stirring speed could induces the coalescence and breakdown of the emulsion globules. It resulted in the unstable primary emulsion and favors the transport of the internal dispersed phase toward the external continuous aqueous phase. When others parameters are remained constant, increasing the stirring speed will increase the shear rate. As a result, the stream will be more turbulence then it will enhance the mass transfer. The turbulence of the system is important to confirm the even distribution of the cadmium in the external phase.

3.8 Effect of the initial feed concentration

The chemical potential due to the concentration difference between the feed and internal phase is a significant driving force for the diffusion process. The extraction efficiency of cadmium was studied at initial feed concentrations of 10 ppm, 30 ppm, 50 ppm, 70 ppm, 100 ppm, and 150 ppm. Data describing the effect of the initial feed concentration on the extraction efficiency are shown in

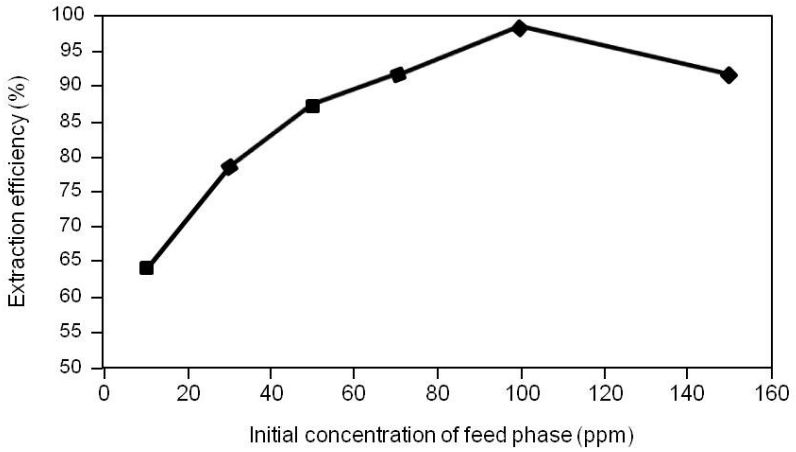

Fig. 9 Effect of the initial concentration of feed phase on the extraction efficiency of Cd(II). Span 80 = 4 wt.%; TOA = 4 wt.%; stripping solution (NH_4OH) = 3 M; ratio of membrane to internal phase = 3; emulsification time = 15 min; treatment ratio = 5; initial pH of feed solution = 1.53; stirring speed = 250 rpm; extraction time = 15 min

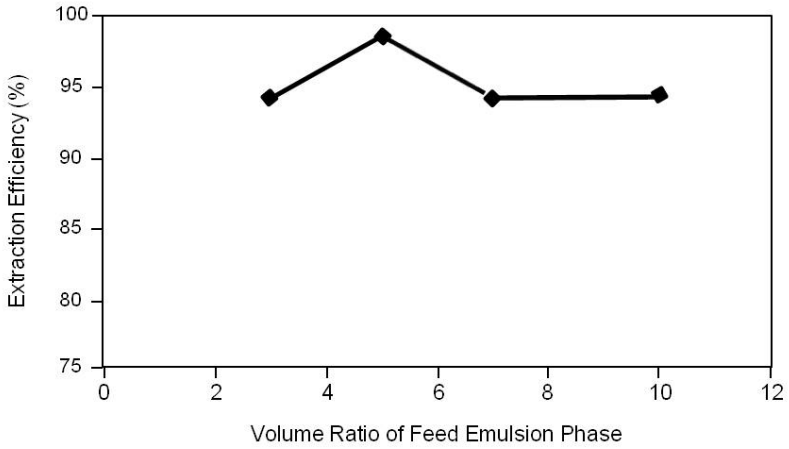

Fig. 10 Effect of the volume ratio of the feed to the emulsion on the extraction efficiency of Cd(II). Span 80 = 4 wt.%; TOA = 4 wt.%; stripping solution (NH_4OH) = 3 M; ratio of membrane to internal phase = 3; emulsification time = 15 min; initial concentration of Cd(II) = 100 ppm; initial pH of feed solution = 1.53; stirring speed = 250 rpm; extraction time = 15 min

Fig. 9. As shown in the figure, the extraction efficiency increased with an increase in the initial feed concentration due to the higher chemical potential between the feed and the internal phase. However, in the present study, at feed concentrations greater than 100 ppm, the extraction efficiency was found to be decreased. It can be explained that as plenty of cadmium diffused into the internal droplets, the rest need to permeate more deeply within the emulsion globule. Therefore, an increase in the cadmium concentration lengthen the diffusion path (Sengupta, Sengupta *et al*. 2006, Kumbasar 2008) and ultimately reduce the extraction rate. The observed decrease in the extraction efficiency was also attributed to the fact that greater amounts of carrier were required to transport the larger quantity of cadmium (Basualto, Poblete *et al*. 2006).

3.9 Effect of the volume ratio of the feed to the emulsion phase

The effect of the volume ratio of the feed to the emulsion phase was studied at ratios of 3, 5, 7, and 10. The treatment ratio is an indicator of the stability of the emulsion in a particular system. As shown in Fig. 10, when the (stability of the emulsion was low (i.e., a ratio of 10), the extraction efficiency was also notably low. As the treatment ratio decreased to 7, a slight increase in the extraction efficiency was observed. However, when the treatment ratio decreased to 5, the extraction efficiency increased significantly. At this ratio, the highest extraction efficiency (> 98%) was attained. When the treatment ratio was less than 5, the extraction efficiency decreased sharply, due to an increase in membrane breakage. The swelling phenomenon occurred at lower treatment ratio promoted the formation of larger globules and decreased the mass transfer area. Interactions among globules were also enhanced by an increase of emulsion volume, which led to the coalescence and re-dispersion of globules. Consequently, the membrane ruptured and the encapsulated cadmium was released into the feed phase, as demonstrated by Sengupta *et al.* Sengupta, Sengupta *et al.* 2006).

4. Conclusions

The removal of low concentrations of cadmium from wastewater was studied using emulsion liquid membranes, and various parameters were evaluated. In the current investigation, ultrasound was used to produce a stable w/o emulsion, and Cd(II) extraction was favored when trioctylamine, ammonia, and Span 80 in kerosene was used as a dissolving carrier, internal stripping solution, and surfactant, respectively. The optimal conditions were obtained at an emulsification time of 15 minutes, Span 80 concentration of 4 wt.%, TOA concentration of 4 wt.%, extraction time of 15 minutes, stirring speed of 250 rpm, initial feed concentration of 100 ppm, volume ratio of the emulsion to feed phase of 1:5, and initial feed pH of 1.53. Under optimal conditions, the Cd(II) removal rate was greater than 98%.

Acknowledgments

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