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CADMIUM REMOVAL USING VEGETABLE OIL BASED EMULSION LIQUID MEMBRANE (ELM): MEMBRANE BREAKAGE INVESTIGATION

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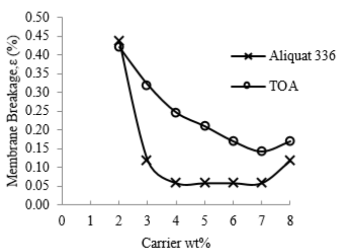
Graphical abstract



Abstract

The aim of this research is to quantify the occurrence of membrane breakage in vegetable oil based Emulsion Liquid Membrane (ELM). Basically, ELM consists of three main phases; internal, external and membrane. In this work, the membrane phase was prepared by dissolving Span 80 as surfactant and Aliquat 336 as carrier in commercial grade corn oil. As a way to promote sustainable development, vegetable oil which is environmentally benign diluent was incorporated in the formulation of ELM. The influence of several important parameters towards membrane breakage were studied. They are carrier and surfactant concentration, W/O volume ratio, emulsification time, internal phase concentration as well as stirring speed. Based on the data obtained, emulsion prepared using 4 wt% Aliquat 336 and 3 wt% Span 80 resulted in the most stable emulsion with only 0.05% membrane breakage. The emulsion was produced using W/O volume ratio of 1/3 and it was homogenized with the assistance of ultrasound for 15 min. Moreover, emulsion produced able to provide a fair balance between emulsion stability and Cd(II) permeability as it able to remove 98.20% Cd(II) ions from the external phase.

Keywords: Emulsion liquid membrane, vegetable oil, membrane brekage, Cd(II) removal

Abstrak

Tujuan utama kajian ini adalah untuk menyiasat kewujudan pemecahan membran pada Membran Cecair Emulsi (MCE). Pada dasarnya, MCE terdiri daripada tiga fasa utama iaitu fasa dalaman, fasa membran dan fasa luaran. Dalam kajian ini, fasa membran telah disedia menggunakan Span 80 sebagai surfaktan dan Aliquat 336 sebagai pembawa yang dilarutkan dalam minyak jagung bergred komersial. Sebagai salah satu usaha untuk menerapkan pembangunan mampan, minyak sayuran yang merupakan pelarut mesra alam telah digunakan dalam formulasi ELM. Pengaruh beberapa parameter yang penting terhadap pemecahan membran telah dikaji. Antara parameter yang terlibat ialah kepekatan pembawa dan surfaktan, ratio isi padu W/O, masa emulsifikasi, kepekatan fasa dalaman dan juga kelajuan kacau. Berdasarkan data yang diperolehi, emulsi yang disediakan menggunakan 4 wt% Aliquat 336 dan 3 wt% Span 80 telah menunjukkan kestabilan emulsi yang tinggi dengan hanya 0.05% pemencahan membran direkodkan. Emulsi tersebut menggunakan ratio isi padu W/O sebanyak 1/3 dan ia telah dihomogen menggunakan ultrabunyi selama 15 min. Selain itu, emulsi tersebut juga telah mecapai keseimbangan yang baik diantara kestabilan emulsi dan juga pemerasapan Cd(II) dimana sebanyak 98.20%% Cd(II) ion telah berjaya diekstrak daripada fasa luaran.

Kata kunci: Membran Cecair Emulsi, minyak sayuran, pemecahan membrane, penyingkiran Cd(II)

1.0 INTRODUCTION

Naturally, Cd(II) is a metal which can be found deposited in the earth crust. Excessive human exposure to Cd(II) could cause headache, nausea, vomiting, depression, lethargy, kidney damage, renal disorder, asthma, cough and neurologic signs such as seizures, ataxia and increased thirst [1]. In addition, high concentration of Cd(II) in human body will inhibit the production of progesterone [2] and laboratory data implicate Cd(II) as prostate carcinogen [3]. Extensive usage of Cd(II) in the production of Nickel-Cadmium batteries as well as in plating and coating industries resulted in the presence of high Cd(II) concentrations in the industrial wastewater. Lack of efficient treatment of water containing Cd(II) prior to its discharge to environment could cause catastrophe to human being and aquatic life.

Realizing its deleterious effects towards humans, tremendous efforts have been carried out to find an efficient way to reduce the concentration of Cd(II) in aqueous media. Among existing techniques available are metal precipitation, ion exchange and solvent extraction [4]. Unfortunately, these techniques face some inherent limitations for instance low efficiency, sensitive operating conditions, production of secondary sludge, high capital and operating costs as well as high cost for further disposal [5]. Emulsion Liquid Membrane (ELM) was invented by Li [6] and it was found successful in removing various types of metal ions such as copper [7, 8], cadmium [9] and cobalt [10] from aqueous solution. It consists of internal (W_1) and external phase (W_2), and they were separated by the immiscible organic membrane phase (O) thus, forming $W_1/O/W_2$ (water-in-oil-in-water) emulsion system. In this multiple emulsion system, the primary water-in-oil (W_1/O) emulsion is prepared first before dispersing it in a second aqueous phase (W_2) [11]. The membrane phase which consists of carrier, surfactant and diluent encapsulates the internal phase (W_1) in forming the primary water-in-oil (W_1/O) emulsion.

The process of Cd(II) extraction is facilitated by carrier via the formation of solute-carrier complex. This complex will diffuse across the membrane phase and Cd(II) ions will be stripped into the internal phase. Once stripped, the metal ions will remain and the free carrier will diffuse back to the external-membrane interface to form another new complex with Cd(II) extractable ions. Other than metal ions separation, ELM in different formulation is extremely versatile and useful for different applications including toxic separation in blood [12], separation of hydrocarbon [13] and carbon dioxide separation [14]. Attractive features of ELM are high efficiency, easily operated, high selectivity, high interfacial area for mass transfer, requirement of little organic solvent and scope of continuous operation [15]. Furthermore, ELM is estimated to be about 40% cheaper than the conventional extraction processes for heavy metal removal in industry [16].

On the other hand, diluent is an important component in ELM formulation as it responsible to reduce the total viscosity of the membrane phase. Conventionally, ELM applies petroleum derivatives as its diluent. This type of diluent, which forms major component of the organic membrane phase is classified as non-renewable, flammable, difficult to handle, easily volatile and hazardous to humans as well as aquatic life. Due to limited supply, price inconsistency of petroleum based diluent could affect the total operational cost of ELM. In complying with the principle of sustainable development, vegetable oil has been incorporated in various configurations of liquid membrane [17, 18], but not in the emulsion type. Vegetable oil such as corn oil, soybean oil and sunflower oil possess similar properties which are low melting point, low specific gravity, high flash point and non-volatile. Most importantly, these vegetable oils have low dielectric constant value (~3) which makes them non-polar [19] and their aliphatic property allows them to be immiscible in the external phase. Also, the stability of the emulsion can be improved due to high viscosity of the vegetable oil.

Despite its beneficial characteristics for separation of solute, ELM suffers from emulsion instability. Stability of emulsion could be disrupted by membrane breakage, coalescence and emulsion swelling [20]. Membrane breakage causes leakage of internal phase to the external while emulsion swelling occur as a result of water transportation from the external phase into the internal. This phenomena has retarded the extraction process and severe environmental problem would occur if petroleum derivatives were to be used continuously as diluent [5]. It is identified that the factors affecting emulsion stability are membrane formulation, method of preparation and the condition under which the emulsion is contacted with a reactant phase [21].

The main objective of this study is to incorporate vegetable oil as diluent in the membrane phase and hence focuses on producing a stable emulsion system for Cd(II) extraction. Apart from emulsion stability, this literature will provide the data on Cd(II) extraction efficiency to ensure that a fair balance between emulsion stability and Cd(II) permeability is achieved. In this present study, the investigation on the parameters which governs the emulsion viscosity and its stability will be conducted. Carrier and surfactant concentration, emulsification time and W/O volume ratio will be studied, followed by internal phase concentration as well as stirring speed.

2.0 EXPERIMENTAL

2.1 Chemicals

Commercial grade of corn oil, non-ionic surfactant (Span 80 from Merck) and carrier (Trioctylamine and Aliquat 336 purchased from Merck and Sigma Aldrich, respectively) were used in the preparation of membrane phase while the external phase was prepared by dissolving $CdCl_2$ (Sigma Aldrich) in HCl solution. On the other hand, the internal phase was prepared using ammonia (Merck). Otherwise stated, all solutions were prepared using deionized water.

2.2 Emulsion Preparation for Cd(II) Extraction

Surfactant (1-6 wt%) and carrier (2-8 wt%) were dissolved in corn oil to prepare the membrane phase. The preparation of emulsion started with careful pouring of internal phase into the prepared membrane phase according to a specific ratio (1/6-1/2). Then, this immiscible mixture was emulsified, assisted by intensive ultrasonication at frequency of 22.5 kHz. A commercial ultrasonic (USG-150) equipped with titanium horn was used for this purpose. The tip of the horn was ensured to be placed symmetrically at the internal-membrane interface and the process took place for 5 to 17 min. The volume of emulsion produced were 30 mL, where 10 mL was used for its viscosity measurement using viscometer (Brookfield DV-III) at ambient temperature while the remaining was used for Cd(II) extraction. A constant ratio of 1:5 was selected as the treating ratio and they were stirred for 15 min at 100 to 600 rpm. The initial concentration of $CdCl_2$ in the external phase is 150 ppm and it was kept constant for the entire experiment.

2.3 Stability Study

After Cd(II) extraction process ended, the immiscible mixture was left for settling to allow complete separation of the external phase and the emulsion. After 10 min, the external phase was taken out for pH and Cd(II) concentration measurement. Membrane breakage,ε (%) were calculated based on H^+ ions concentration change in the external phase which can be determined via pH measurement using the following Equations [21]:

$$\varepsilon(\%) = \frac{V_s}{V_i} \times 100 \quad (1)$$

Where V_i is the initial volume of the internal phase while V_s is the volume of the internal phase leaked into the external phase which is defined by:

$$V_s = V_{Ext} \frac{10^{-pH_0} - 10^{-pH}}{10^{-pH} - C^i_{H^+}} \quad (2)$$

Where V_{Ext} denotes the initial volume of the external phase, $C^i_{H^+}$ is the initial concentration of H^+ in the internal phase while pH_o and pH is the pH of external phase before and after extraction of Cd(II), respectively. The pH of the solution was measured using Fisher Scientific accumet AB15 pH meter.

2.1 Cd(II) Removal Efficiency

Atomic Absorption Spectrophotometer (Shimadzu AA-6650) was used to determine the concentration of Cd(II) at a wavelength of 228.8 nm. The efficiency, E(%) of Cd(II) removal was calculated using the following equation:

$$E(\%) = \frac{(C_o - C_t)}{C_o} \times 100 \quad (3)$$

Where C_o is the initial concentration of Cd(II) in the external phase while C_t is the concentration of Cd(II) in the external phase after 15 min of extraction.

3.0 RESULTS AND DISCUSSION

3.1 Effect of Carrier Type and Concentration

In Type II Facilitated Transport, carrier plays an important role in ensuring the effectiveness of solute extraction since it is responsible in the formation of complex with the solute in the external phase and to transport them across the membrane phase. However, previous studies have revealed several implications of carrier type and its concentration towards membrane property, stability and extraction efficiency. This study was design to compare the performance of trioctylamine (TOA) and trioctylmethylammonium chloride (Aliquat 336) as carrier in the membrane phase. The selection of these carriers in this comparative study was made due to their property of highly selective towards Cd(II) ions, as reported by Kumbasar [22] and Ahmad *et al*. [23]. At varying concentrations, their effects on membrane breakage,ε (%) is presented in Figure 1.

The figure clearly shows that 4 wt% of Aliquat 336 is sufficient to yield the most stable emulsion with only

0.06% membrane breakage. Good emulsion stability towards membrane breakage was achieved with the help of surfactant properties possessed by Aliquat 336. However, increasing its concentration beyond 4 wt% does not improve the stability of the emulsion. This is due to the excess concentration of Aliquat 336 used which in turn, could promote emulsion swelling. This phenomena also led to membrane layer thinning, making it prone to breakage. In the case of TOA, the lowest membrane breakage (0.15%) can be obtained using higher concentration of TOA (7 wt%) but breakage has worsened beyond this point. By comparing the data available in Figure 2, it is noted that a more viscous emulsion was made using Aliquat 336 and the viscosity increase together with the carrier concentration. However, an opposite effect was observed in the case of TOA where less viscous emulsion was formed as the carrier concentration increase, causing it to have poor stability. Less viscous emulsion were unable to withstand the shear provided by the impeller thus, resulting in high membrane breakage. Also, unnecessarily high TOA concentration has caused high competitive adsorption with the surfactant molecules due to their opposite behaviour [24] thus, reducing the membrane stability.

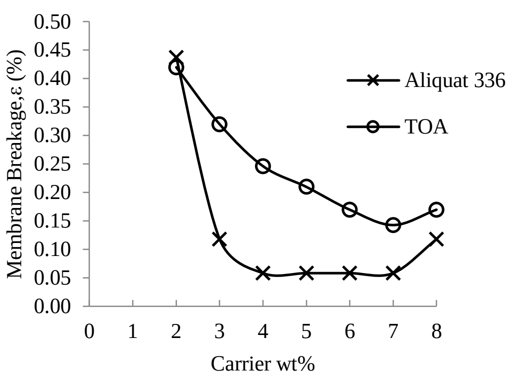


Figure 1 Effect of type of carrier and its concentration on membrane breakage

Although more stable emulsion were formed with the application of viscous carrier, but it is reported that the viscosity of emulsion could affect the extraction efficiency of ELM. Usage of viscous component in the membrane phase could cause the formation of large emulsion droplets during dispersion, resulting in low removal efficiency. However, usage of 4 wt% Aliquat 336 showed good extraction efficiency as it able to remove up to 98.00% Cd(II) ions from the external aqueous phase. Hence, 4 wt% Aliquat 336 will be used as carrier for the rest of this study.

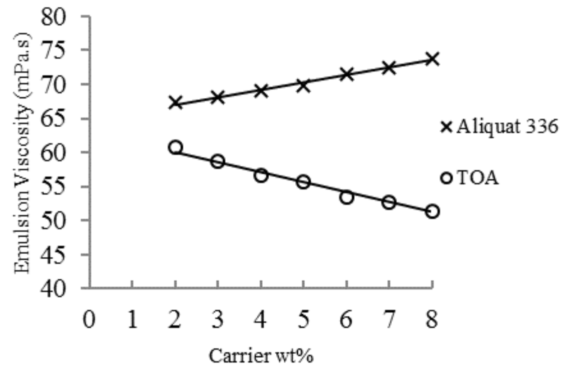


Figure 2 Plot of emulsion viscosity against carrier concentration

3.2 Effect of Surfactant Concentration

Surfactant plays an important role in emulsion stabilization as it reduces the interfacial tension between the two immiscible phases. Hydrophile-Lipophile Balance (HLB) value of 4.3 made Span 80 nonpolar and it allows the formation of water-in-oil emulsion. While keeping other parameters constant, experiments were designed at varying Span 80 concentrations to investigate its influence on membrane breakage,ε (%) and the data obtained is presented in Figure 3. Also, data in Figure 4 is useful to investigate the effects of Span 80 concentration on emulsion viscosity. Data provided shows that surfactant has a huge impact towards stability of an emulsion as well as its viscosity. Membrane breakage was significantly reduced as the concentration of Span 80 increases from 1 to 3 wt% due to the reduction of interfacial tension between the water and oil phases. Moreover, this condition favors the formation of smaller and even more stable emulsion droplets. However, no improvement of emulsion stability was observed beyond 3 wt% of Span 80. In addition, increasing its concentration to 6 wt% has caused the formation of micelle in the membrane phase [25], resulting in poor membrane stability. Micelles were formed as the surfactant molecules arrange themselves into an organized molecular assemblies where it usually occurred at high concentration of surfactant [26].

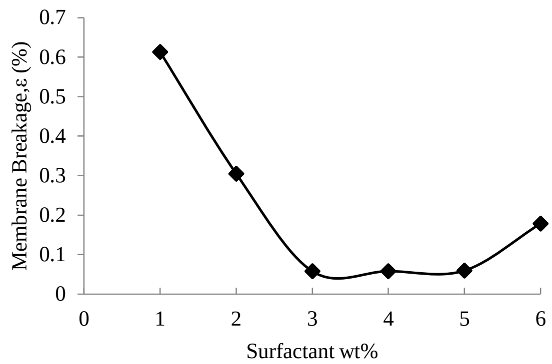


Figure 3 Effect of surfactant concentration on membrane breakage

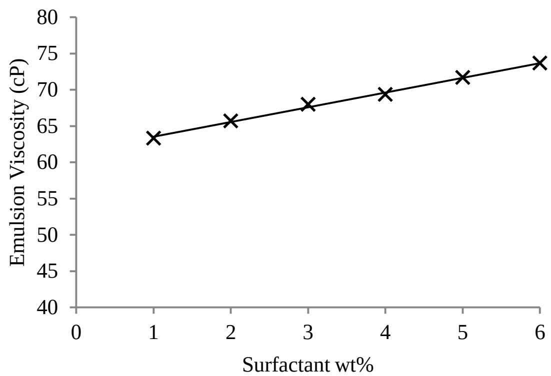


Figure 4 Plot of emulsion viscosity against surfactant concentration

Although it is beneficial to have a stable emulsion, but unnecessarily high concentration of Span 80 has resulted in the formation of a highly viscous emulsion, as can be seen in Figure 4. This condition is not preferred during the extraction process due to formation of large emulsion globules as well as high mass transfer resistance as a consequent of surfactant molecules occupancy. Data available in Figure 3 suggested that 3 wt% Span 80 is enough to produce a stable emulsion as increasing its concentration will neither benefit the emulsion stability nor extraction kinetics. Usage of surfactant at minimal but adequate amount is the key in ensuring high stability of emulsion and at the same time, allowing it to perform extraction process effectively. At this optimum point, 98.10% of Cd(II) ions were successfully removed.

3.3 Effect of W_1/O Volume Ratio

Figure 5 shows the effect of W_1/O (internal phase/membrane phase) volume ratio on membrane breakage,ε (%). To investigate the effect of the volume ratio on membrane breakage, the ratio was varied from 1/6 to 1/2, while maintaining other parameters constant. It is identified that the most stable emulsion was formed at volume ratio of 1/3 with only 0.05% membrane breakage. As can be seen in Figure 6, reducing the volume ratio from 1/2 to 1/3 has caused the emulsion to be more viscous and the emulsion stability was improved, but not beyond the volume ratio of 1/3. Usage of lower volume ratio resulted in thicker membrane film [27], causing it to be highly resistance towards membrane breakage. Also, the presence of surfactant concentration at the interface of membrane-external too can be affected by the W_1/O volume ratio [28] which could significantly affect the emulsion stability. Although the strength of the emulsion wall was improved by using greater volume of membrane phase, but its usage at excessive amount turns out to be counterproductive. Reducing the ratio beyond 1/3 has caused poor membrane stability and at the same time, producing a highly viscous emulsion. This condition has caused an increment in mass transfer resistance and usage of great volume of membrane phase will affect the total operational cost of ELM.

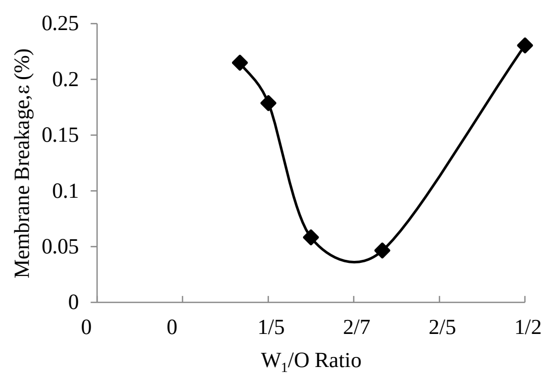


Figure 5 Effect of W_1/O ratio on membrane breakage

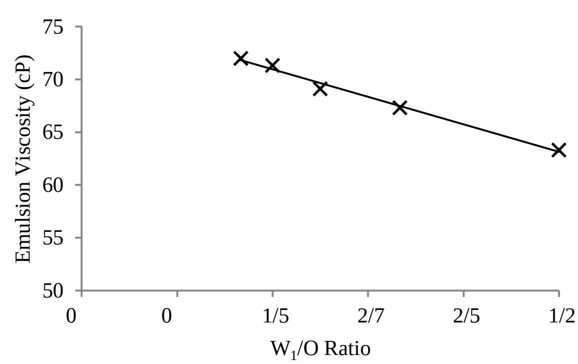


Figure 6 Plot of emulsion viscosity against W_1/O ratio

Conversely, increment of the volume ratio will inhibit the encapsulation of internal phase droplets thus, creating larger emulsion globules. As a consequent, thinner membrane layer was formed [22], exposing the emulsion to greater chances of membrane breakage. This condition retards the emulsion's extraction ability as the interfacial area for solute transfer is reduced. From Figure 5, it is found that the increment of the internal phase volume resulted in higher membrane breakage while at ratio of 1/2, phase inversion was observed. This situation has caused the oil to be dispersed instead of water, causing the hydrophilic part of the emulsion to dissolve in the external phase easily. At its most stable form, the emulsion removed 98.10% Cd(II) ions from the external phase.

3.4 Effect of Emulsification Time

Experiments were carried out under the same operating condition as mentioned earlier, but the duration for emulsification was varied to study its effect on membrane breakage. In ensuring a stable and uniform emulsion are produced, sufficient time for emulsification must be employed during the emulsion preparation step. The duration of ultrasonic exposure during emulsion preparation was varied from 3 to 17 min and its effect on membrane breakage,ε (%) is presented in Figure 7. It is found that 15 min of ultrasonication is required to produce a stable emulsion with only 0.05% membrane breakage. Ample time for exposure has allowed the production of emulsion with smaller aqueous internal phase droplets and this condition has enhanced the homogeneity of the dispersed phase [29]. From the figure, short emulsification time (<15 min) was found to be insufficient to produce a stable emulsion. Insufficient time for homogenization will cause the droplet size to be larger and hence, promoting coalescence. On the other hand, prolong emulsification time (>15 min) does not improve the emulsion stability due to high internal shearing, leading to very high number of small droplets which is conducive to their diffusion into external phase [30]. 98.15% Cd(II) ions were removed from the external phase using the emulsion prepared for 15 min.

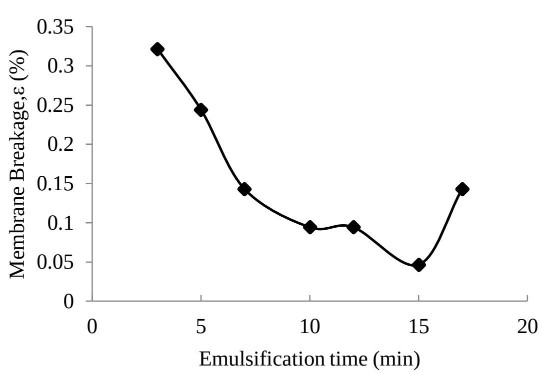


Figure 7 Effect of type of emulsification time on membrane breakage

3.5 Effect of Internal Phase Concentration

The effect of internal phase concentration on membrane breakage,ε (%) is shown in Figure 8. The ammonia concentrations were varied from 0.05 to 1.0 M. As can be seen from the figure, internal phase prepared with 0.1 M ammonia resulted in the lowest membrane breakage. Increasing the ammonia concentration to 0.2 M did not improve the emulsion stability while at higher concentration, the stability was further reduced. Furthermore, increasing the concentration of internal phase has caused high pH gradient between the internal and external phase. This huge difference in ionic strength will promote the transportation of water from the external into the internal phase, causing the emulsion to swell. As a consequent, the membrane layer will become thinner, leading to membrane breakage. Also, Chiha *et al*. [31] claimed that further increment of ammonia concentration has caused a reaction to occur between ammonia and Span 8, and could affect the properties of the surfactant. Apart from minimal membrane breakage, usage of 0.1 M ammonia as internal phase has recorded highest Cd(II) removal efficiency (98.20%). Increasing the internal phase concentration does not benefit the Cd(II) extraction capability as the number of moles of ammonia needed to react during the stripping process were proven to be in excess even 0.1 M of ammonia is used. Thus, it is not necessary to use high concentration of internal phase as it does not benefit the emulsion stability as well as its extraction efficiency.

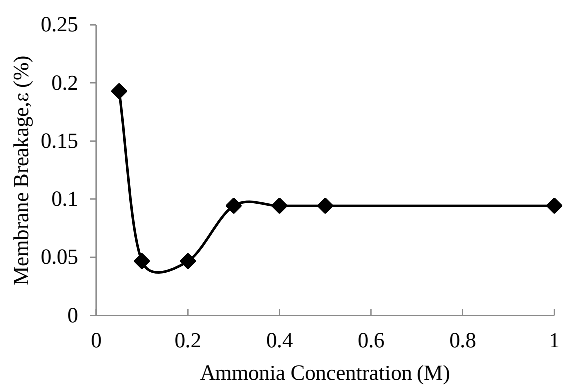


Figure 8 Effect of internal phase concentration on membrane breakage

3.6 Effect of Stirring Speed

In providing high surface area for solute extraction, the emulsion needs to be mobilized. Optimum stirring speed must be identified to ensure that the emulsion is well dispersed in the external phase and at the same time able to maintain its stability. A set of experiment was performed to study the effect of stirring speed on membrane breakage,ε (%) and the data obtained is presented in Figure 9. At low stirring speed (<400 rpm), minimal membrane breakage was noted as a result of insufficient shear provided by the impeller to disperse the emulsion. Low speed of stirring resulted in large emulsion globules to be formed, thereby increasing the thickness of the membrane phase. Although low membrane breakage was recorded, slow speed of stirring does not enhance the solute extraction process as large emulsion globules reduces the available area for solute transfer [32].

On contrary, fast stirring speed was proven not to be advantageous [29] either to emulsion stability or solute removal efficiency. It can be seen clearly from Figure 9 that increasing the speed beyond 400 rpm has caused the membrane breakage to worsen. High membrane breakage can be expected at faster speed of stirring as the emulsion could not withstand the excessive shear provided by the impeller as well as the wall of the contactor [24]. This condition has caused the membrane wall to rupture easily and hence, releasing the extracted solute back into the external. Since the emulsion is made using viscous component, the emulsion stability was maintained even at stirring speed of 400 rpm due to its rigid membrane wall. At this speed, only 0.05% of membrane breakage was noted and 400 rpm was found to be the "critical" speed for stirring. Appropriate stirring speed is essential in providing high mass transfer area to enhance the process of solute extraction. In this system, it is found that the emulsion able to remove 98.20% Cd(II) ions from the external phase while keeping a minimal membrane breakage.

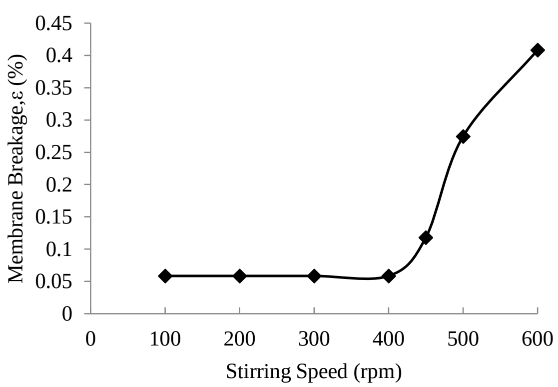


Figure 9 Effect of stirring speed on membrane breakage

4.0 CONCLUSION

The incorporation of vegetable oil as diluent in the formulation of ELM was explored and the stability of the emulsion produced was reported. The effect of several parameters on membrane breakage,ε (%) was studied in this present work. They are carrier and surfactant concentration, W/O volume ratio, emulsification time, and internal phase concentration, followed by stirring speed.

Based on the data recorded, application of high carrier and surfactant concentration does not benefit the system as excessive amount of both components have caused the membrane breakage to worsen. Minimal membrane breakage was obtained using low W_1/O volume ratio but it must be homogenized for 15 min to obtain a stable and uniform emulsion. Only 0.05% membrane breakage was recorded after all parameters have been optimized. It was found that emulsion produced with viscous component resulted in lower membrane breakage, but with some limitations. This is due to the fact that the strength of the membrane wall was improved by using highly viscous component in the membrane phase. This situation has caused the membrane wall to become more resistance towards shear. Although high mass transfer resistance were claimed to exist by using highly viscous emulsion, but the results obtained shows that the emulsion produced capable in removing 98.20% Cd(II) ions from the external phase at its most stable form.

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