Stability Study of Emulsion Liquid Membrane via Emulsion Size and Membrane Breakage on Acetaminophen Removal from Aqueous Solution Using TOA

Nur Dina Zaulkiflee, Abdul Latif Ahmad,* Jayasree Sugumaran, and Nuur Fahanis Che Lah

ABSTRACT: The purpose of this study is to explore the emulsion liquid membrane stability for acetaminophen (ACTP) removal from aqueous solution. In this work, the membrane phase was prepared by dissolving trioctylamine (TOA) with kerosene and Span80. The stability of the emulsion in terms of emulsion size, membrane breakage, and its efficiency in removing ACTP was considered for the optimization of parameters. Investigation on the stability of emulsion was carried out by manipulating the concentration of stripping agent, agitation speed, extraction time, and treat ratio. The best condition to produce a very stable emulsion was achieved at 0.1 M of stripping agent concentration, with 300 rpm of agitation speed for 3 min of extraction time with a treat ratio of 3:1. Eighty-five percent of ACTP successfully stripped into the emulsion with minimum membrane breakage of 0.17% through this experiment.

1. INTRODUCTION

Recently, there has been a growing realization of pharmaceutical contaminants of emerging concern (CEC) in the aquatic environment at concentrations that are adequate for causing catastrophic effects in living organisms. Other than human consumption, veterinary usage also contributes to the release of CEC into the environment. Chemical compounds such as acetaminophen (ACTP), carbamazepine, diclofenac, ibuprofen, and salicylic acid can be easily detected in the water. Although these components exist in small concentrations, they still lead to chronic hazards in the long run. To make matter worse, there is some concern regarding the potential “cocktail” effects of different species of pharmaceutical contaminants mixed together. Thus, due to the increasing demand for acetaminophen (ACTP) in many applications, it is essential to extract acetaminophen from biological production waste. The more substantial environmental crisis can be caused by the improper treatment of these chemicals. According to Alistair, pharmaceutical wastes are discharged to the environment by multiple paths such as livestock treatments, manufacturing process, aquaculture treatments, improper disposal of worn containers and pristine medicine, and treatment of pet animals.

One of the most studied groups of emerging contaminants is pharmaceutical contaminants, which have been widely publicized in the ng/L to μg/L range. Nearly 3000 various substances are used as pharmaceutical ingredients, which include molecules with different physicochemical and biological properties. The majority of medical substances are managed orally, while some drugs are either metabolized or remain intact before being excreted. Therefore, a mixture of pharmaceuticals and their metabolites penetrate municipal sewage and sewage treatment plants. For example, several types of pharmaceutical CECs such as acetaminophen, atenolol, furosemide, and metformin have been detected in Langat River, Malaysia. According to Lyons, global surveys found 713 pharmaceuticals (of which 142 are transformation products) in the environment, and it was reported that 631 (of which 127 are transformation products) are above their detection limits.

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The emulsion liquid membrane (ELM) has a high interfacial area-to-volume ratio for mass transfer, so the system is capable of recovery of solute even at low concentration selectively. This process, which is considered as economical due to its low energy consumption and solvent quantity, enables us to simultaneously extract and strip. Thus, it is a suitable method to apply to remove acetaminophen in water. Despite the promising features of ELM, the major drawback of ELM is its instability, and this phenomenon has impeded the widespread applications of ELM on a larger scale. The stability of an emulsion is defined as liquid membrane resistance toward high shear stress during solute extraction. Thus, an unstable liquid membrane tends to be ruptured or broken apart, which diminishes some of the solute separations that have been achieved. According to Kumar et al., instability of emulsion occurred consequently due to the presence of two thermodynamically unstable interfaces.

Enormous studies have been conducted to minimize the occurrence of emulsion instability to achieve better extraction efficiency. However, emulsion stability remains a great challenge that would hinder its wide applications. There are three main phenomena that could cause instability of emulsion, which are membrane breakage, emulsion swelling, and coalescence. It is usually governed by emulsion rupture and leakage, causing a decrease in stripping phase volume. This causes the mass transfer driving force; the concentration gradient reduced and increases the external feed concentration while lowering the extraction efficiency. The instability may be caused by the emulsion formulation and condition of emulsification. Therefore, the purpose of this research was to remove acetaminophen from aqueous solution, with a focus on these factors that are emulsion size and membrane breakage. The effects of stripping agent concentration, agitation speed, extraction time, and treat ratio toward emulsion diameter and membrane breakage were explored. Therefore, emulsion stability was explored for the removal of acetaminophen (ACTP) from aqueous solution.

2. EXPERIMENTAL METHOD

2.1. Chemicals. Generally, there are two categories of ELMs that are water-in-oil-in-water (W/O/W) and oil-in-water-in-oil (O/W/O) systems, which comprise of the membrane and internal and external (feed) phases. The external phase contains analytical grade ACTP and was dissolved in hydrochloric acid, HCl solution accordingly. The preparation of the membrane phase requires diluent (kerosene), nonionic surfactant (Span80), and carrier (Tri-octylamine, TOA). The internal phase consists of a stripping agent (ammonia in liquid form, NH₃). All of the chemicals and reagents used in this study were analytical grade.

2.2. Analytical Instruments. Fisher Scientific accumet AB15 pH meter was used to measure the pH for every sample of the solution. The pH meter was calibrated using standard buffer solutions with calibration at pH 4, 7, and 10. All readings were taken during the stable reading at ambient temperature (25 ± 1). An Olympus optical microscope with a camera and an image analysis software, ImageJ, was used to measure the size of the droplets for water-in-oil, W/O, emulsion and emulsion globules. The concentration of ACTP was determined spectrophotometrically by UV–vis spectrophotometer at a wavelength of 243 nm.

2.3. Emulsion Formulation. Primary W/O emulsion is composed of a membrane phase and an internal phase. The membrane phase formed by mixing surfactant, Span80 and carrier, and TOA in a diluent, kerosene, for 5 min at 500 rpm. In the internal phase, ammonia was then added in a ratio (internal phase to membrane phase) of 1:3. Commercial ultrasonic (USG150) equipped with a titanium horn was used for the emulsification of the mixture to form W/O emulsion. The emulsion was required to be freshly prepared prior to all steps of the study. To capture the emulsion globule image, a tiny drop of the emulsion was dispersed onto a glass slide containing a pool of external phase to form a W/O/W system. The images obtained were analyzed and measured three times to observe and get an average diameter value of the emulsion size. The emulsion size is expressed as droplets diameter or Sauter diameter ($d_{32}$), which represents the average surface diameter as follows

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

(1)

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

2.4. Stability Study. Emulsion stability is important in the application of ELM, and it has been a problem in the industrial applications of the ELM process. Thus, to conquer this problem, it is crucial to sustain the desired level of stability. In this research, the optimum conditions for stable emulsion were determined experimentally. The stability study of the emulsion was carried out by manipulating four parameters such as stripping agent concentration, agitation speed, extraction time, and treat ratio. The external feed phase at a fixed ACTP initial concentration was mixed with freshly prepared emulsion and stirred. Upon completion of agitation, the portion of the external phase was taken for pH measurement. Membrane breakage, $\epsilon$ (%) were calculated based on the change in the H⁺ ion concentration in the external phase, which is determined via pH meter according to the following equation

$$\epsilon = \frac{V_i}{V_i} \times 100$$

(2)

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

$$V_i = V_{\text{Ext}} \frac{10^{-pH_i} - 10^{-pH}}{10^{-pH} - C_{\text{OH}^-}}$$

(3)

where $V_{\text{Ext}}$ is the external phase initial volume, pHᵢ and pH are the external phase, initial pH and the external phase pH after being in contact with emulsion after stirring, respectively. $C_{\text{OH}^-}$ is the initial concentration of OH⁻ in the internal phase.

2.5. Extraction Study. The extraction and stripping reactions involved during the reaction mechanism of ACTP removal have been elucidated at the external–membrane interface. ACTP chemically react with TOA, eq 4, while at the membrane-stripping interface, the ACTP-TOA complex diffuses to the internal interface through the membrane phase by reacting with ammonia (eq 5).
The extraction efficiency is then calculated using eq 6, where $C_0$ is the ACTP initial concentration (ppm), while $C_f$ is the ACTP final concentration at the end of the extraction process.21

$$E = \left(1 - \frac{C_f}{C_0}\right) \times 100 \%$$

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of Stripping Agent Concentration.

Another crucial factor in designing a stable ELM is choosing the adequate stripping agent concentration. The concentration varied at 0.05, 0.1, 0.15, and 0.2 M, as presented in Figure 1. Based on the graph, the results show that increasing the concentration of ammonia resulted in a decrease in membrane breakage. At low stripping agent concentration, there was an inadequate stripping agent to strip acetaminophen from the membrane phase, whereby the process decelerated and caused the acetaminophen complex in the liquid membrane to be saturated. These results are in line with those of Ng et al.22 Meanwhile, at higher ammonia concentration, more carrier molecules were generated as more solute is stripped. However, the increase of concentration up to 0.2 M causes membrane breakage to increase as a result of the high pH gradient of the internal and external phases. The large difference in ionic strength encourages the water to flow into the internal phase, causing the emission to swell and the extraction efficiency to reduce.23 Consequently, the membrane layer becomes thinner and triggered emulsion breakage. This situation is in line with a study conducted by Ahmad et al.24 to extract cadmium. Thus, it can be concluded that 0.1 M of ammonia is the best stripping agent concentration in this study.

#### 3.2. Effect of Agitation Speed.

High agitation speed is required in the furtherance of creating a uniform dispersion on a broad interfacial area. However, this can also increase the shear energy, which leads to emulsion instability such as membrane breakage. Thus, agitation speed plays an important role in ELM stability where appropriate speed must be selected. The effect of agitation speed to emulsion size was explored at agitation speeds of 200–500 rpm with an interval of 100 rpm as demonstrated in Figure 2. The percentage of membrane breakage was highest at a low agitation speed of 200 rpm. This is due to the insufficient shear energy to disperse the emulsion in the external feed phase and larger globules were formed. Consequently, it results in coalesced globules and emulsion breakage occurred. Similar results were found by Kumbasar,25 stating that low agitation speed causes the ELM globules not well dispersed and formations of large globules in an emulsion. Similar results were also found by Othman et al.26 in the recovery of chromium using ELM. As the agitation speed increases to 300 rpm, the membrane breakage decreases. Thus, this indicates that the higher the agitation speed, the higher the shear rate. This results in more turbulence conditions, which enhance the mass transfer of the ELM process. High agitation speed is preferable to produce fine droplets with larger surface area, whereby the interfacial area of the feed solution and emulsion liquid membrane solution increases. Thus, membrane stability also increases. These results are in agreement with those of Datta et al.27 for aniline removal using ELM. However, accelerating the agitation speed beyond the optimal value is detrimental to membrane stability problems. Further increase of agitation speed up to 500 rpm causes an increment of emulsion breakage. An increase in agitation speed results in unstable primary emulsion and favors leakage of the internal dispersed phase toward an external phase. Even though membrane breakage is higher, the size of the emulsion globule formed was smaller at higher agitation speed. This condition caused the thinning of interfacial film and rapid coalescience of emulsion globule, which eventually leads to membrane breakage. It demonstrates that the rise of the mass transfer area originates from the formation of smaller globules. The globules were incapable to compensate for the
release effect of the internal phase reagent through emulsion breakup. This phenomenon was also faced by other researchers upon using excessive speed. Valenzuela et al.28 found that excessively high agitation speed could induce coalescence and breakdown of emulsion globule. These results are also in line with those of Chaouchi and Hamdaoui.29 Thus, the agitation speed of 300 rpm was chosen to obtain a stable emulsion in this study.

3.3. Effect of Extraction Time. The contact time that is also known as extraction time between the emulsion phase and the external feed phase was studied. The extraction time was investigated by varying the time at 1, 3, 5, and 7 min. Figure 3 presents the effect of extraction time against emulsion stability. Based on the results, at 1 min, 22% of emulsion breakage was observed. This may be due to inadequate contact time, which consequently promotes the formation of easily ruptured large-size emulsion globules. This, in turn, causes the leakage of the stripping agent into the external feed phase. Meanwhile, the emulsion stability improved as the extraction time was increased from 1 to 3 min. A full emulsion dispersion to form the W/O/W interface occurs with increasing contact time.30 Hence, it is believed that this duration of extraction time is decent enough for a stable emulsion. Besides, the emulsion size also decreases with extraction time, which is attributed to a more uniform size of globule dispersion, thus promoting exceptional emulsion stability. In different circumstances, as the extraction time increases, the emulsion breakage also increases. Results show that 19 and 39% of emulsion breakage were detected at 5 and 7 min, respectively. Longer extraction time leads to the dispersion of smaller emulsion globules but consequently also leads to the coalescence of emulsion globule and emulsion breakage. This is parallel with the size of emulsion, which increases as the extraction time increases. This proved that the larger emulsion globules were formed at longer extraction time. In addition, longer extraction time also causes more water transport into the internal phase, leading to membrane swelling followed by emulsion breakage. The breakage of the emulsion phase at longer extraction time was also reported by Kulkarni and Mahajani.31 These results also in line with the study by Ooi et al.32 Besides, Ahmad et al.33 also reported that prolonged extraction time caused emulsion instability. Therefore, 3 min of extraction time was selected as the best condition to produce a stable emulsion for acetaminophen removal.

3.4. Effect of Treat Ratio (External Feed Phase: Emulsion). It is crucial to select a satisfactory treat ratio as it governs the interfacial mass transfer over the emulsion liquid membrane. The external feed phase volume was varied while the volume of the emulsion was kept constant. To explore the effect of treat ratio (external feed phase to emulsion), the treat ratio is varied at 3, 5, and 9. Figure 4 represents the stability of the emulsion of different treat ratios. Based on Figure 4, the results show that at the treat ratio of 3, the lowest emulsion size and membrane breakage were achieved. This is due to the low volume of emulsion, which causes the system to be dispersed properly, resulting in a smaller and stable emulsion. This indicates that smaller emulsion size increases the mass transfer due to a larger interfacial area. Further, an increase in the treat ratios of 5 and 9 results in higher emulsion size and membrane breakage. Membrane breakage occurs at a high treat ratio due to the difference in osmotic pressure, causing the rupture of emulsion globule. The greater number of water molecules in the external feed phase was how the target osmotic pressure difference was sustained.34 A study by Hasan et al.35 revealed that an increase in the external phase volume results in a reduction of membrane area per total external volume. Besides, the emulsion size increases as the treat ratio increases due to the decreasing volume of the internal solution toward the external feed phase at fixed emulsion volume. Datta et al.36 revealed that in terms of emulsion size, a high treatment ratio is not preferable since it provides a bigger size with a smaller contact area. Globules interactions were enhanced for a higher volume of emulsion and lead to coalescence of globules and rupture of membrane.36 Hence, the optimum treat ratio with the smallest emulsion size and membrane breakage selected for this study is 3:1.

3.5. Extraction Efficiency. The ACTP extraction efficiency under the best conditions of parameters according to the emulsion size and membrane breakage was investigated. The summary of the results is tabulated in Table 1. To achieve
Table 1. Summary of Results Based on Parameters Studied

| Parameters                  | Conditions |
|-----------------------------|------------|
| Stripping agent concentration | 0.1 M      |
| Agitator speed              | 300 rpm    |
| Extraction time             | 3 min      |
| Treat ratio                 | 3:1        |
| Membrane breakage           | 0.17%      |
| Emulsion sauter diameter    | 0.75 μm    |
| Extraction efficiency       | 85%        |

the highest extraction efficiency in the ELM system, a stable emulsion formulation is needed. This is because unstable liquid membrane tends to get ruptured; as a result, the extracted solute is discharged back into the external phase, consequently causing lower extraction efficiency, while it is nullified to some extent. As a matter of fact, the release of the internal phase does not only affect the separation efficiency but further contaminates the external phase with the stripping agent. The result obtained on the stability study showed that the highest extraction efficiency achieved was 85%, with a minimum membrane breakage of 0.17% and emulsion diameter of 0.75 μm, as depicted in Figure 5. The emulsion prepared with the most optimal parameter was found to be stable, which was due to the formation of the smallest droplet size of water in oil and thus low membrane breakage. As a result, maximum extraction efficiency can be achieved for the removal of ACTP from aqueous solution.

4. CONCLUSIONS

The outcome of emulsion diameter and membrane breakage was reported, where several parameters were studied such as stripping agent concentration, agitation speed, extraction time, and treat ratio. Throughout this study, the best conditions were found to be at the stripping agent concentration of 0.1 M, 300 rpm of agitation speed with 3 min of extraction time, and a treat ratio of 3:1. Based on the best conditions achieved, the results obtained bestow emulsion diameter d_{50} of 0.75 μm and membrane breakage of 0.17% with an extraction efficiency of 85%.

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