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Cadmium removal from aqueous solution by emulsion liquid membrane (ELM): influence of emulsion formulation on cadmium removal and emulsion swelling

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ABSTRACT

This work aims to investigate the best formulation of Emulsion Liquid Membrane to be used for cadmium removal from aqueous solution. The parameters involved in this study are carrier (Aliquat 336) and surfactant (Span 80) concentration, emulsification time as well as initial W/O (water-in-oil) volume ratio. Their effects on cadmium removal efficiency, E(%) were investigated together with their influence on emulsion swelling, $\delta(\%)$. The emulsion globule was observed under a microscope to track its size change as the extraction process took place and the data were later used to quantify the occurrence of emulsion swelling. Corn oil was used as diluent to dissolve 3 wt.% of both, Aliquat 336 and Span 80 in forming the membrane phase. W/O mixture at volume ratio of 0.33 was homogenized for 12 min to prepare the emulsion and it was found to effectively remove 98.15% of cadmium at minimal swelling (34.24%).

Keywords: Emulsion liquid membrane; ELM stability; Emulsion swelling; Cadmium extraction; Vegetable oil

1. Introduction

Stability of Emulsion liquid membrane (ELM) system could be disrupted by membrane breakage, coalescence as well as emulsion swelling. In the case of emulsion swelling, it is mainly caused by transportation of water from the external phase into the internal, and it is classified into two main types; osmotic and entrainment swelling [1]. The phenomena has caused

the emulsion to become prone to membrane breakage as the membrane thickness is reduced [2] hence, resulting in poor extraction efficiency while at certain extent, it is nullified. In fact, swelling of emulsion could harm the overall ELM performance as it decreases the driving force for solute extraction besides diluting the final solute concentration in the internal phase [3]. As a consequent, this phenomenon limits the extensive applications of ELM in larger scale.

Two mechanisms of water transport in W/O/W (water-in-oil-in-water) emulsion system that caused

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swelling of emulsion were reported by Wen and Papadopoulos [4]. Via the first mechanism, the water is said to be transported as the effect of surfactant hydration where the hydrophilic part of the surfactant is hydrated at the membrane-external interface and later dehydrated as it reaches the membrane-internal interface. The second mechanism is reverse micellization. This phenomenon normally occurs in emulsion having thick membrane layer where the reverse micelles were formed at membrane-external interface and it later migrates to the membrane-internal interface. Apart from these two mechanisms, emulsion swelling can be mediated by water co-extraction and it took place even in the absence of any osmotic pressure gradient [5]. Also, swelling can occur due to entrainment of external phase as a result of repeated coalescence and re-dispersion of emulsion globules during the dispersion process [6].

Despite instability issues, ELM which was invented by Li [7] has been applied widely for heavy metal removal from aqueous solution. This includes copper [8], cobalt [9], and cadmium [10]. As for cadmium, usage of ELM has resulted in a very high removal efficiency at its optimum condition. Moreover, based on our previous work [11] using TOA as carrier, more than 98% of cadmium ions were removed from the aqueous solution, thus proving the feasibility of ELM. Effectiveness of ELM in separating solute is attributed to its beneficial features; large surface area to volume ratio, simultaneous extraction and stripping process in a single unit, highly selective and does not require much energy as well as time. However, finding the optimum condition in ELM operation is realized to be important in ensuring high removal efficiency.

Basically, ELM consists of internal, membrane, and external phase. The membrane phase is made up of surfactant, carrier and diluent and this phase is responsible in separating the internal and external phase as well as providing high surface area for solute transfer. As for cadmium, it is known to be insoluble in the membrane phase and hence, requires a carrier to mediate its transportation across the membrane phase. Once stripped in the internal phase, cadmium ions remain and the free carrier diffuses back to the external-membrane interface to form another new complex with cadmium extractable ions. This mechanism is known as the Type II Facilitated transport. In conventional ELM formulation, petroleum derivatives such as kerosene [10] and hexane [12] were used as diluent in forming the membrane phase. These types of diluents were normally selected due to their characteristics of low viscosity, readily available and nonpolar. Despite their effectiveness in the ELM formulation for solute removal, the diluent itself is toxic and

harmful to the environment as well as human health, outweighing their advantages in separation field. Application of safer solvent such as vegetable oil was continuously explored in few other configurations of liquid membrane such as bulk [13] and supported [14]. However, incorporation of non-petroleum-based chemical as diluent in ELM is still scarce.

In this study, the emulsion will be developed by incorporating corn oil as diluent and hence, its performance on cadmium removal efficiency, E(%) as well as on emulsion swelling, $\delta(\%)$ will be evaluated. Effect of four parameters; carrier and surfactant concentration, emulsification time and initial W/O volume ratio will be studied. Observation of emulsion swelling was made using a microscope, while the removal efficiency will be calculated using the data obtained from a spectrophotometer. The main interest of this study is to discover the optimum point for each parameter to allow maximum cadmium removal efficiency to be achieved and at the same time, ensuring the stability of the emulsion. In fact, not much work have been done to optimize the parameters involved in ELM system by taking into consideration these two important aspects at the same time.

2. Experimental

2.1. Chemicals

The three main phases of the emulsion (membrane, internal and external) were prepared individually. The membrane phase was made by dissolving non-ionic surfactant (Span 80 from Merck) and carrier (Aliquat 336 from Sigma Aldrich) in commercial grade of corn oil. The external phase was prepared by dissolving 150 ppm CdCl₂ (Sigma Aldrich) in HCl solution and the pH was adjusted to 1.0 before any extraction process took place. On the other hand, the internal phase was prepared using 0.1 M Ammonia solution (Merck). Otherwise mentioned, all solutions were prepared using deionized water and the experiments were conducted at ambient temperature.

2.2. Procedure

2.2.1. Cadmium extraction

The membrane phase was prepared by dissolving adequate amount of Aliquat 336 (1–6 wt.%) and Span 80 (1–6 wt.%) in corn oil. W/O emulsion was made by adding the internal phase to the membrane phase prior to intensive emulsification with the help of ultrasonic at frequency of 22.5 kHz. A commercial ultrasonic (USG-150) equipped with titanium horn

was used in this process and it was carried out for 15 min unless stated. After pouring the prepared emulsion to the external phase at ratio 1:5, the content of the vessel was stirred at 400 rpm for 20 min. Stirring speed, extraction time and emulsion to external phase ratio were kept constant throughout the entire experiment. Finally, the concentration of cadmium in the external phase was measured using Atomic Absorption Spectrophotometer (Shimadzu AA-6650) at wavelength of 228.8 nm and the efficiency of cadmium removal, E(%) was calculated using Eq. (1):

Cadmium removal efficiency,
$$E(\%) = \frac{(C_o - C_t)}{C_o} \times 100$$

where C_0 is the initial concentration of cadmium in the external phase while C_t is the concentration of cadmium after 20 min of extraction.

2.2.2. Emulsion swelling investigation

The size of the emulsion globules were observed using Olympus BX51 M optical microscope equipped with a 3.0 MP camera and an image analysis software. The emulsion was sampled every 5 min as the extraction process took place. To capture the emulsion globule image, a tiny drop of the emulsion was placed onto a glass slide containing pool of external aqueous phase to form a W/O/W system. A single emulsion globule was focused and the image was captured. The image obtained was analyzed to observe the fate of internal droplet size as emulsion swelling were caused by the expansion of this phase due to water transfer. The change of the emulsion globule diameter was recorded as *S*(*t*) using Eq. (2) [15]:

$$S(t) = \frac{D(t)}{D(0)} \tag{2}$$

where D(t) is the diameter of the emulsion globule at time t while D(0) is the initial diameter of the emulsion globule and the data is later plotted against time. Change of W/O volume ratio can be expected as water permeates from the external phase into the internal, using equation derived from mass balance. W/O volume ratio, $R_{\rm W/O}(t)$ at specific time was calculated using the following equation [15]:

$$R_{\text{W/O}}(t) = 1 - \frac{1}{S^3(t)} [1 - R_{\text{W/O}}(0)]$$
 (3)

where $R_{\rm W/O}(t)$ and $R_{\rm W/O}(0)$ is the W/O volume ratio at time t and initial W/O volume ratio, respectively. The data were later used in calculating the percentage of emulsion swelling, $\delta(\%)$ by comparing the value of $R_{\rm W/O}(t)$ and $R_{\rm W/O}(0)$ using Eq. (4):

Emulsion swelling,
$$\delta(\%) = \frac{R_{\rm W/O}(t) - R_{\rm W/O}(0)}{R_{\rm W/O}(0)} \times 100$$
 (4)

3. Results and discussion

3.1. Effect of carrier (Aliquat 336) concentration

The change of the emulsion globule diameter with time were recorded as S(t) and the data are plotted in Fig. 1. It is clearly seen from the figure that emulsion made of more than 3 wt.% Aliquat 336 showed a significant increment of emulsion globule size at early extraction period and the gradient of S(t) with respect to time were found to be increasing together with the carrier concentration. On the other hand, Figs. 2 and 3 were provided to show the images of emulsion globule size change and the swelling percentage, δ (%) data as a function of carrier concentration, respectively. The occurrence of severe emulsion swelling can be directly noted from the images in Fig. 2 as the internal phase undergoes significant expansion when more than 3 wt.% Aliquat 336 was incorporated in the membrane phase. From the quantitative data of emulsion swelling displayed in Fig. 3, it is identified that the swelling of emulsion is minimal at 1-3 wt.% of Aliquat 336 but it has abruptly increased to 82.53% at 4 wt.% of Aliquat 336. The trend continued as the concentration was further increased.

Increasing emulsion swelling trend in Fig. 3 at high concentration of carrier, especially > 4 wt.% is probably due to the surfactant property of Aliquat 336

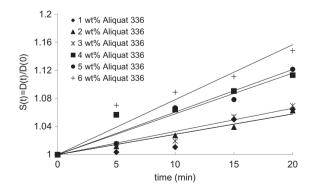


Fig. 1. Plot of S(t) vs. time.

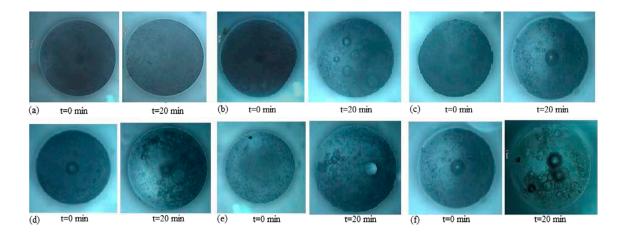


Fig. 2. Images of emulsion globule size change at various Aliquat 336 concentration: (a) 1 wt.%, (b) 2 wt.%, (c) 3 wt.%, (d) 4 wt.%, (e) 5 wt.%, and (f) 6 wt.%.

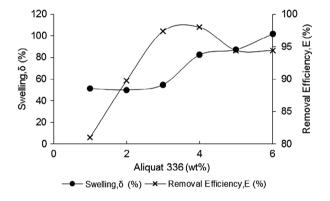


Fig. 3. Effect of Aliquat 336 concentration on emulsion swelling and cadmium removal efficiency.

[16]. Presence of high Aliquat 336 concentration in the emulsion has allowed permeation of water across the membrane phase, causing the internal phase to swell. The observation made in Fig. 3 is also a consequent of carrier-solute complex formation [17]. This is due to the fact that the complex could co-transport water molecules across the membrane phase and higher amount of carrier available has enhanced emulsion swelling occurrence.

The performance of ELM in removing cadmium was evaluated and the data of cadmium removal efficiency, E(%) can be found in Fig. 3. Data from the figure suggests that increment of Aliquat 336 concentration in the membrane phase has a huge contribution to the extraction capability of the system. It is conceivable that the increase of carrier concentration in the membrane phase, and hence, at the membrane-external aqueous interface enhances the formation of metal-carrier complexes [3]. This situation has resulted

in increasing extraction of cadmium from the external phase through the membrane layer. At low concentration, insufficient amount of carrier caused low E(%) to be recorded and it increases gradually as the concentration increases. From the figure, high E(%) was achieved using 3–4 wt.% of Aliquat 336. However, further increment of Aliquat 336 concentration to 5 wt.% and beyond does not benefit the system. Rather than enhancing the performance of the system, severe emulsion swelling also occurred (Fig. 3) as a consequent of high carrier concentration. Eventually, it causes release of the extracted solute back to the external phase due to thinning of membrane layer, resulting a decline of efficiency as illustrated in Fig. 3.

Two major observations can be made as the concentration of Aliquat 336 increases; it causes instability of emulsion and increment of emulsion viscosity which leads to enhancement of mass transfer resistance, thus causing extraction capability to decline. Since carrier is the most expensive component in the emulsion, its usage at high concentration is not necessary as it is only responsible in facilitating the transportation of insoluble solute across the membrane phase via the formation of complex. Only 3 wt.% of Aliquat 336 will be used as carrier for the rest of this study.

3.2. Effect of surfactant (Span 80) concentration

While keeping other parameters constant, the effects of varying Span 80 concentration on emulsion swelling were studied and the data obtained are presented in Figs. 4–6. Illustration of S(t) vs. time data is provided in Fig. 4 while Fig. 5 shows the images of emulsion globules change. According to these figures,

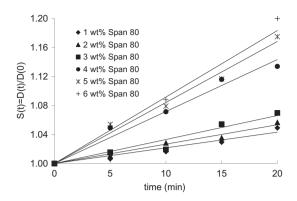


Fig. 4. Plot of S(t) vs. time.

the changes of emulsion globule diameter were found to be huge due to swelling of the emulsion as the concentration of Span 80 increases beyond 3 wt.%. This condition has resulted a large gradient of S(t) with respect to time and the data available were later transformed into percentage of emulsion swelling, $\delta(\%)$ as plotted in Fig. 6. From the figure, it is identified that severe emulsion swelling, $\delta(\%)$ was recorded at 4 wt.% and thereafter.

Significant increment of swelling were noted as Span 80 concentration increases from 3 to 4 wt.%. This phenomenon was observed due to several reasons and one of them is the formation of fine emulsion droplets. According to Juang and Lin [18], a great amount of surfactant available allows it to form an adsorbed monolayer onto the emulsion droplets, hence, govern the surface area produced. Although it is beneficial to have a large interfacial area for solute extraction, this condition has permitted more water to permeate into

the internal phase, mostly due to osmotic pressure gradient [4].

Besides, due to Span 80's amphiphilic property, it could be easily hydrated and cause swelling to occur [15]. This can be attributed to the fact that Span 80 is having low HLB value [19] and it is classified as strong hydrophile [5]. Water is spontaneously transported across the membrane phase as the hydrophilic portion of the surfactant is hydrated at the membrane-external interface and gets dehydrated on the other side of the membrane [15]. As higher concentration of surfactant is available in the system, larger amount of water could be transported across the membrane phase via this mechanism, hence, severe emulsion swelling occurred [4]. This phenomenon can be directly observed in Fig. 5, especially when 4–6 wt.% Span 80 were used.

Meanwhile, the effect of varying Span 80 concentration on cadmium removal efficiency, E(%) was studied and the data obtained are presented in Fig. 6. It is noted that by increasing the surfactant concentration from 1 to 3 wt.% has improved the removal efficiency of cadmium (from 89.30 to 98.00%), but not thereafter. The enhancement of E(%) was mainly attributed to the fact that smaller emulsion globules were formed as the surface tension between the immiscible phases was reduced due to the presence of sufficient amount of surfactant [3]. This condition led to the formation of larger contact area between the emulsion and the external phase [20].

On contrary, counterproductive results were recorded as the concentration of Span 80 increases beyond 3 wt.%. Apart from emulsion instability as illustrated in Fig. 6, this situation was observed due to

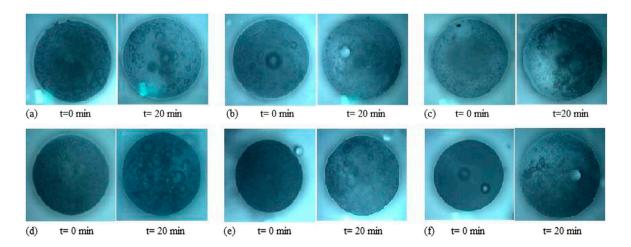
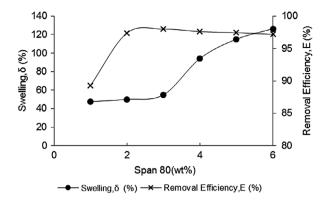
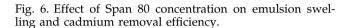


Fig. 5. Images of emulsion globule size change at various span 80 concentrations: (a) 1 wt.%, (b) 2 wt.%, (c) 3 wt.%, (d) 4 wt.%, (e) 5 wt.%, and (f) 6 wt.%.





two other reasons; surfactant occupancy which enhances the mass transfer resistance, and it increases emulsion viscosity, causing larger emulsion droplets formation during dispersion [21]. In addition, saturation of Span 80 at the membrane-external interface due to excessive amount of surfactant available has caused the formation of a barrier for solute transport at the interface, thus decelerate solute permeation [22].

In compensating the mass transfer resistance and the emulsion stability, the usage of 3 wt.% of Span 80 was found to be appropriate. According to emulsion stability as well as the efficiency data, irrelevant increment of Span 80 concentration has neither benefited the emulsion stability nor the extraction efficiency. By using 3 wt.% of Span 80, only 54.95% emulsion swelling were recorded alongside maximum cadmium removal efficiency (98.00%).

3.3. Effect of emulsification time

In observing the effects of emulsification time on cadmium removal efficiency as well as emulsion swelling, the W/O mixture was emulsified at various duration, ranging from 7 to 17 min. Fig. 7 shows the data of *S*(*t*) vs. time, while Fig. 8 provides the images of emulsion globules change at varying emulsification time. Based on these figures, emulsion prepared for 17 min showed the largest expansion of the internal phase as well as the emulsion globule diameter while the one prepared for 15 min showed the least. By taking the available data of S(t), the emulsion swelling, $\delta(\%)$ was calculated and presented in Fig. 9. According to the data in this figure, application of too short or too long emulsification time has neither assisted in the formation of a stable emulsion. Swelling of emulsion was found to lessen as the emulsification time increases from 7 to

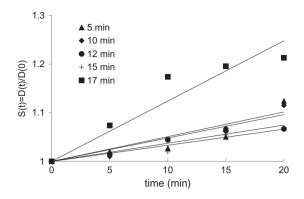


Fig. 7. Plot of S(t) vs. time.

15 min, but not thereafter. Beyond 15 min, abrupt increment of emulsion swelling was noted.

As can be seen from Fig. 9, occurrence of high emulsion swelling was observed at minimal emulsification time and it is mainly due to the formation of large emulsion droplets that coalesce quickly [3]. As the time for emulsification prolongs, the water and oil mixture were said to be homogenized properly [23]. However, extending the time to 17 min has resulted in severe emulsion swelling and according to Malik et al. [3], this condition is a consequent of entrainment of the external phase during the dispersion of emulsion globules for extraction purpose. Besides, emulsion swelling could also easily occur as the emulsion's shape is distorted. This phenomenon is a result of surfactant degradation at elevated temperature of the emulsion during long emulsification process.

Cadmium removal efficiency data as a function of emulsification time are presented in Fig. 9. According to the figure, E(%) recorded increases gradually as the emulsification time increases from 7 to 12 min. This observation was noted mainly due to the fact that a stable and homogenized emulsion was produced at sufficient emulsification time [24]. From the data available in Fig. 9, maximum E(%) was recorded at 12 min of emulsification where 98.05% of cadmium ions were removed.

Low E(%) was recorded at minimal emulsification time due to the formation of large internal phase droplets, causing a reduction in the transfer area of solute [20]. At this point, the time was said to be insufficient to produce a sufficiently small emulsion globule and as a result, poor extraction efficiency is recorded in Fig. 9. On the other hand, sufficient time for emulsification process has allowed the production of smaller emulsion droplets [3], leading to large interfacial area for solute transfer at the membrane-external interface. Based on the data in Fig. 9, extending the emulsification time from 12 to 15 min does not enhance the removal

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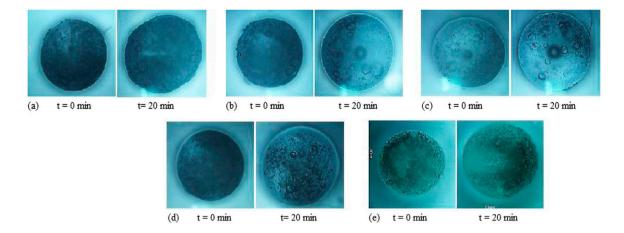


Fig. 8. Images of emulsion globule size change at various emulsification time: (a) 7 min, (b) 10 min, (c) 12 min, (d) 15 min, and (e) 17 min.

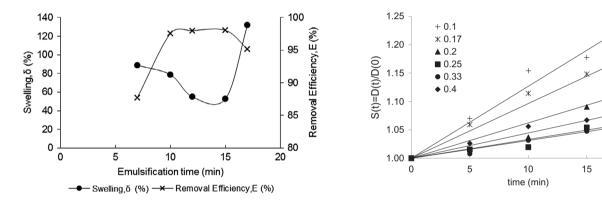


Fig. 9. Effect of emulsification time on emulsion swelling and cadmium removal efficiency.

efficiency significantly. On top of that, application of longer emulsification time (17 min) has negatively

longer emulsification time (17 min) has negatively affected the efficiency. Hence, 12 min is taken as the optimum point due to low emulsion swelling (52.81%) recorded, whereas 98.05% of cadmium were removed.

3.4. Effect of initial W/O volume ratio

Experiments were design at varying W/O volume ratio to investigate its influence on emulsion swelling, $\delta(\%)$. The ratio were varied, ranging from 0.1 to 0.4 and the change of emulsion globule diameter with time, S(t) was investigated. The data obtained are plotted in Fig. 10, whereas Fig. 11 provides the images of the emulsion globule observed under a microscope. As can be seen from the figures, emulsion prepared using low W/O volume ratio showed the greatest change in emulsion globule size. Emulsion prepared using W/O ratio of 0.1 recorded the largest S(t) and

Fig. 10. Plot of S(t) vs. time.

the data available were transformed into the plot of emulsion swelling, $\delta(\%)$ vs. W/O volume ratio, shown in Fig. 12. From the figure, it is identified that the swelling of emulsion has reduced dramatically from 436.61% with the usage of W/O volume ratio 0.1 to 34.24% at ratio of 0.33.

The emulsion swollen badly at low W/O volume ratio mainly due to the presence of high amount of organic membrane phase containing surfactant, which reported to facilitate water permeation [4]. Since the internal phase volume is relatively small compared to the membrane phase, the effective amount of surfactant to adsorb the interfacial tension at the water-oil interface decreases [25], leaving behind a great sum of excess surfactant molecules. These excess surfactant molecules tend to form secondary emulsion and eventually, entrained the external phase [2].

In fact, similar trend was documented by Yan and Pal [15] who claimed that high volume of membrane phase used in ELM system has caused the excessive

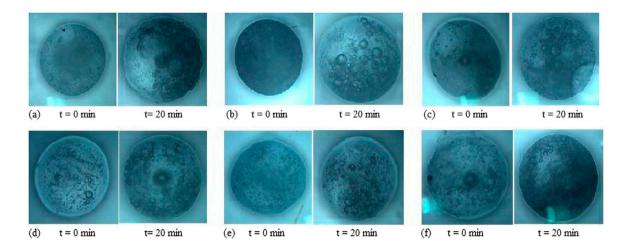


Fig. 11. Images of emulsion globule size change at various W/O ratio: (a) 0.1, (b) 0.17, (c) 0.2, (d) 0.25, (e) 0.33, and (f) 0.4.

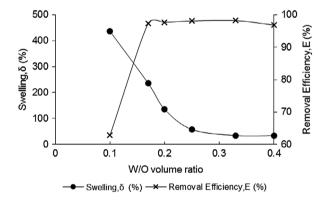


Fig. 12. Effect of initial W/O volume ratio on emulsion swelling and cadmium removal efficiency.

surfactant to assist the occurrence of emulsion swelling due to surfactant hydration [26]. Additionally, the occurrence of remarkable emulsion swelling at low W/O volume ratio as observed in Fig. 12 is also attributed to the encapsulation of tiny water droplet at the interface due to the existence of reverse micelle [4].

Investigation on the performance of ELM for cadmium removal at varying W/O ratio was carried out and the data available are presented in Fig. 12. According to the figure, highest removal efficiency was recorded using W/O volume ratio of 0.33 where 98.15% of cadmium ions were successfully removed. Sharp increment of E(%) was noted as the ratio increases from 0.1 to 0.33 but it dropped beyond this point. This condition is directly related to the viscosity of the emulsion produced. Emulsion with high viscosity was formed at lower W/O volume ratio which was claimed to cause difficulties in dispersing the

emulsion during extraction process [27]. As a result, larger emulsion globules were dispersed in the external phase, causing a decrease in surface area to volume ratio of the emulsion [20].

In addition, poor performance of ELM with the application of low W/O volume ratio as illustrated in Fig. 12 can also be attributed to the surfactant occupancy at the water-oil interface. This condition has further enhanced the mass transfer resistance [28]. On the other hand, improvement of cadmium removal efficiency was achieved as the W/O volume ratio increases due to the reduction of membrane layer thickness. This is due to the fact that thinner membrane layer was formed using higher W/O volume ratio, thus resulting in shorter path for solute transportation [29]. Unfortunately, too high W/O volume ratio has caused the encapsulation of the internal phase to be inhibited [30] and larger emulsion globules with thin layer of membrane phase were formed. This condition has lessen the interfacial area available for solute transport while the thin membrane layer has caused the membrane to break easily, releasing the extracted solute back into the external phase [31]. This phenomenon is probably the main cause of major decline of E(%) as the W/O volume ratio was further increased to 0.40, as demonstrated in Fig. 12.

Hence, the optimum point selected for this parameter is 0.33 as it recorded the best emulsion stability as well as excellent cadmium removal efficiency. By using this ratio, only 34.24% of emulsion swelling was recorded and at the same time, 98.15% of cadmium ions were removed.

4. Conclusions

Extraction of cadmium using ELM was reported and the parameters studied are carrier and surfactant concentration, initial W/O volume ratio as well as emulsification time. The impact of emulsion formulation on cadmium removal efficiency, E(%) and emulsion swelling, $\delta(\%)$ can be clearly seen as the parameters varied.

- (1) Carrier is the major component in the membrane phase as it responsible in extraction of solute while surfactant has great contribution to the stability of the emulsion. However, the data obtained shows that unnecessarily high concentration of both components has caused the emulsion swelling to worsen and it does not benefit the extraction kinetics.
- (2) Prolong emulsification time has resulted in coalescence, leading to emulsion instability. On the other hand, initial W/O volume ratio has greatly affected the swelling and removal efficiency as the thickness of the membrane layer is depending on this parameter.

Throughout this study, the optimum parameters were found to be 3 wt.% of Aliquat 336 and Span 80 dissolved in corn oil as the membrane phase. W/O mixture with ratio of 0.33 was emulsified for 12 min in forming the emulsion to remove 98.15% of cadmium at minimal emulsion swelling (34.24%).

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List of Symbols

$C_{\rm o}$	_	initial concentration of cadmium (ppm)
C_t	_	final concentration of cadmium (ppm)
D(t)	_	diameter of the emulsion globule at
		time t (μm)
D(0)	_	initial diameter of the emulsion
		globule (μm)
Ε	_	removal efficiency (%)
$R_{W/O}(0)$	_	initial W/O volume ratio (dimensionless)
$R_{\rm W/O}(t)$	_	W/O volume ratio at time t
,		(dimensionless)
S(t)		change of the emulsion globule diameter
		(dimensionless)
δ	_	emulsion swelling (%)
		0 . /

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