Stability Study on Acetaminophen Removal from Aqueous Solution using TOA via Emulsion Liquid Membrane

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Abstract. The aim of this study is to develop a stable emulsion liquid membrane for acetaminophen removal through membrane breakage. In this work, Trioctylamine (TOA), Span 80 and kerosene were used as carrier, surfactant and diluent, respectively in membrane phase while ammonia solution was used as a stripping agent in the internal phase. Research was conducted on various parameters such as stripping agent concentration, agitation speed, extraction time and treat ratio. The stripping agent concentration was varied from 0.05 M to 0.2 M while agitation speed was investigated at 200 rpm to 500 rpm. The best condition achieved for acetaminophen removal from aqueous solution via emulsion liquid membrane were at 0.1M of stripping agent using 300 rpm agitation speed for 3 minutes of extraction time with a treat ratio of 3:1. Investigation on membrane breakage revealed the lowest membrane breakage achieved was 0.17%.

1. Introduction
The generation of large amount of wastewater from various usage is one of the critical pollution problems arising in this era nowadays. In recent years there is an increasing awareness of pharmaceutical contaminants in the environment. Pharmaceutical contamination in rivers is widespread with hundreds of drugs found at low concentrations. One of the main abundantly used pharmaceuticals are acetaminophen (ACTP), which is also known as Paracetamol. It is primarily used as analgesics and antipyretics. It is a drug used to relieve pain and to suppress inflammation in a way similar to steroids without side effects. Although the anti-inflammatory effect is weak, the impact on the environment is not different from others. The water solubility of ACTP is high, resulting in its easily accumulation in aquatic environment [1]. As reported by Kim, Choi [2], ACTP is one of the most frequently detected pharmaceuticals in sewage treatment plant effluents, drinking water or surface water.

Major portion of the pharmaceutical’s products were removed by conventional wastewater treatment processes. ACTP wastewater is mainly treated by chemical oxidation processes such as electrochemical, ozonation, H₂O₂ oxidation, TiO₂ photocatalysis and solar photoelectro-Fenton oxidation [3]. However, the application of conventional treatment process in wastewater treatment plants is unable to completely remove the residues. Thus, among the existing methods, one of the promising methods for ACTP removal is by emulsion liquid membrane (ELM). ELM process involves four main steps which are emulsion preparation, solute extraction, emulsion separation and demulsification. ELM system is created by forming a primary emulsion which consists of organic and
aqueous phase stabilized by surfactant. The concept of ELM separation is a solute-carrier complex formed when the carrier selectively combines with solute ions at the external membrane phase. Therefore, ELM still can work appropriately even in the low concentration of solute.

ELM is relatively cheap with high flux rate, high extraction efficiency and environmental-friendly [4] but coalescence and emulsion swelling resulting in low emulsion stability are considered as its disadvantages. The major drawback of ELM is its instability, and this phenomenon has impeded the widespread applications of ELM in larger scale. The stability of an emulsion is defined as how resistant the liquid membrane towards high shear stress during solute extraction in ELM process. Thus, unstable liquid membrane tends to be ruptured or broken apart which will diminish some of the solute separation which has been achieved [5]. Emulsion instability occurs through various physical mechanisms such as swelling, breakage and coalescence.

Therefore, this research is expected to develop a stable ELM system, which to be dispersed to extract the targeted solute from aqueous solution through parameters optimization. Several factors affecting emulsion stability will be examined such as stripping agent concentration, agitation speed, extraction time and treat ratio. These parameters were investigated in order to obtain its best stable formulation for removal of ACTP. This research contributes to the knowledge and technology whereby the success of this research will be helpful in the application of wastewater treatment.

2. Materials and Methods

2.1. Materials

In this present work, the Acetaminophen (ACTP) is used as the external feed phase, Trioctylamine as carrier, Sorbitan Monooleate (Span 80) as surfactant, Kerosene as diluent and Ammonia as stripping agent. All chemicals used to produce emulsion liquid membrane are analytical grade and were purchased from Sigma Aldrich of Merck.

2.2. Analytical Procedures

Analytical procedures involved in this experiment consisted of pH measurement. pH for every sample was taken using Fisher Scientific accumet AB15 pH meter. The pH meter is calibrated with a three-point calibration using standard buffer solutions of pH 4.00, 7.00 and 10.00. The electrode of the pH meter needs to be immersed at appropriate depth in the solution. The pH reading was taken during stable reading at room temperature (25±1).

2.3. Production of Emulsion

The emulsion was prepared by via emulsification method before being dispersed into the external feed solution. The membrane phase was prepared by mixing Trioctylamine (TOA) and Span 80 in kerosene. The internal aqueous phase of ammonia solution was then added to the membrane organic phase where the volume ratio is internal aqueous phase to membrane phase is 1:3. These phases were then emulsified using the ultrasonic probe (USG-150). Then, 10 ppm of ACTP feed solution, was prepared by dissolving the desired amount of solute ACTP in HCl solution as the external feed phase solution.

2.4. Stability Study

Stable emulsions are defined as those that are persist without phase separation over a period of time. The stability of emulsion in emulsion liquid membrane is favoured by several parameters. In order to optimize the emulsion stability, several parameters were investigated such as stripping agent concentration, agitation speed, extraction time and treat ratio. The membrane breakage at various conditions were also determine.
2.4.1. Membrane Breakage

Membrane breakage, ε (%), were calculated based on H+ ions concentration change in the external phase which are determined via pH meter according to the following equation [6]:

$$\varepsilon (\%) = \frac{V_e}{V_i} \times 100$$  \hspace{1cm} (1)

where, $V_i$ is the initial volume of the internal phase while $V_e$ is the volume of the internal phase leaked into external phase which can be calculated by mass balance as shown in equation below.

$$V_e = V_{\text{Ext}} \times \frac{10^{-pH_e} - 10^{-pH}}{10^{-pH_{\text{OH}^-}} - C_{\text{OH}^-}^i}$$  \hspace{1cm} (2)

where, $V_{\text{Ext}}$ is the initial volume of external phase, $pH_e$ 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. $C_{\text{OH}^-}^i$ is the initial concentration of OH- in the internal phase.

3. Results and Discussion

3.1. Effect of Stripping Agent Concentration

The effect of stripping agent concentration was investigated by varying the concentration at 0.05, 0.1, 0.15 and 0.2 M as presented in Figure 1. As the concentration of ammonia increases, the membrane breakage decrease. At low stripping agent concentration, there was insufficient stripping agent to strip acetaminophen from membrane phase. Meanwhile as the concentration increases, more solute is stripped resulting in more carrier molecules generated. However, further increase of the concentration up to 0.2 M causes the membrane breakage to increase. This is due to the high pH gradient between the internal and external phase where the large difference in ionic strength promotes the transportation of water into the internal phase causing emulsion swelling [7]. Consequently, this will trigger emulsion breakage. Thus, 0.1 M of ammonia was selected as the best stripping agent concentration in this study.

![Figure 1. Effect of Stripping Agent Concentration to Membrane Breakage](image-url)
3.2. Effect of Agitation Speed

Agitation speed plays an important role in ELM stability where an appropriate speed must be selected. The effect of agitation speed on emulsion diameter was investigated at agitation speeds of 200 rpm, 300 rpm, 400 rpm and 500 rpm as shown in Figure 2. At an agitation speed of 200 rpm, the percentage of membrane breakage were at the highest. This is due to the insufficient shear energy to disperse the emulsion in the external feed phase and larger globules were formed and thus emulsion breakage occurred. Similar results were found by Kumbasar [8], stating that low agitation speed causes the ELM globules cannot be well dispersed and the formations of large globules. As the agitation speed increases up to 300 rpm, the membrane breakage decrease. High agitation speed is preferable to produce fine droplets with larger surface area and improved membrane. Further increase of agitation speed up to 500 rpm is detrimental for membrane stability problems where it results in increment of emulsion breakage. The increase of agitation speed results in unstable primary emulsion and favors the leakage of internal dispersed phase to the external continuous aqueous phase. Valenzuela, Araneda [9] found that excessively high agitation speed could induce coalescence and breakdown of emulsion globule. Therefore, an agitation speed of 300 rpm was chosen to obtain a stable emulsion in this study.

![Figure 2. Effect of Agitation Speed to Membrane Breakage](image)

3.3. Effect of Extraction Time

The effect of extraction time was investigated by varying it at 1, 3, 5 and 7 minutes as presented in Figure 3. 22% of emulsion breakage was observed at the first 1 minute. This may be due to the insufficient contact time which leads to the formation of easily ruptures emulsion globules thus causing the leakage of stripping agent into the external feed phase. However, the emulsion stability was improved when the extraction time was increased from 1 to 3 minutes. Complete emulsion dispersion to form W/O/W interface occurs with increasing contact time [10]. Thus, it is believed that the extraction time is adequate enough for a satisfactory stable emulsion. As the extraction time increases, the emulsion breakage also increases. Membrane breakage of 19% and 39% was observed at 5 and 7 minutes respectively. Longer extraction time causes more water transport into the internal phase which leads to membrane swelling followed by emulsion breakage. Ahmad, Kusumastuti [11] also reported that prolonged extraction time caused emulsion instability. Hence, 3 minutes of extraction time was selected as the best condition to produce a stable emulsion for acetaminophen removal.
3.4. Effect of Treat Ratio

The treat ratio was varied by changing the volume of external feed phase and kept constant the volume of the W/O emulsion. The treat ratio is varied at 3, 5 and 9 as shown in Figure 4. Results show that at treat ratio 3, lowest membrane breakage was achieved. This is due to the low volume of emulsion which causes the system to be dispersed properly resulting in a stable emulsion. Further increase in treat ratio of 5 and 9 results in higher membrane breakage. Membrane breakage occurs at high treat ratio due to the difference in osmotic pressure between the emulsion and the external feed phase causing the rupture of emulsion globule [12]. Globules interactions were enhanced for higher volume of emulsion and leads to coalescence of globules and membrane ruptured [13]. Hence, the best treat ratio with the lowest membrane breakage is at a treat ratio of 3:1.

4. Conclusion

This study succeeded in choosing the best parameters and operating conditions for the stability study of emulsion liquid membrane on membrane breakage. The effect of emulsion diameter to membrane
breakage was reported where several parameters were studied which are the stripping agent concentration, agitation speed, extraction time and treat ratio. Throughout this study, the best condition was found to be a stripping agent concentration of 0.1 M, agitation speed of 300 rpm, extraction time of 3 minutes and a treat ratio of 3:1 with a membrane breakage of 0.17%.

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