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Removal of Acetaminophen from Aqueous Solution by Emulsion Liquid Membrane: Emulsion Stability Study

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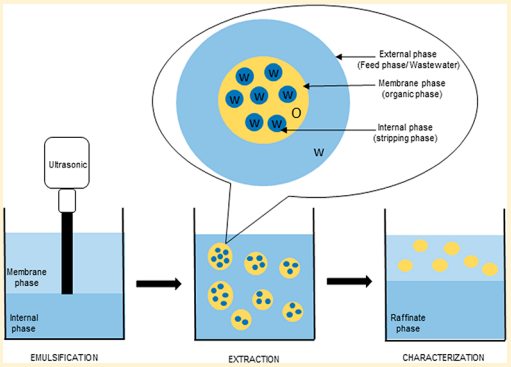
ABSTRACT: This study focused on the investigation of emulsion stability, membrane breakage, and emulsion swelling of an emulsion liquid membrane for acetaminophen (ACTP) removal. Stability of the emulsion as well as its effectiveness in removing ACTP from aqueous solution were considered for the optimization of parameters. Parameters involved are carrier and surfactant concentration, emulsification time, as well as volume ratio of membrane to internal phase. The effects of membrane breakage and emulsion diameter on the removal capacity of ACTP were also studied. Results showed that the optimal conditions to produce a very stable emulsion and to achieve maximum ACTP removal efficiency were found to be 4 wt % of trioctylamine (TOA) and Span 80, W/O volume ratio of 3, and 10 min of emulsification time. The prepared emulsion was found to effectively remove 85% of ACTP at minimal membrane breakage of 0.19%.



1. INTRODUCTION

Environmental pollution has existed for centuries but started to be significant following the industrial revolution in 19th century which in turn has raised many critical issues on a vast and unprecedented scale around the globe. Pollution occurs when there is an introduction of contaminants into the natural environment where it can cause damage to the environment and harm plus discomfort to humans and other living species. It is one of the greatest challenges that the world is facing today and increases day by day causing irreparable damage to Mother Earth. Thus, as our environment changes, so does the need to become increasingly aware of the problems that surround it.

While the current generation continues to make efforts to remediate and minimize traditional pollutants in the environment, other "emerging" environmental contaminants are now warranting attention which are labeled as "contaminants of emerging concerns" or known as CECs.[1] These contaminants are widespread in the aquatic and terrestrial environments, and include anthropogenic and naturally occurring chemicals, pharmaceuticals, and personal care products (PPCPs), metabolites and transformation products of PPCPs, illicit drugs, engineered nanomaterials, and antibiotic resistance genes. Even though they are not yet regulated in drinking water supplies and are not commonly monitored in the environment, these contaminants have the potential to cause adverse ecological and human health effects even at low levels of concentration.[2]

Over the past few years, there has been an increasing awareness of pharmaceutical CECs in the aquatic environment at concentrations capable of causing detrimental effects toward aquatic organisms. This is because they are introduced not only by humans but also through veterinary usage resulting in their continuous release to the environment.[3] It is estimated that approximately 3000 different substances are used as pharmaceutical ingredients including painkillers, antibiotics, and impotence drugs. The presence of pharmaceutical CECs in environmental waters is due to incomplete removal in wastewater treatment or diffuse-source contamination, which are threats to drinking waters, estrogenic possibility, and also adverse effects to both humans and wildlife. The major concern of pharmaceutical CECs is that they were usually designed specifically to maximize their biological activity at low doses and target certain metabolic, enzymatic, or cell-signaling mechanisms.[4] In addition, the development of bacterial resistance from release of antibiotics and the decrease in biodegradation of leaves and other plants which serve as primary food source for aquatic life are also one of the major concerns of pharmaceutical CECs.[5]

Some of the most abundantly used pharmaceuticals are acetaminophen, carbamazepine, cimetidine, and diltiazem, and six sulfonamide related antibiotics.[6] Acetaminophen (ACTP) also known as paracetamol is widely used to relieve pain or suppress inflammation. According to Petrie et al.,[7] 2015, the

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prescription of ACTP is estimated to be more than 2 000 000 kg whereby 20% of the excretion unchanged resulting with a mean maximum amount of contaminants found on surface water around 2382 ng/L. The composition of pharmaceutical wastewater according to a pharmaceutical occurrence in Langat River according to Al-Odaini et al.[8] had a detected concentration of acetaminophen of 350.3 ng/L. With that, paracetamol is categorized as one of the alarming CECs.[9] The presence of acetaminophen in wastewater and drinking water can cause ecological effects because continuous introduction into the environment can lead to overwhelming transformation rates. According to Carlos A Rey-Mafull et al.,[10] acetaminophen acts on the basis of a pharmacological effect by inhibiting prostaglandin synthesis, cellular mediators responsible for the pain relief. At therapeutic doses, ACTP is relatively safe; however, overdose concentrations of ACTP are dangerous as it can cause liver failure, gastrointestinal disease, centrilobular necrosis, and hepatotoxic potential.[11]

Conventional treatment processes applied to wastewater treatment plants fail to completely remove pharmaceutical compounds. Removals during wastewater treatment are generally good; however, notable concentrations remain in final effluents because of the relatively high influent concentrations encountered.[12] Therefore, integration of conventional wastewater treatments with advanced technologies has become of great interest especially liquid membranes. There are three configurations of liquid membrane which are bulk, supported, and emulsion. Among those three, the emulsion liquid membrane was given more attention due to having high interfacial area which enables the system to selectively recover solute. Emulsions are playing an important role in a variety of fields such as foodstuffs, cosmetics, pharmaceuticals, laundry and cleaning, lubricants, and many more since emulsions function as an alternative of conventional methods.[13] Furthermore, the emulsion liquid membrane (ELM) has successfully recovered solute even in very low concentrations by almost no loss of organic solution. In addition, the combination of extraction and stripping processes in one stage contributes economically. Thus, it is a suitable method to implement to remove acetaminophen CECs in water. Unfortunately, despite the promising features of ELM, this process is not widespread because of the swelling of the emulsion and emulsion instability. The stability of the emulsion is defined as resistance of the liquid membrane to rupture under high shear stress during solute extraction in the ELM process.[14] Hence, the best performance of solute extraction could be achieved by employing an optimally stable emulsion.

There are many factors affecting emulsion stability, and one of them is emulsion diameter. Both methods of emulsification and membrane compositions play an important role in producing a stable emulsion associated with the droplet size of the emulsion.[4,15] Emulsion droplet size is represented by Sauter mean diameter.[16] Large droplet diameters result in poor stability and extraction efficiency. The other factor affecting emulsion stability is membrane breakage. Emulsion breakage results in decreasing of extraction efficiency by the release of entrapped pollutants. Membrane rupture occurs when there is an increase of feed phase pH which causes the spill out of internal phase to the feed phase.[4]

Therefore, this research emphasizes the stability of the liquid membrane for the acetaminophen removal from aqueous solution to achieve a high acetaminophen extraction with a stable emulsion. This study will focus on the emulsion size droplet factors as well as the membrane breakage. The effects of surfactant concentration, carrier concentration, emulsification time, and ratio of membrane to internal phase on the emulsion diameter and membrane breakage were studied. All of these parameters in this study were repeated at least 3 times to obtain an accurate result. Furthermore, the removal efficiency was also investigated on the influence of emulsion diameter. Overall, application of this technique to solutions containing ACTP stock solutions was investigated for removal of acetaminophen (ACTP) using trioctylamine (TOA) as extractant, Span 80 as surfactant, kerosene as membrane phase, and ammonia as stripping solution.

2. EXPERIMENTAL METHOD

2.1. Chemicals. Kerosene was used as diluent to dissolve a nonionic surfactant, Span 80, and carrier, trioctylamine (TOA), purchased from Merck and Sigma-Aldrich, respectively. These chemicals were chosen to be used in this study since it resulted in the lowest breakage percentage as well as best emulsion stability.[17−21] In addition, for ionization of the acetaminophen complex and TOA as well as adjustment of the pH of the solution, hydrogen chloride (HCl) was used. Ammonia (NH_3) was used for the internal phase. The aqueous solution of acetaminophen (ACTP) was prepared from ACTP stock solution by dissolving analytical-grade ACTP purchased from Sigma-Aldrich in deionized water. Other chemicals and reagents used in this study are all analytical grade and were purchased from Merck.

2.2. Analytical Instruments. The pH of the solution was measured using a Fisher Scientific accumet AB15 pH meter, and all readings were taken at ambient temperature. The measurement of emulsion globule size was measured using an Olympus optical microscope equipped with a camera. The concentration of ACTP was determined spectrophotometrically by a UV−vis spectrophotometer at the maximum absorbance of ACTP.

2.3. Emulsion Formulation. The membrane phase which contains Span 80 as surfactant (2−8 wt %) and trioctylamine (TOA) as carrier (2−8 wt %) is dissolved in kerosene. The membrane phase was then stirred at 500 rpm for 5 min using a magnetic stirrer. Then, the emulsion was performed by pouring ammonia, the internal phase, into the prepared membrane phase according to a specific 1:3 internal phase to membrane phase ratio. The immiscible mixture was then emulsified assisted by a commercial ultrasonic (USG-150) instrument equipped with a titanium horn at an emulsification time of 5−20 min to form the W/O emulsion. The emulsion was then measured directly after its formation. The droplet diameter can be expressed as a Sauter diameter (d_{32}) which represents the average surface diameter as follows:[3]

$$d_{32} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} = 6\frac{V}{A} \quad (1)$$

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

2.4. Stability Study. The prepared W/O emulsion was then poured into the external aqueous phase containing the ACTP ions at a fixed initial concentration of 10 ppm. Extraction was conducted at volume ratio of emulsion to external phase of (1:3, 1:5, 1:9). The system was stirred with a

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magnetic stirrer at 250 rpm for 15 min, and samples were taken from the external aqueous phase for pH and ACTP concentration measurement. Membrane breakage, ε (%), was calculated on the basis of H^+ ion concentration change in the external phase which is determined via pH meter according to the following equation:

$$\varepsilon\ (\%) = \frac{V_s}{V_i} \times 100 \tag{2}$$

where V_i is the initial volume of the internal phase, and V_s is the volume of the internal phase leaked into external phase which can be calculated by a mass balance as shown in the following equation.

$$V_s = V_{ext}\frac{10^{-pH_0} - 10^{-pH}}{10^{-pH} - C^i_{OH^-}} \tag{3}$$

Here, V_{ext} is the initial volume of external phase, pH_0 and pH are the initial pH of external phase and pH of external phase in contact with emulsion after a certain time of stirring, respectively. $C^i_{OH^-}$ is the initial concentration of OH^- in the internal phase.

2.5. Extraction Study. An extraction study is carried out by calculating the efficiency, E (%), of the removed ACTP ions from the concentration of ACTP ions removed from the external phase using the following equation:

$$\text{extraction efficiency, } E\ (\%) = \frac{C_0 - C_f}{C_0} \times 100 \tag{4}$$

where C_0 is the initial concentration of ACTP in the external phase (mg/L), and C_f is the final concentration of ACTP at the end of extraction process. The concentration of ACTP in the solution was determined by a UV−vis spectrophotometer at the maximum absorbance of ACTP.

The extraction chemistry of ELM systems is basically the same as in solvent extraction.[12] The emulsion liquid membrane system involving W/O/W emulsion consists of an emulsion including the membrane and aqueous internal phase dispersed in a continuous external phase. The mechanism of carrier-facilitated transport of ACTP by ELM transfer across a liquid membrane using trioctylamine (TOA) as carrier is schematically presented in Figure 1.[5,6] The general complexation reaction between ACTP and TOA can be expressed by eq 5.

Feed-membrane side reaction:

$$(NR_3)_{org} + (C_8H_9NO_2{-}H^+)_{aq} \leftrightarrow (C_8H_9NO_2{-}H^+NR_3)_{org} \tag{5}$$

At the external-membrane interface, ACTP chemically reacts with TOA to form 1 mol of acid−carrier complex ($C_8H_9NO_2{-}H^+NR_3$). The complex then diffuses through the membrane phase to the internal interface by reacting with ammonia as shown in eq 6.

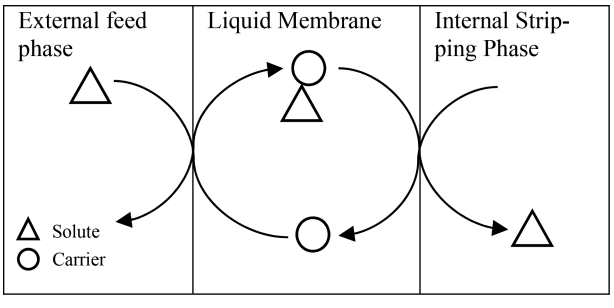

Figure 1. Mechanism of coupled transport in ELM.

Stripping-membrane side reaction:

$$(C_8H_9NO_2{-}H^+NR_3)_{org} + (OH^-)_{aq} \leftrightarrow (C_8H_9NO_2{-}H^+OH^-)_{aq} \tag{6}$$

Here, NR_3 represents TOA, $C_8H_9NO_2$ represents ACTP, $C_8H_9NO_2{-}H^+NR_3$ represents the ACTP−TOA complex, and OH^- represents ammonia.

The ammonia in the internal phase reacts with the acid−carrier complex ($C_8H_9NO_2{-}H^+NR_3$) to strip ACTP into the internal phase. Mass transfer in this system is governed by the carrier present in the membrane phase as well as the ion concentration gradient between external and internal aqueous solution.

3. RESULTS AND DISCUSSION

3.1. Effect of Surfactant Concentration. Surfactant plays an important role in emulsion stabilization as it reduces the interfacial tension between two immiscible phases. A surfactant was added as an emulsifier to act as a protective barrier between the external and internal phases, thus preventing emulsion breakage. The effect of surfactant concentration on the emulsion diameter was studied by varying surfactant concentrations at 2, 4, 6, and 8 wt %. Figure 2 shows the

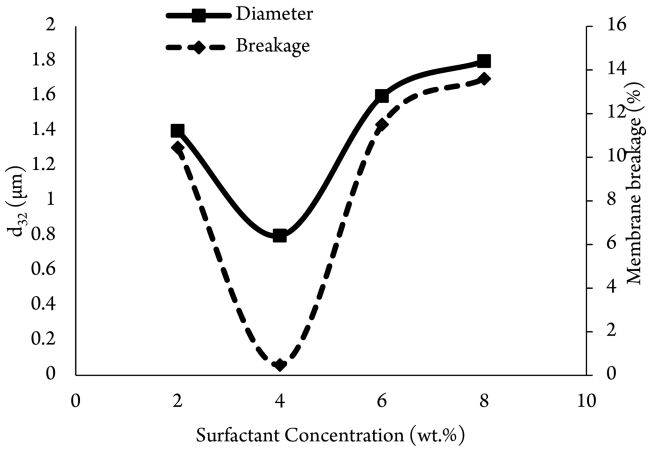

Figure 2. Effect of surfactant concentration on the emulsion diameter and membrane breakage. (Experimental conditions: [TOA] = 4 wt %; organic to internal ratio = 3:1; emulsification time = 10 min; diluent = kerosene.)

droplets size of the W/O emulsion produced by different surfactant concentrations. At low concentration, it is seen that water-in-oil emulsion droplet diameters are high. This is because the emulsion is unstable because of insufficient surfactant to reduce oil−water interfacial tension which causes high interfacial tension, leading to the difficulty in the dispersion of emulsion droplets, and with that, a bigger emulsion droplet will be formed.[4] Thus, coalescence happened and increases the droplet diameter. Increasing the surfactant concentration significantly enhanced the emulsion stability. An increment of the surfactant concentration will increase the emulsion stability and reduce the emulsion leakage as reported by several researchers.[22,23] At a higher surfactant concentration, more surfactant is absorbed at the interface between the oil membrane phase and internal aqueous phase, thus

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enhancing the strength of the adsorption layer and increasing stability. In addition, the increase in surfactant concentration also enhances stability because of the reduction of interfacial tension between the water and oil phases. However, a further increase of the surfactant concentration increased the emulsion droplet diameters and resulted in the formation of an unstable emulsion at high surfactant concentration. The destabilization of emulsion occurred because of rapid coalescence between the droplets despite the high amount of droplets formed. Joshi et al.[24] also observed the destabilization of emulsion at high surfactant concentration. Furthermore, excess of Span 80 above its critical micelle concentration tends to form surfactant aggregates in the liquid membrane phase where it promotes water transport between two aqueous phases and causes breakage and swelling.[25] Othman et al.[19] also reported that the instability of the emulsion with increase in surfactant concentration is due to Ostwald ripening of emulsion droplets, which in turn leads to an increase in swelling and leakage. The d_{32} was in the order of 4, 2, 6, and 8 wt %. The smallest d_{32} was 0.81 μm while the highest d_{32} was 1.85 μm. Therefore, the effect of surfactant concentration to the membrane breakage was investigated. As described above, the amount of surfactant must be considered very well to obtain a stable emulsion. It was analyzed that emulsion stability increased slightly with the increase of surfactant concentration until 4 wt % and then decreased as the surfactant concentration increased. At lower interfacial tension, stability is reduced to the coalescence of the smallest droplets formed.[16] Increasing its concentration caused the formation in the micelle as the surfactant molecules arranged themselves into organized molecular assemblies in the membrane phase resulting in poor membrane stability.[14] Beyond that concentration, the membrane breakage increased sharply. This is due to the decrease of interfacial tension between the phases, forming finer droplets.

3.2. Effect of Carrier Concentration. A carrier plays an important role in ensuring the effectiveness of solute extraction since it is responsible in the formation of a complex with the solute. For an investigation of the effect of carrier on the emulsion diameter, TOA concentration was varied at 2, 4, 6, and 8 wt %. The effect of carrier concentration on the emulsion droplet diameter is shown in Figure 3. The Sauter diameter decreased with the increase of carrier concentration from 2 to 4 wt %. Good emulsion stability toward membrane breakage was achieved as the carrier concentration increased. Increasing the carrier concentration over a certain limit also can raise the osmotic pressure in the internal as compared to the external.[26,27] In addition, a high amount of carrier present in the ELM could also bring the increment in mass transport resistance where the accumulation of complex occurred during the process.[28] However, increasing its concentration beyond 4 wt % does not improve the stability of the emulsion. This is because excessive concentration of TOA could in turn promote emulsion swelling which decreases the efficiency of the process and later causes the membrane layer to become thinner, making it prone to breakage.[29] The high content of carrier in the membrane is not beneficial because of the increase in viscosity, which leads to larger globules.[30] A similar result was found by Chakraborty et al.[15] (2004); incorporation of a carrier in the membrane phase increases membrane breakage, resulting in the rapid transfer of internal feed phase to external phase. The effect of carrier concentration on membrane breakage is presented in Figure 3. From this figure, it is seen that, for carrier concentrations ranging from 2 to 4 wt %, the

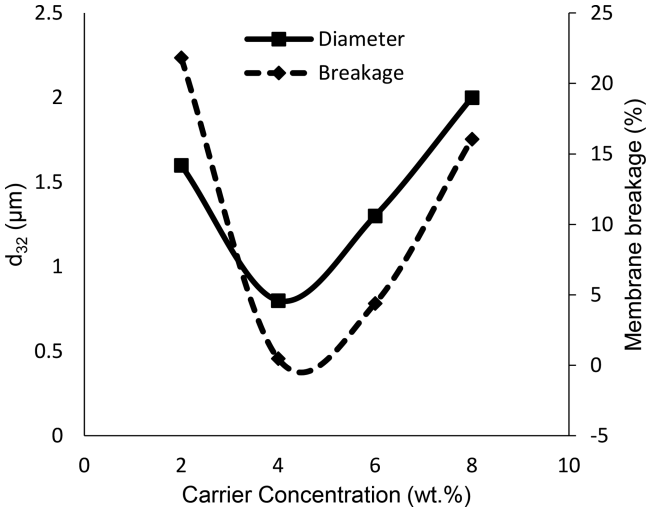

Figure 3. Effect of carrier concentration on the emulsion diameter and membrane breakage. (Experimental conditions: [Span 80] = 4 wt %; organic to internal ratio = 3:1; emulsification time = 10 min; diluent = kerosene.)

membrane breakage decreases with increasing the carrier concentration. A high concentration of carrier may trigger emulsion breakage due to the interfacial properties of the solute−carrier complex which loses the internal phase solution. Because of the increase of interfacial tension, increasing carrier concentration resulted in larger emulsion size. The instability of W/O emulsions results in the membrane breakage, causing the split of internal phase into external phase. The carrier concentration was found at 4 wt % to obtain the best membrane stability.

3.3. Effect of Emulsification Time. Sufficient time for the emulsification process must be employed to ensure that a stable and uniform emulsion is produced. For a study of the effect of emulsification time on emulsion diameter, an emulsion was prepared at varied times in the range 5−20 min. Figure 4 demonstrates the effect of emulsification time on water-in-oil emulsion stability. Longer emulsification time

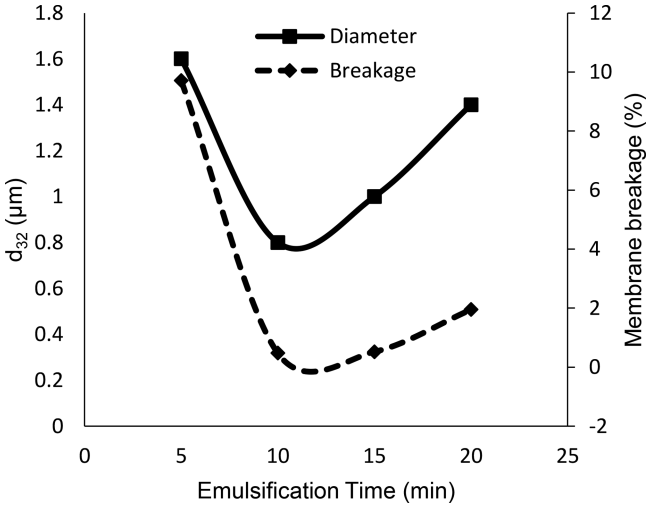

Figure 4. Effect of emulsification time on the emulsion diameter and membrane breakage. (Experimental conditions: [TOA] = 4 wt %; [Span 80] = 4 wt %; organic to internal ratio = 3:1; diluent = kerosene.)

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produced smaller emulsion diameter and a more stable emulsion, and the intensity of the solution is also enhanced. It is seen that, at a shorter time, the Sauter diameter, d_{32}, is high. This indicates that a short emulsifying time produces an unstable emulsion because the mixture of organic membrane and aqueous internal solution was not well-homogenized. Gaikwad and Pandit[31] reported that a short emulsification time leads to higher breakage percentage due to insufficient time to produce a sufficiently small emulsion droplet which causes the tendency of larger droplets to coalescence with one another. Similar results were obtained by Gasser et al.[23] who found that short emulsification time causes significant emulsion instability due to the coalescence of larger droplets. At 10 min of emulsifying time, the emulsion formed is more stable. This is because the emulsion will be more homogeneous with more internal phase entrapped in the membrane phase. Hence, smaller internal droplets were formed. This indicates that, at a longer emulsification time, a greater number of fine droplets were produced. When these droplets become smaller, more time is needed for coalescence to occur.[32] The result is in agreement with Djenouhat et al.[33] who observed that the homogeneity of the dispersed phase enhanced with ample time for exposure. A further increase in the emulsification time leads to an unstable emulsion. Emulsions with longer emulsification time face higher shear which leads to emulsion breakage. In addition, the effectiveness of the surfactant will decrease because of intense emulsification causing the surfactant to drop out from the water−oil interface. This will increase the interfacial tension and form a larger droplet causing it to easily break. Ng et al.[34] reported that coalescence of internal droplets at prolonged emulsification time was observed. The best membrane stability was reached at an emulsification time of 15 min, implying the steady state condition. It is observed that, at emulsification time higher than 15 min, the breakage percentage increased.

3.4. Effect of Volume Ratio of Membrane to Internal Phase. Membrane to internal phase ratio is an important factor to achieve optimum emulsion stability. For an investigation of the effect of volume ratio of membrane to internal phase on the emulsion diameter and membrane breakage, volume ratio of membrane to internal phase was varied at 2, 3, and 5. Figure 5 represents the stability of the prepared emulsion of various volume ratios. A low volume ratio of membrane to internal phase inhibits the encapsulation of internal phase droplets thus producing larger droplet diameters. Consequently, this will result in a thinner membrane layer enhancing membrane breakage. This result is in line with Ahmad et al.[35] where high internal phase volume resulted in higher membrane breakage. Even though the strength of the emulsion wall was improved by using a greater volume of membrane phase, its excessive amount can be counterprotective. A high volume ratio will produce a highly viscous emulsion where the membrane solution produces a thicker emulsion wall that prevents the internal phase from diffusing in. In addition, this increases the mass transfer resistance, and the high volume usage will also affect the total operational cost of ELM. A high volume ratio of membrane to internal phase also increases the surface tension; hence, it is harder for the emulsion droplets to disperse, and as a consequence, larger droplets will be produced.[4] Hence, the ratio of membrane to internal phase must be used precisely to obtain a more stable emulsion with greater amount of droplet

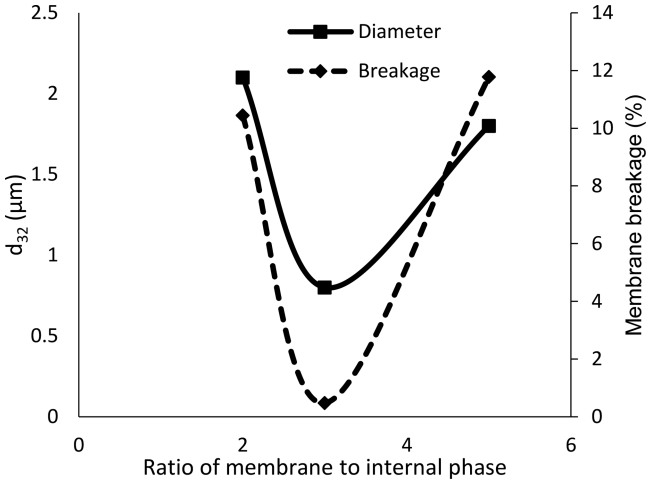

Figure 5. Effect of ratio of membrane to internal phase on the emulsion diameter and membrane breakage. (Experimental conditions: [TOA] = 4 wt %; [Span 80] = 4 wt %; emulsification time = 10 min; diluent = kerosene.)

formation. In this research, the smallest d_{32} was reached at a volume ratio of membrane to internal phase of 3:1.

3.5. Removal Efficiency. The ACTP removal efficiency is shown in Figure 6. It is seen that the efficiency decreased with

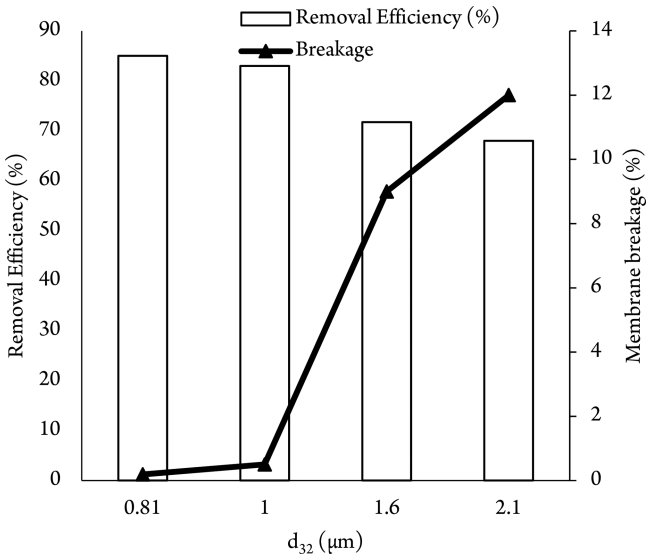

Figure 6. Effect of emulsification diameter on the removal efficiency and membrane breakage.

the increase of d_{32}. This is due to smaller droplet diameters giving a larger mass transfer area and a greater number of droplets. The highest removal efficiency was obtained at the smallest d_{32}. In this research, the highest removal efficiency was 85%, with a final acetaminophen concentration of 1.5 ppm whereby the initial concentration was at 10 ppm. This shows that the ultrasound emulsification is more beneficial compared to the mechanical agitation method since it produces stable emulsions and a high removal efficiency of ACTP. The effect of emulsion diameter on membrane breakage was also observed in this research. The results showed that a small droplet diameter tends to have better breaking resistance and rapid extraction. This result was also observed by Li et al.[36] This can be seen in Figure 6 which shows that membrane

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breakage increased with the increase of emulsion diameter. The lowest membrane breakage of 0.19% was reached at the smallest emulsion diameter of 0.81 μm.

4. CONCLUSION

The stability of the emulsion based on diameter size and membrane breakage has been investigated. An emulsion was produced using trioctylamine as carrier, kerosene as diluent, and Span 80 as surfactant. Effects of several parameters on emulsion stability were studied. They were carrier and surfactant concentration, W/O volume ratio, emulsification time, and volume ratio of membrane to internal phase, followed by removal efficiency. Within the scope of the current study, the highest separation was found to be at 4 wt % of trioctylamine and 4 wt % Span 80 dissolved in kerosene as the membrane phase at an emulsification time of 10 min with a volume ratio of membrane to internal phase of 3:1. At this condition, it gave the smallest d_{32} of 0.81 μm, with the lowest breakage of 0.19%. Membrane breakage at the rate of ~0.1% is allowable for a practical process.[37] The obtained results show that the produced emulsion is capable of removing 85% of acetaminophen from the external phase at its most stable form.

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Notes

The authors declare no competing financial interest.

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