Emulsion liquid membrane for cadmium removal: Studies on emulsion diameter and stability

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ABSTRACT

This paper presents a comprehensive study on emulsion diameter and removal capacity of Cd(II) from aqueous solution using emulsion liquid membrane (ELM). The liquid membrane consists of trioctylamine (TOA) as a carrier, kerosene as an organic diluent, ammonia as a stripping solution and Span 80 (sorbitan monooleate) as an emulsifying agent, prepared using ultrasonic. The important parameters affecting the emulsion diameter for recovery of Cd(II) including emulsification time, surfactant concentration, carrier concentration, and volume ratio of membrane to internal phase were systematically studied. The effects to membrane breakage were also investigated. The effect of emulsion diameter on the removal capacity of Cd(II) was also studied as its important role in the permeation process. The results showed that the emulsion diameter ranging from 0.878 up to 2.46 μm. The highest removal capacity was 0.493 mg Cd/ml emulsion while the lowest membrane breakage was 0.117% were obtained at the smallest emulsion droplets diameter.

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1. Introduction

In 2010, about 85% cadmium compounds such as cadmium sulfide and cadmium oxide/hydroxide are used in rechargeable nickel-cadmium batteries [1]. Cadmium has also used in pigments, coatings, stabilizers, specialty alloys and electronic compounds. As a result, the industrial liquid waste is therefore potential sources of cadmium which is a kind of harmful heavy metals. Much of the cadmium entering fresh waters may be rapidly adsorbed by particulate matter [1]. The high toxicity of this metal causes an important environmental impact which not only affects aquatic life but also human life. Therefore, the removal of this ion from wastewater is very important.

Many methods have used in waste water treatment generated by industrial processes such as solvent extraction, electro coagulation, activated carbon adsorption, ion exchange, emulsion liquid membrane (ELM), etc. Among them, extraction processes using ELM, invented by Li [2] in 1968, have received significant attention for their potential as a technique for treatment of industrial liquid wastes due to the high interfacial area for mass transfer, the ability to remove and to concentrate selectively or collectively, and the requirement of only small quantities of organic solvent. However, the need to obtain desired level of stability is very important in order to overcome the obstacle of the application of ELM at industrial scale. Its commercial applications on the removal of heavy metals are still limited by the emulsion instability that can decrease the extraction efficiency [3,4].

One of the factors determining the emulsion stability as well as the extraction efficiency is membrane breakage. In extraction process, stirring is done to disperse emulsion phase in continuous feed phase. The emulsion should be stable enough against the stirring to extract the metal into the internal phase. Emulsion breakage results in decreasing of extraction efficiency by the release of entrapped metal. The increase of feed phase pH indicates the membrane rupture which causes the spill out of internal phase to the feed phase.

The other factor affecting emulsion stability is emulsion diameter. In this matter, both the methods of emulsification and membrane compositions play an important role to produce stable emulsion which is associated to droplet diameter of emulsion [4,5]. Large droplet diameters result in poor stability and extraction efficiency [6] because of a low surface-to-volume ratio [7]. Emulsion droplets in the range 0.8–3 μm combine rapid extraction rates, good stability and are readily broken by electrostatic means [6]. Small emulsion diameter will provide a stable emulsion and a larger mass transfer area thus increasing the extraction efficiency. If the droplet diameters are too small, however, the emulsion is very difficult to break by any mechanical means [6]. In addition, too many of them are packed into each organic globule and consequently the liquid membrane becomes too thin and ruptures easily [7].

There are two methods used to produce emulsion in ELM process, i.e. mechanical agitation and ultrasonication [4]. In case of cadmium extraction, mechanical agitation such as stirrer, mixer, and homogenizer is the most common method used in published literatures

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[8–14]. Till date, no information about ultrasound emulsification for recovering cadmium found in the literature. Neither did the study on the emulsion diameter and membrane breakage in cadmium removal. In fact, generally mechanical agitation produces bigger emulsion diameter and relatively longer processing time than that of ultrasound emulsification [15]. Ultrasound emulsification does not only consume the least energy and surfactant but also can be potentially scaled up which make the process feasible [4]. Nevertheless, for ELM separation process, ultrasound emulsification must be managed very well; otherwise it may produce too stable emulsions in relatively short times, causing another problem in the following demulsification process.

In this study, ultrasonic was used to produce emulsion. The effects of emulsification time, surfactant concentration, carrier concentration and ratio membrane to internal phase on the emulsion diameter and membrane breakage were studied. Furthermore, the removal capacity of cadmium was also investigated on the influence of emulsion diameter. In view of this, application of this technique to solutions containing Cd(II) was investigated for removal of Cd(II) using trioctylamine (TOA) as extractant, Span 80 as surfactant, kerosene as membrane phase, and ammonia (NH_3) as stripping solution.

2. Materials and methods

2.1. Chemicals

All reagents used were of analytical grade. All aqueous solutions were prepared with deionized water. The trioctylamine (TOA) as extractant was used without further purification. The surfactant used was Span 80. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust feed phase pH. TOA, Span 80, NH_3, HCl, and NaOH were obtained from Merck. The aqueous solutions of cadmium were prepared from its cadmium chloride provided by Sigma Aldrich. The diluents used were commercial grade.

2.2. Analytical instruments

The droplet sizes of w/o emulsions were measured using Olympus optical microscope equipped with camera. The solution pH was measured using Fisher Scientific accumet AB15 pH meter. The concentration of cadmium was determined spectrophotometrically using Atomic Absorption Spectrophotometer AA-6650 Shimadzu at wavelength of 228.85 nm.

2.3. Procedure

2.3.1. Emulsion formation

Unless otherwise stated, the emulsion formation was done by mixing 45 ml of the membrane phase containing 4 wt.% of carrier with 4 wt.% of surfactant Span 80 in kerosene. The membrane phase was stirred at 500 rpm for 5 min using magnetic stirrer. To this mixture, 15 ml of the stripping aqueous solution, 3 M NH_3 solution, was added. The solution was then emulsified in a double glass cylindrical jacket, allowing water-cooling of the emulsification cell. A commercial supply ultrasonic USG-150 equipped with titanium horn mounted at the top of the cylindrical glass cell was used at emulsification time of 15 min to form the w/o emulsion. The emulsion was then measured directly after its formation.

The droplet diameter can be expressed as Sauter diameter (d_{32}) which is representing the average surface diameter as follow [16]:

$$d_{32} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} = 6\frac{V}{A} \tag{1}$$

where n_i, d_i are the number and diameter of droplets belonging to the ith class, while V and A are the total volume and area of the dispersed phase, respectively.

2.3.2. Extraction of cadmium

The prepared w/o emulsion was then poured into the external aqueous phase containing the cadmium ions at concentration of 100 ppm. Extraction was conducted at volume ratio of emulsion to external phase of 1:5. The system was stirred with a magnetic stirrer at 250 rpm for 15 min. Samples were taken from the external aqueous phase for analysis. In all experiments the results were taken in terms of the concentration of cadmium ions removed from the external phase. A summary of the experimental conditions for the ELM is presented in Table 1.

The removal capacity, denoted as removed cadmium mass per unit volume of emulsion, was calculated by the relation given by Mortaheb et al. [13]:

$$\boldsymbol{Removal\ capacity} = \left[\frac{(C_o - C)}{R_{ew}^o}\right] \times 10^{-3} \tag{2}$$

where C_0 is the initial concentration of cadmium ions in the external phase and C is the cadmium ion concentration in the external phase after contact. R_{ew}^0 is volume ratio of emulsion to external phase.

The percentage of membrane breakage (ε) is calculated using the following equation:

$$\varepsilon = \frac{V_s}{V_{int}} \times 100\% \tag{3}$$

where V_s is volume of internal phase leaked into external phase by splitting and V_{int} is initial volume of internal phase. While V_s can be calculated by mass balance:

$$V_s = V_{Ext}\frac{10^{pH0-14} - 10^{pH0-14}}{10^{pH0-14} - C_{OH^-}^{int}} \tag{4}$$

where V_{ext} is the initial volume of external phase, pH_0 and pH are the initial pH of external phase and pH of external phase being in contact with emulsion after a certain time of stirring, respectively. $C_{OH^-}^{int}$ is the initial concentration of OH^- in the internal phase.

Emulsion liquid membrane system involving w/o/w emulsion consists of emulsion including membrane and aqueous internal phase dispersed in a continuous external phase. The extractant reacts with the metal ion at the interface between the feed phase and the membrane phase to form the metal-extractant complex. The complex diffuses from this interface through the membrane phase, to the interface between the membrane phase and the aqueous internal phase, where stripping reaction occurs and the stripping agent in the aqueous internal phase strips metal ion into the aqueous internal phase. The stripping reaction also regenerates the extractant, which

Table 1
Experimental conditions for the ELM.

External phase	
pH	5.1
Volume (mL)	300
Cd(II) Conc. (ppm)	100
Internal phase	
Volume (mL)	15
[NH_3] (M)	3
Organic solution	
Volume (mL)	45
Diluent	Kerosene
[TOA] (wt.%)	4
Span 80 (wt.%)	4
Emulsification time (min)	15
Extraction time (min)	15
Extraction speed (rpm)	250

diffuses across the membrane phase and back to the interface adjacent to the aqueous feed phase to complete the facilitated transport cycle. The extractant is also called "carrier" in that it carries metal ions through the membrane phase [17]. The facilitated transport mechanism of Cd (II) transfer across a liquid membrane is shown in Fig. 1. The mechanisms of extraction and stripping processes of cadmium (II) through an ELM are explained by the following equations [9,12,18]:

1. TOA (shown as R_3N) of the organic membrane phase reacts with H^+ of the external phase

$$[R_3N]_{(org)} + [H^+]_{(aq)} + [Cl^-]_{(aq)} \rightleftharpoons [R_3NH^+Cl^-]_{(org)}$$
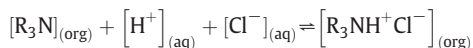
2. In the feed phase, $CdCl_4^{2-}$ exchanges with Cl^- of $[R_3NH^+Cl^-]$ in the organic membrane phase

$$2[R_3NH^+Cl^-]_{(org)} + [CdCl_4^{2-}]_{(aq)} \rightleftharpoons [(R_3NH)_2CdCl_4]_{(org)} + [2Cl^-]_{(aq)}$$
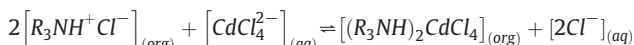
3. NH_3 in the internal phase reacts with $[(R_3NH)_2CdCl_4]$ to strip cadmium (II) into the internal phase

$$[(R_3NH)_2CdCl_4]_{(org)} + [2OH^-]_{(aq)} \rightleftharpoons 2[R_3N]_{(org)} + [CdCl_4^{2-}]_{(aq)} + [2H_2O]_{(aq)}$$
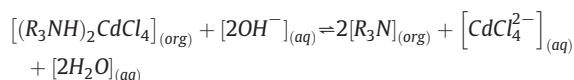
Some studies on cadmium removal by ELM used NH_3 as stripping solution [11,12]. By using NH_3, the studies resulted in the highest efficiency among the other. In this research, 3 M ammonia was used as stripping solution. If it is assumed that all the Cd was stripped by ammonia, the maximum concentration of $Cd(OH)_2$ will be 6.656×10^{-3} g/100 mL. Therefore, there should be no precipitation occurred since the solubility of $Cd(OH)_2$ i.e. 2.6×10^{-2} g/100 mL is higher than the maximum $Cd(OH)_2$ formed.

3. Results and discussion

3.1. Effect of emulsification time

To study the effect of emulsification time to emulsion diameter, emulsion was prepared at varied time in the range of 5–30 min. The prepared emulsion was then used to extract cadmium. The variations of the Sauter diameter, d_{32}, as a function of the emulsification time are presented in Fig. 2. Longer emulsification time produced smaller emulsion diameter and more stable emulsion. Intensity of the solution is also enhanced by longer emulsification time. The mixture will be more homogeny, more internal phase will be shrunk and entrapped in the membrane phase, producing finer droplets diameter. Related to fine droplets, greater number is produced at longer emulsification time. When these drops become smaller they will
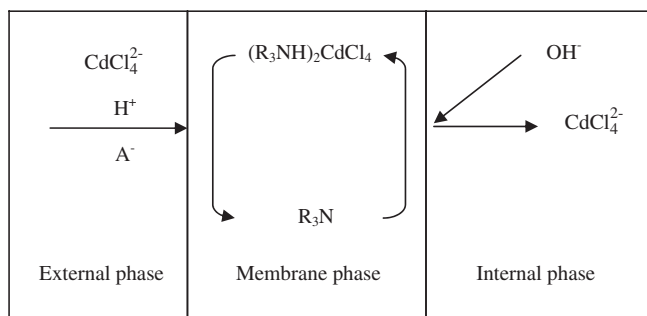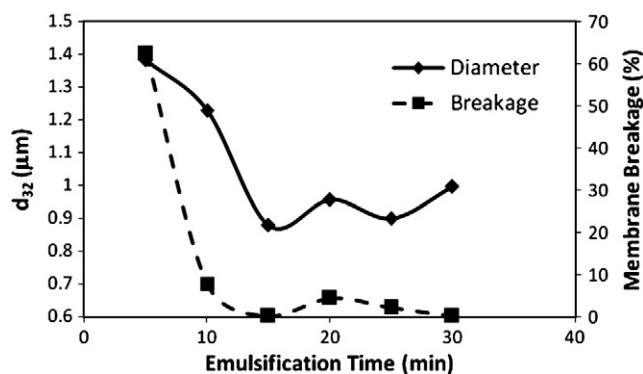

Fig. 2. Effect of emulsification time on the emulsion diameter and membrane breakage. Span 80 = 4 wt.%; TOA = 4 wt.%; volume ratio of membrane to internal phase = 3/1; $NH_3 = 3$ M; diluent = kerosene.

take much more time to coalesce [19]. However, too much emulsion droplets facilitate coalescence phenomenon, so the emulsion droplets become bigger. Another factor increasing droplets diameter at longer time is water transport phenomena.

Based on the experiment, the smallest droplets diameter was reached at emulsification time of 15 min. The increase of emulsification time until 30 min caused the increase of droplets diameter as described above.

Fig. 2 also illustrates the influence of emulsification time on the membrane breakage. An increase of irradiation time (5–15 min) results in the reduction of membrane breakage. The best membrane stability was reached at emulsification time of 15 min, implying the steady state condition. It is observed that at emulsification time higher than 15 min the breakage percentage increased. The high cavitation increases the number of small droplets, which is responsible for their diffusion into external feed phase. The insufficient irradiation time (below 15 min) leading to higher breakage percentage due to the larger size of the droplets that tend to coalesce with each other [20].

3.2. Effect of surfactant concentration

Effect of surfactant concentration on the emulsion diameter was studied by varying surfactant concentrations at 2 wt.%, 4 wt.%, 6 wt.%, and 8 wt.%. Fig. 3 shows the droplets size of w/o emulsion produced by different surfactant concentration. It is seen that emulsion droplets diameter decreased as the surfactant concentration increased from 2 wt.% to 4 wt.%. At low surfactant concentration, the coverage of membrane interface is incomplete caused by insufficient surfactant. Therefore, coalescence happened and raised the d_{32}. Lack
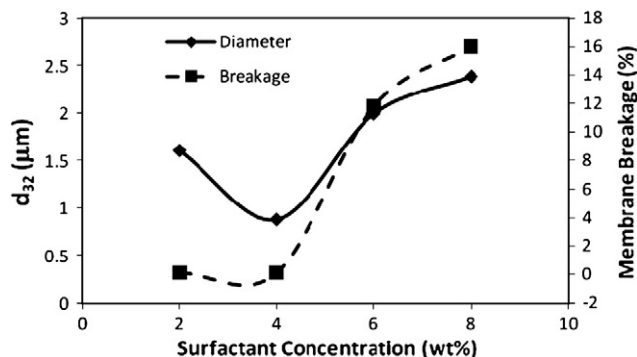

Fig. 3. Effect of surfactant concentration on the emulsion diameter and membrane breakage. Emulsification time = 15 min; TOA = 4 wt.%; volume ratio of membrane to internal phase = 3/1; $NH_3 = 3$ M; diluent = kerosene.

Fig. 1. Facilitated transport mechanism of Cd(II) transfer across a liquid membrane.

of surfactant also causes the high surface tension, leading to the difficult dispersion of emulsion droplets. Hence bigger emulsion droplets will be produced. Abismail [15] also observed that with non ionic surfactants, droplet size is further reduced above the critical micelle concentration (cmc), perhaps because of the solubility of the non ionic in both phases. Further increase in surfactant concentration up to 8 wt.% increased the emulsion droplets diameter. This phenomena probably caused by the droplets coalescence due to the excess surfactant or micelles adsorbed onto the surface of emulsion droplets [15]. The d_{32} was in the order of 4 wt.%<2 wt.%<6 wt.%<8 wt.%. The smallest d_{32} was 0.878 μm while the highest d_{32} was 2.38 μm. These results agree with the range suggested by Li et al. [6] who produced w/o emulsion at d_{32} of 0.8 to 3 μm. At surfactant concentration of 7 vol% and using higher power of 93 W, Juang and Lin [21] produced w/o emulsion at smaller d_{32} of 50 nm.

The effect of surfactant concentration to the membrane breakage was investigated. As described above, the amount of surfactant must be considered very well to obtain stable emulsion. It was analyzed that emulsion stability increased slightly with the increase of surfactant concentration until 4 wt.%. Beyond that concentration, the membrane breakage increased sharply. This is due to the decrease of interfacial tension between the phases, leading to form more fine droplets. Above its critical micelles concentration, surfactants tend to form aggregates in the bulk solution. The aggregates promote water transport to external phase which causes breakage while to internal phase causes swelling [22].

3.3. Effect of carrier concentration

To investigate the effect of carrier on the emulsion diameter, TOA concentration was varied at 2 wt.%, 4 wt.%, 6 wt.%, and 8 wt.%. The effect of carrier concentration on the emulsion droplets diameter is shown in Fig. 4. The d_{32} decreased as the increase of carrier concentration from 2 wt.% to 4 wt.%. The increase of carrier concentration does not favor the emulsification process particularly at ultrasonic power<30 W [18], seen by the increase of d_{32} as the carrier concentration was increased until 8 wt.%. The water transport phenomena happened in the higher carrier concentration leading to more serious swelling effect. Instead of using high carrier concentration, separation ability and removal capacity can be increased by occupying higher ultrasonic power. Chakraborty and Bart [23] found the similar result, incorporation of carrier in the membrane phase increases membrane breakage, resulting into the rapid transfer of internal feed phase to external phase. The high content of carrier in the membrane is not beneficial due to the increase in viscosity, which leads to larger globules. Also, the increasing concentration of carrier promotes the permeation swelling, which dilutes the aqueous receiving phase and decreases the efficiency of the process [24].
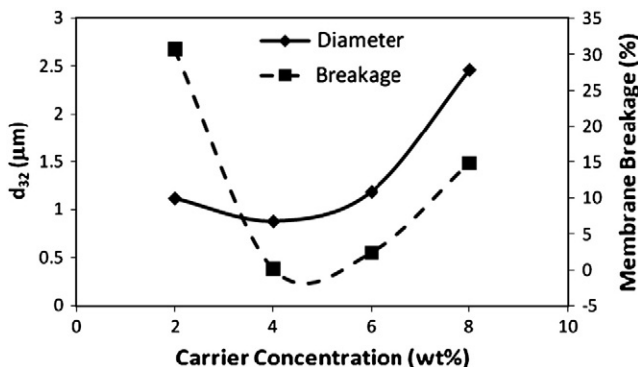
Effect of carrier concentration to membrane breakage is presented in Fig. 4. From this figure, it is seen that for carrier concentrations ranging from 2 wt.% to 4 wt.%, the membrane breakage decreases with increasing the carrier concentration. This may be due to the interfacial properties of the carrier. Emulsion stability decreased beyond that concentration. The instability of w/o emulsions results in the membrane breakage, causing the split of internal phase into external phase. To get the best membrane stability, carrier concentration was found to be 4 wt.%.

3.4. Effect of volume ratio of membrane to internal phase

To investigate the effect of volume ratio of membrane to internal phase on the emulsion diameter and membrane breakage, volume ratio of membrane to internal phase was varied at 2, 3, and 5. Profile of emulsion diameter as a function of volume ratio membrane to internal phase is shown in Fig. 5. Low volume ratio of membrane to internal phase produce big droplets diameter. This is due to insufficient amount of membrane solution causing the internal phase cannot be completely entrapped. At lower ratio, the internal phase tends to leak into the external phase, enhancing the membrane breakage. Conversely, high volume ratio of membrane to internal phase also produce big droplets diameter. Too much membrane solution produce thicker emulsion wall that prevents the internal phase from diffusing in. The increase of membrane phase volume also increases the surface tension hence the emulsion droplets are harder to be dispersed. As a consequence, larger droplets will be produced. The higher surface tension also leads to higher membrane breakage. Hence, the ratio membrane to internal phase must be used precisely. In addition, Abismail [15] stated that at equal volume, phase inversion tends to occur in ultrasound emulsification. In this research, the smallest d_{32} was reached at volume ratio of membrane to internal phase of 3/1.

3.5. Removal capacity of cadmium

The removal capacity of cadmium as a function of emulsion diameter is shown in Fig. 6. It is seen that removal capacity decreased with the increase of d_{32}. This is due to smaller droplets diameter give larger mass transfer area and greater number of droplets. The highest removal capacity was obtained at the smallest d_{32}. In this research, the highest removal capacity was 0.493 mg Cd/ml emulsion. For comparison with other study [13] in which emulsion was prepared using mechanical agitation, the removal capacity was only 0.44 mg Cd/ml emulsion at 15 min of emulsification time and initial concentration of cadmium of about 100 ppm. This indicates that the ultrasound emulsification is more beneficial, not only produces stable emulsions
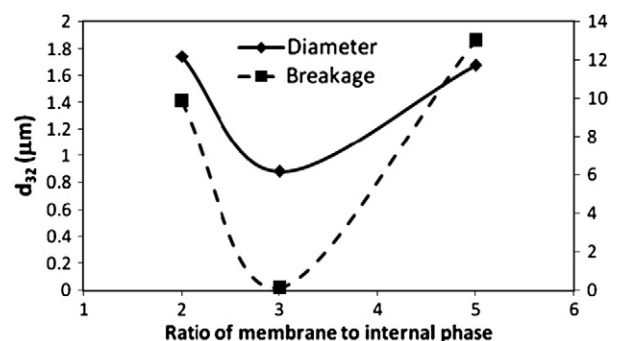

Fig. 4. Effect of carrier concentration on the emulsion diameter and membrane breakage. Emulsification time = 15 min; Span 80 = 4 wt.%; volume ratio of membrane to internal phase = 3/1; NH$_3$ = 3 M; diluent = kerosene.

Fig. 5. Effect of volume ratio of membrane to internal phase on the emulsion diameter and membrane breakage. Emulsification time = 15 min; Span 80 = 4 wt.%; TOA = 4 wt.%; NH$_3$ = 3 M; diluent = kerosene.
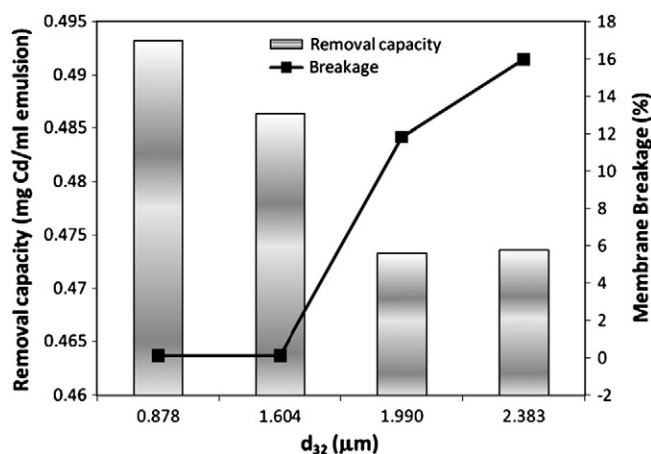
Fig. 6. Effect of emulsion diameter on the removal capacity of cadmium and membrane breakage. Emulsification time = 15 min; Span 80 = 4 wt.%; TOA = 4 wt.%; volume ratio of membrane to internal phase = 3/1; NH₃ = 3 M; diluent = kerosene; initial cadmium ions concentration = 100 ppm; C^o_{ew} = 1/5; extraction stirring speed = 250 rpm; extraction time = 15 min.

but also gives a high removal capacity of cadmium compared to mechanical agitation method.

The effect of emulsion diameter to membrane breakage was also observed in this research. The results showed that small droplet diameter tends to have better breaking resistant and rapid extraction as obtained by Li, et al. [6]. This can be seen at Fig. 6 which describes that membrane breakage increased as the increase of emulsion diameter. The lowest membrane breakage of 0.117% was reached at the smallest emulsion diameter of 0.878 μm. Membrane breakage at the rate of ~0.1% is allowable for a practical process [25].

4. Conclusion

In this work, a w/o type emulsion was prepared using ultrasound by dissolving carrier trioctylamine, internal stripping solution ammonia, and surfactant Span 80 in kerosene for Cd(II) removal from waste water. The use of ultrasound emulsification has been proven to be a useful method to produce a stable emulsion with small diameter. In this research, the optimum condition was obtained at emulsification time of 15 min, Span 80 concentration of 4 wt.%, TOA concentration of 4 wt.% and volume ratio of membrane to internal phase of 3/1. The optimum condition gave the smallest d_{32} of 0.878 μm, the lowest breakage of 0.117% and the highest removal capacity of 0.493 mg Cd/ml emulsion.

Acknowledgments

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