STUDY OF BEHAVIOR AND MECHANISM OF WATER-IN-OIL-WATER EMULSION INSTABILITY IN EMULSION LIQUID MEMBRANE: MEMBRANE BREAKAGE

Nur Dinnie Shazlyn Binti Mohd Noor Salizan, Meor Muhammad Hafiz Shah Buddin

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract— ***Emulsion liquid Membrane (ELM) consist of three main phases which are membrane phase, internal phase and external phase. However, ELM performance is heavily affected by the emulsion stability, where one of it is the membrane breakage. Emulsions are metastable colloids that are made of two immiscible liquids, where one being dispersed in the other within the sight of a surface-active agent. This research work aims to investigate the occurrence of water-in-oil-in-water (W/O/W) emulsion instability in ELM. To identify the best operating parameters to achieve minimal water-in-oil-water emulsion instability to allow high copper removal efficiency. Parameter involves in this study are homogenization time and speed, carrier concentration and surfactant concentration. Data recorded shows that 8000rpm, 15 min of homogenization, 4 wt% of carrier and 4 wt% of surfactant resulted in the minimum membrane breakage. At this condition, 0.14% of breakage was recorded .***

Keywords—Emulsion Liquid Membrane, Breakage, Emulsion Stability

I. INTRODUCTION

1.1 Research Background

Emulsion liquid membrane (ELM) is a liquid membrane based on process initially proposed by Li (1989) [2] where a primary emulsion is dispersed in the feed phase to be treated. It is one of a way that very useful and alternative for the recovery of different compound contained in wastewater. Basically , ELM comprises of three phases as shown in Figure 1, consisting of membrane phase, internal phase and external phase [3].

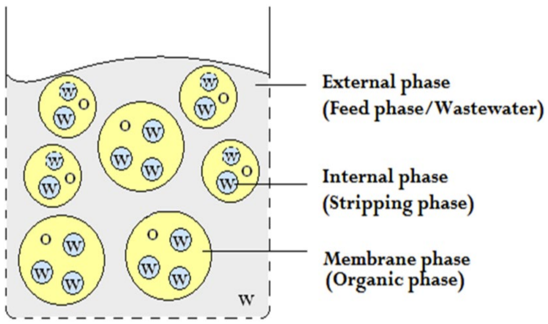

Figure 1: The phase presence in a water-in-oil-in-water emulsion (W/O/W). where O= Oil (Yellow) and W= Water.(Martinelli et al, 2015).

The membrane phase consists of surfactant, diluent and carrier. While the external phase is the water that carries the metal or other element of interest and for the internal phase is the liquid that traps the recover the solutes. For the organic phase or known as membrane phase, it consists of surfactant to ensure the stability of the emulsion, besides the membrane phase is made up of carrier and diluent [1].

ELM technique is commonly used for element of metal ions extraction and organics recovery. ELM was reported to successfully remove many kind of heavy metals. This method was proven to be effective based on report on the extraction of Chromium (III) by Hartati et al. (2007) [5], while Ahmad et al. (2015) extracted Cd(II) ions. This is because ELM offers fast process of the extraction and allows single phase operation of a stripping extraction process.

Basically, ELM is prepared via three main steps as shown in Figure 2 [6]. First step is the preparation of membrane phase and internal phase prior to emulsification. The emulsification process produces the primary water-in-oil (W/O) emulsion. This process was followed by the dispersion of the primary emulsion in the external phase which forming the water-in-oil-in-water (W/O/W) emulsion. Solutes will be extracted due to the presence of carrier in ELM.

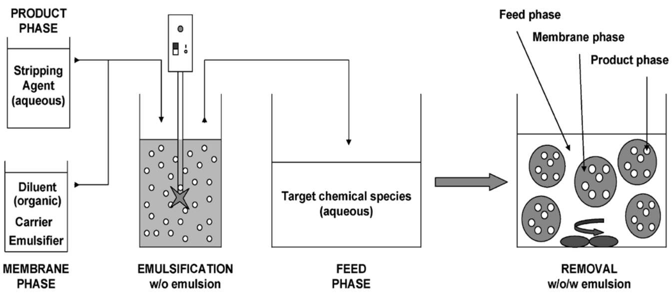

Figure 2: Diagram of steps of an emulsion liquid membrane process (León at el., 2017)[2].

Emulsion liquid membrane (ELM) system has its own advantages such as high interfacial area for mass transfer because of the size of the aqueous phase droplets are small, high diffusion rate of the metal ion through the membrane, simultaneously performance of extraction and stripping in the same system and have a variety elements and other compound in industrial where it capable for a treating at a higher speed with a high degree of the effectiveness [7].

Eventhough nowadays there are many research reported on the ELM application for the removal of the heavy metals from waste solution, their efficiency is highly dependent on the emulsion stability. Emulsions are metastable colloids that are made of two immiscible liquids, where one being dispersed in the other within the sight of a surface-active agent. Due to high specific surface areas, that is resulting from the dispersion procedure are not specifically favored, and therefore the emulsions are thermodynamically unstable and it was expected to make a break [8]. Emulsion stability is affected by emulsion swelling, membrane breakage and coalescence. Stability of the emulsion globules is literally known as one of the most serious problems in the application of the ELM to the separation of industrial waste[9]. The membrane breakage includes rupture of the emulsion, leading to loss of internal phase. As referring to the researcher stated before which study of emulsion liquid membranes stability by Gheorghe et al. (2008), it concerns on the emulsion stability where it was proven that by removing phenol using emulsion liquid membranes the stability of the emulsion liquid membrane was maintained and stable during the operating time other than preparation of a mixture that contain surfactants.

W/O/W emulsion process is probably having a problem on the stability which is caused from the mixing process in the emulsion membrane extraction which are mainly known as a problem that occur in emulsion liquid membrane, that is membrane breakage and emulsion swelling.These two components are rarely studied in detail during the emulsion stability for removal of Cu(II) ions. In fact, the mechanism that causes the stability to be distrupted is scarce. Just a few of scientists have investigated the emulsion breakage. Bunge et al., 2010 have revealed that the leakage of the internal phase is in range (1 to 5%), however apparently not significant, can still profoundly influence the emulsion performance. Besides that, Ho and Li have investigated that the small amount of initial leakage that comes from the internal phase which produced from the emulsion expansion to the membrane of the feed can be attributed due to the lack of efficient and ideal encapsulation from the internal phase which consist in the membrane matrix. Nakashio et al., 2007 have investigated the impact of various surfactants (the surfactant alkyl chain effect) on the emulsion separation. Prior distributed work by Abou-Nemeh and Van Peteghem revealed that the emulsion breakage passes through a minimum for a certain composition of the membrane.

In this study, the removal of Cu(II) ions from aqueous solutions by emulsion liquid membrane is proposed. The membrane phase will be made by using Bis(2-ethylhexyl) phosphate as carrier and Span 80 as surfactant, dissolved in the kerosene. On the other hand, hydrochloric acid (HCl) as the internal phase has been suggested. Achieving maximum solute removal efficiency has always been the target for any liquid membrane system. However, failing to identify the best condition to achieve best emulsion stability could cause maximum removal efficiency impossible to be identified accurately. The effect of the different operating parameters will be analyzed.

II. METHODOLOGY

2.1 Chemicals

The chemicals used are Bis(2-ethylhexyl) phosphate, Span 80, Copper (II) sulphate, Hydrochloric acid (HCl), Kerosene, Sodium Hydroxide (NaOH), acetic acid and Sodium acetate anhydrous.

Table 1: Chemicals used and their role

Phases	Chemicals
Membrane phase	Organic solvent: Kerosene Surfactant: Span 80 Carrier: Bis(2-ethylhexyl) phosphate (D2EHPA)
Internal phase	Hydrochloric acid (HCl)
Stripping phase	Sodium Hydroxide (NaOH)
Extraction	Copper (II) sulphate dissolved in Acetate Buffer (Acetic Acid and Sodium Acetate)

2.2 Emulsion Liquid Membrane Preparation

The first step are emulsion preparation in which emulsion was prepared by mixing membrane phase containing Bis(2-ethylhexyl) phosphate (D2EHPA) (at 0 to 8 wt%) as carrier, and Sorbitan monooleate (Span 80) as surfactant (at 0 to 5 wt%) in Kerosene which act as organic solvent. The solution was then stirred for 5 minutes at of 300 rpm prior to its mixing with internal phase (HCl). Next, the emulsion was produced by homogenizing the membrane and internal phase at ratio of 1: 3 (by volume). Homogenization process was carried out using Homogenizer (WITEG HG-15D) at varying speed and time (shown in Figure 3).

Figure 3: Set up of W/O/W emulsion preparation.

This process allowed water to be dispersed in the oil thus, forming the primary water-in-oil (W/O) emulsion. The process was then continued by dispersed it in the external phase which contains Copper (II) ions. 100 ppm of Copper (II) Sulphate was dissolved in Acetate Buffer solution where the pH was kept constant at 4 unless mentioned. Mixing process of these phases resulted in the formation of W/O/W emulsion. The emulsion was then stirred at 300 rpm for 15 minutes.

2.3 Stability Analysis

Once the process of extraction ended, the external phase was taken out to measure its final pH. The data obtained is useful to calculate the percentage of breakage of membrane. Equation (1) below calculates the volume of internal phase leaked into the external phase, Vs:

$$V_S = V_{Ext}\,\frac{10^{-pHo} - 10^{-pH}}{10^{-pH} - C^{i}_{H+}} \qquad (1)$$

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.

Calculated leaked volume of internal phase was later converted into percentage ratio of leaked volume to initial volume of internal phase. Such as, with a ratio of 3:1 of 30 mL of ELM solution will give a 10 mL of HCl solution. Besides that, volume percent is also can be defined as (2):

Breakage (%) = [(volume of internal phase leaked into the external phase (Vs)/(initial volume of internal phase)] x 100% (2)

Four parameters involved in this study. They are homogenizer speed and time, carrier concentration and surfactant concentration.

III. RESULT AND DISCUSSION

In this research, there are four significant parameter that has been observed. They are the effect of homogenization time and speed, the effect on carrier concentration and the effect on surfactant concentration.

3.1 Effect of Homogenization Time and Speed

The study was carried out at homogenization speed range of 5000rpm to 1500rpm while the time was varied from 5 to 20 minutes. On the other hand, the carrier and surfactant concentration were kept constant at 4 wt% and 5 wt% respectively.

Based on the data recorded, ELM produced at maximum speed (1500rpm) recorded the lowest membrane breakage at short period of time. However, at longer homogenization time, 8000rpm showed promising result. Sufficient amount of time and appropriate speed of homogenization are crucial factors to entrap the internal phase into the membrane. During the emulsification, the large droplets are initially deformed, elongated and subsequently broken into smaller one due to shear force applied on it. Therefore as the homogenization time increases, the size of the droplets decreases, more stable emulsion formed [10]. On the other hand, insufficient time of homogenization process leads to the formation of large emulsion droplets which later tend coalesce easily. On contrary, fine droplets of emulsion requires more time to coalesce hence, the data reported at 8000 rpm and 10000 rpm. Djenouhat et al. (2008)[11] reported similar trend. It was claimed due to the homogeneity of the produced emulsion. Smaller emulsion droplets is favorable due to the requirement of high interfacial area for mass transfer to extract the solute in internal phase.

Apart from stabilized emulsion, smaller emulsion droplets with higher interaction would also increase the viscosity of the emulsions. This factor also has contributed to the better emulsion stability, as reported by Ahmad et al. (2015)[12]. Homogenization time and speed are related to the amount of energy added to produce the emulsion. Through this, by adding more energy, the smaller droplets are produced. However, the case did not apply to 15000 rpm. This is due to the excessive shear provided to the emulsion during homogenization process. Also, effect of temperature has contributed to the observation.

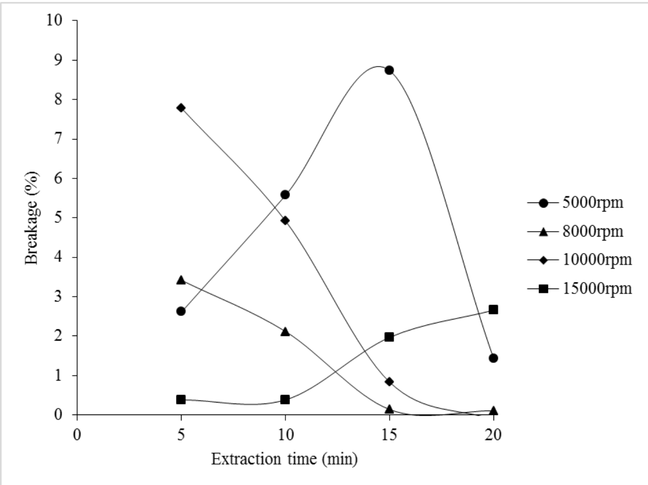

Figure 4: Effect of Homogenization Time and Speed

Therefore it was conclude that on this parameter, a high mixing of speed used and the longer the duration it takes during the experiment will give the best results.

3.2 Effect of Carrier Concentration

The experimental runs were performed by using various carrier concentrations (Bis(2-ethylhexyl) phosphate) within the organic membrane phase in the range of 0 wt% to 7 wt%. The concentrations of the Bis(2-ethylhexyl) phosphate or normally known as D2EHPA, within the organic phase were determined from the same amount of internal phase of pH 4. The experimental conditions were kept constant at emulsification speed 8000 rpm, emulsification time 15 min, internal phase. It was observed that the carrier concentration also plays a key role in the emulsion stability. Data recorded is as shown in Figure 5.

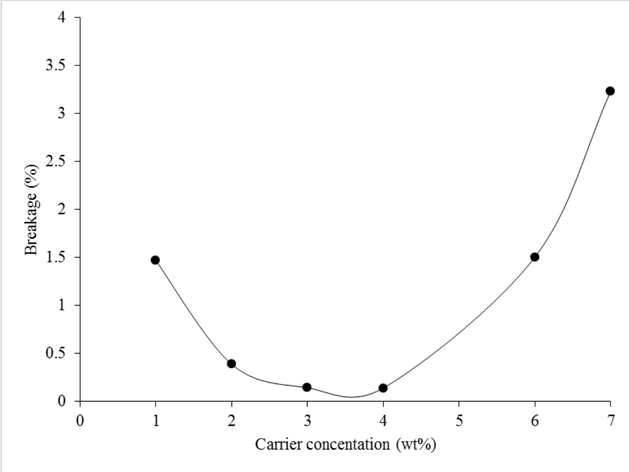

Figure 5: Effect of Carrier Concentration

From the result shown in Figure 5, it could be observed that increasing the amount of carrier has improved the stability (until 4 wt%). It is claimed that high carrier concentration causes osmotic swelling which in turns promotes breakage[13] . Beyond that, the membrane has shown significant increment. Increasing the amount of carrier has two effects: the viscocity of membrane phase, which limits the extraction rate, decreases by increasing the carrier concentration and hence the carrier acts as thinner layer for the membrane phase. At the same time, increasing the carrier concentration over a certain limit decreases the stability of the emulsion. High carrier concentration causes competitive adsorption with surfactant molecules [14]. In this context, surfactant is unable to reduce the interfacial tension thus, causing the emulsion to be unstable. Large size of emulsion droplets were produced at this condition and tend coalesce easily.

It is well known that the rate of facilitated transport of the solute is directly affected by the amount of carrier that is present in the liquid membrane. On the other hand, an increase in concentration of the carrier in the membrane phase increases the ability of the membrane phase for extraction. However, based on the data obtained, the best value of the carrier concentration was found to be about 4 wt% to avoid high membrane breakage.

3.3 Effect of Surfactant Concentration

The effect of surfactant concentration on the behavior of the emulsion stability was investigated. The experiments were conduct at emulsification speed 8000 rpm with emulsification time 15 min. The concentration of the surfactant was varied from 0% to 5 wt% while the carrier concentration was kept constant at 4 wt%. The effect of surfactant on emulsion stability is presented in Figure 6. It was observed that the emulsion stability improves by increasing the surfactant concentration continuously until 5 wt%. Eventhough high concentration of surfactant increases the stability, it is not preferred as it will cause high mass transfer resistance produced by the thick surfactant film. As reported by Li et al. (1989), the viscocity of the organic phase increases when the surfactant concentration increases, resulting in lowering the emulsion liquid membrane permeation, and diffusivity of complexes in the organic phase is reduced. Although high viscocity of emulsion produced at high surfactant concentration improves the stability but it causes the emulsion difficult to be dispersed properly. Large emulsion globules were formed and swelling can be promoted at high concentration of surfactant [13].

On the other hand, in Figure 6 shows an increase in the surfactant concentration decreases the removal efficiency of Cu(II) ions due to mass transfer resistance caused by the surfactant film. As indicated by Reis et al., the amount of the surfactant in the membrane must be minimal but it must be enough to stabilize the emulsion. So it was concluded that the surfactant concentration must not exceed 4 wt%.

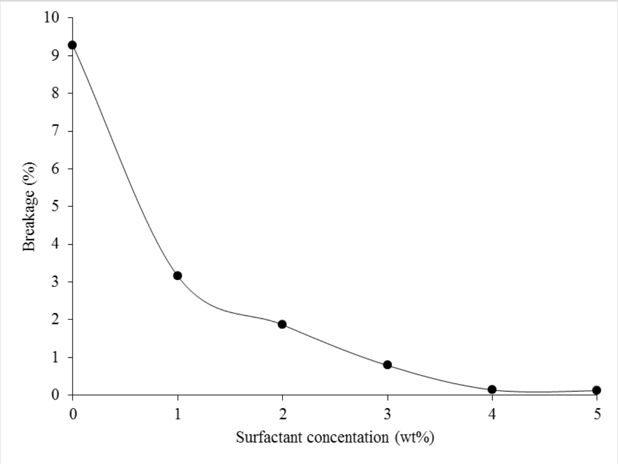

Figure 6: Effect of Surfactant Concentration

IV. CONCLUSION

Based on the research , the objective was obtained. This was shown based on the data recorded where best result achieved through all of the parameter are at the the speed of 8000rpm, 15 min of homogenization, 4 wt% of carrier and 4 wt% of surfactant which it also resulted in the low minimum emulsion breakage. At this condition, 0.14% of breakage was recorded. Therefore, the experiment are completed with a result provided based on the parameter involved.

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REFERENCES

[1] M. T. A. Reis *et al.*, "Removal of phenols from aqueous solutions by emulsion liquid membranes," *J. Hazard. Mater.*, vol. 192, no. 3, pp. 986–994, 2011.

[2] L. León, G. León, J. Senent, and C. Pérez-Sirvent, "Optimization of Copper Removal from Aqueous Solutions Using Emulsion Liquid Membranes with Benzoylacetone as a Carrier," *Metals*, vol. 7, no. 1. p. 19, 2017.

[3] N. Othman *et al.*, "Easy removing of phenol from wastewater using vegetable oil-based organic solvent in emulsion liquid membrane process," *Chinese J. Chem. Eng.*, vol. 25, no. 1, pp. 45–52, 2017.

[4] A. Martinelli, S. Björkegren, R. Karimi, J. Natesan, and M. Ali Ashim, *A New Emulsion Liquid Membrane Based on a Palm Oil for the Extraction of Heavy Metals*, vol. 5. 2015.

[5] I. Hartati and M. E. Yulianto, "(ELM) ON THE CHROMIUM EXTRACTION," vol. 3, no. 1, pp. 28–33, 2007.

[6] A. L. Ahmad, A. Kusumastuti, C. J. C. Derek, and B. S. Ooi, "Emulsion liquid membrane for heavy metal removal: An overview on emulsion stabilization and destabilization," *Chem. Eng. J.*, vol. 171, no. 3, pp. 870–882, 2011.

[7] L. Zhao, D. Fei, Y. Dang, X. Zhou, and J. Xiao, "Studies on the extraction of chromium(III) by emulsion liquid membrane," *J. Hazard. Mater.*, vol. 178, no. 1–3, pp. 130–135, 2010.

[8] A. Gheorghe, A. Stoica, and O. Floarea, "Emulsion liquid membranes stability," *UPB Sci. Bull*, vol. 70, no. 3, 2008.

[9] D. Lu, Y. Chang, W. Wang, F. Xie, E. Asselin, and D. Dreisinger, "Copper and Cyanide Extraction with Emulsion Liquid Membrane with LIX 7950 as the Mobile Carrier: Part 1, Emulsion Stability," *Metals (Basel).*, vol. 5, no. 4, pp. 2034–2047, 2015.

[10] K. Kamarudin, I. Bhatti, S. N Suahadah, U. N Hamzah, and Z. F Mohdfaiz, *Removal of Carbon Dioxide Using Water-in-Oil Emulsion Liquid Membrane Containing Triethanolamine*. 2018.

[11] M. Djenouhat, O. Hamdaoui, M. Chiha, and M. H. Samar, "Ultrasonication-assisted preparation of water-in-oil emulsions and application to the removal of cationic dyes from water by emulsion liquid membrane Part 1 : Membrane stability," vol. 62, pp. 636–641, 2008.

[12] E. Using, "Jurnal Teknologi," vol. 1, pp. 39–46, 2015.

[13] A. A. Mohammed and H. M. Selman, "Journal of Environmental Chemical Engineering Liquid surfactant membrane for lead separation from aqueous solution : Studies on emulsion stability and extraction e ffi ciency," *J. Environ. Chem. Eng.*, vol. 6, no. 6, pp. 6923–6930, 2018.

[14] C. Basualto, M. Poblete, J. Marchese, A. Ochoa, A. Acosta, and J. Sapag, "Extraction of Cadmium from Aqueous Solutions by Emulsion Liquid Membranes using a Stirred Transfer Cell Contactor," vol. 17, no. 7, pp. 1347–1354, 2006.