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Research Paper

Acetaminophen Extraction Study using Vegetable Oil-Based Emulsion Liquid Membrane: The Juxtaposition of Carrier and Internal Phase

Nur Dina Zaulkiflee [1,2], Abdul Latif Ahmad [1,*], Murshid Yaacob [1]

[1] *School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia*
[2] *Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*

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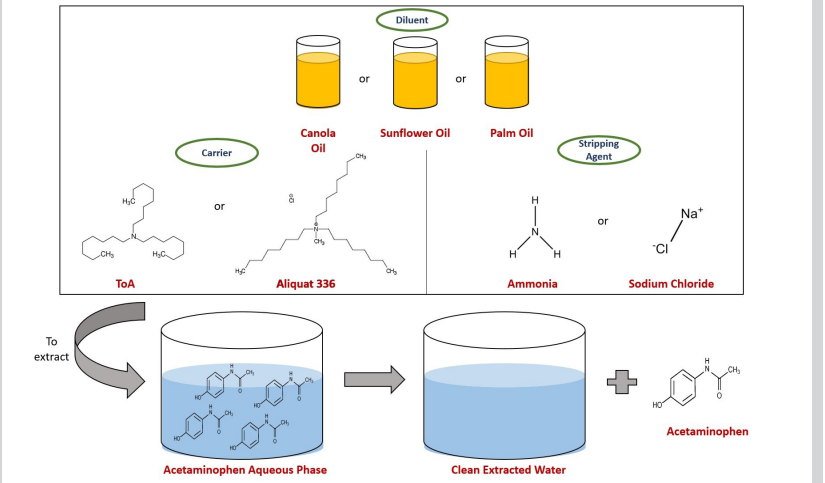
Highlights

- Usage of vegetable oils-based solvent as diluent in the extraction of acetaminophen (ACTP)
- Comparison of carrier and internal phase used for vegetable oils-based ELM in emulsion formulation
- Comparison of extraction efficiency performance of vegetable oils-based ELM in removing ACTP.

Graphical abstract



Abstract

Extraction of Acetaminophen (ACTP) using vegetable oil-based emulsion liquid membrane (ELM) was investigated. ELM consists of membrane and internal phases that form the primary water-in-oil (W/O) emulsion by using an ultrasonic probe while the external phase consists of an ACTP aqueous solution. In promoting a greener development, vegetable oil was incorporated in the formulation of ELM, replacing the hazardous conventional petroleum derivatives diluent. The potential of vegetable oil-based solvent was confirmed via a compatibility study with the carrier and surfactant whereby sunflower oil showed an auspicious potential to be employed as a diluent in ELM formulation. The effect of emulsion formulation parameters of the vegetable oil-based ELM was investigated to obtain its best formulation, by taking into consideration the ACTP extraction efficiency. The extraction study carried out using Trioctylamine (TOA) and Aliquat 336 as carrier and ammonia & sodium chloride (NaCl) as internals phase were compared. The parameters involved are emulsification time, extraction time, and the stirring speed was investigated. These works demonstrated that the ELM system was competent to successfully expel 97.73% of ACTP from aqueous solutions under optimum conditions.

1. Introduction

Pharmaceutical residues are found in the aquatic environment because of drug production, patient, and food production as well as improper disposal. Presence of pharmaceuticals residues in the environment can cause the consumption of it by wildlife and tend to bioaccumulate while humans are exposed through drinking water and ingestion of food. Over consumption of pharmaceuticals residues will be harmful as it contains active ingredients which are designed to have pharmacological effects towards consumer. The focuses and effects of these residues rely upon a mix of various factors including i) properties of the pharmaceutical residue on toxicity, persistence, degradation and versatility ii) timing and source of contamination, iii) technology, operation and removal efficiency of wastewater treatment plant iv) agriculture and veterinary practices and vi) exposure history and

* Corresponding author:E-mail address: chlatif@usm.my (A.L. Ahmad)

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sensitivity of the receiving environment [1]. Many environmental pharmaceutical residues are below concentrations that cause concern, but a significant minority are not. To make matter worse, there is no policy yet on pharmaceutical pollution likewise there is no culprit responsible for these residues. Therefore, even though these residues are at an insignificant amount, finding an effective method is an emerging concern.

One of the most debate pharmaceutical compounds is acetaminophen (ACTP), due to its environmental impact which damaged the aquatic systems and human health. ACTP is an analgesic that have been globally used to temporarily relieve minor aches and pain [2]. However, ACTP toxicity can cause fatal hepatotoxicity and nephrotoxicity that associate with kidney failure, liver damage and in severe cases, it can lead to death [3]. One of the advisable and promising separation techniques to separate contaminants from wastewater is emulsion liquid membrane (ELM) where simultaneous extraction and stripping process occurred [4]. This technique is suitable for separating contaminants as it has the capacity to remove and concentrate specifically contaminants for example metals, hydrocarbons, inorganic species and weak acids or bases. Besides that, ELM requires little quantities of organic solvent which makes it much cheaper up to 40% compared to solvent extraction [5]. ELM is a double emulsion which consist of membrane, internal and external (feed) phases [3]. Normally, the external phase contains the solute while the membrane phase consists of carrier, surfactant, and diluent which help the ELM system to work properly. The internal phase consists of a stripping agent. Water-in-oil (W/O) emulsion is formed with the combination of membrane and internal phase. Separation can be accomplished by solute transport through membrane phase from external to internal phase. The solute will be contained inside the internal phase because of the presence of a striping agent inside the internal phase [6]. The solute reacts with stripping agent inside the internal phase, thus transform into insoluble form in membrane phase. When the extraction is accomplished, the emulsion phase is separated from the external phase and demulsified to recover the internal and membrane phases. Both external and internal phases are miscible whereas membrane phase is immiscible in both phases.

Nevertheless, the concern of ELM is the usage of petroleum-based solvent. Usually, the main constituents of the organic phase are petroleum-based organic solvents for example hexane, heptane and kerosene. These kinds of diluents are liable for various environmental issues nowadays as these diluents are non-renewable, non-biodegradable, toxic and volatile [7]. Thus, new alternatives to these petroleum-based organics are vegetable oil-based solvent which considers as one of the best substitutions as it has the ideal properties of a green solvent to minimize the environmental impacts. These solvents are non-volatile, easy to regenerate and economically viable. Most importantly, these solvent has considerable environmentally favourable attributes and natural surface-active agents that helps in the emulsion stability [8]. Hence, vegetable oils have the potential of being a green alternative solvent. With that, the possibility of using vegetable oil-based solvents such as sunflower, canola and palm oils are investigated in the ELM formulation for the extraction of ACTP.

The rate of separation of ACTP is determined by physical properties which are difference in density of the phases and viscosity [9]. In this research, the difference in density of phases is involved between the ELM and external phase. Better phase separation after extraction can be achieved with higher density difference between both phases. In terms of viscosity, viscous oil is more stable but has a drawback of lowering the mass transport. Lower viscosity of both phases achieves higher phase separation due to the decrease in drag force on the emulsion droplets of the dispersed phase. Due to the above factors, compatibility study needs to be conducted to know which vegetable oils give the highest extraction of ACTP since as far as we could possibly know, barely any announced works are exploring the usage of vegetable oils as a substitute to petroleum-based solvents especially in extraction of ACTP [10]. The optimization of parameters also will determine how good the extraction of ACTP can be achieved by using vegetable oil-based solvent. Therefore, the juxtaposition of vegetable oils for acetaminophen extraction study using emulsion liquid membrane was investigated. In this study, the parameters such as type of diluents (compatibility of diluents), emulsification time, extraction time and stirring speed are examined. Thus, it is crucial to optimize the parameters to study the best ELM formulation for ACTP extraction.

2. Materials and methods

2.1. Materials

Chemicals and reagents used in this study consist of four main components which are carrier, diluent, stripping agent and surfactant. The membrane phase is made up of using commercial vegetable oils such as palm, sunflower and canola oil as the diluent, sorbitan monooleate (Span 80) as the emulsifier and Trioctylamine (TOA) and Aliquat 336 as the carriers were supplied by Sigma Aldrich and Merck respectively. These manufactured grade chemicals were used as acquired. ACTP by Sigma Aldrich was dissolve in acidic solution in order to prepare the external phase of ELM. pH value of the external phase was adjusted using hydrochloric acid (HCL) solution of 37% purity by Merck. Due to the requirement of basic medium as the internal phase, the stripping agent consisted of ammonia solution (NH_4OH) with purity of 25% and sodium chloride (NaCl) aqueous solution provided by Merck.

2.2. Experimental procedure

2.2.1. Compatibility study

Compatibility study needs to be conducted to establish unity between the carrier and surfactant for selecting the best vegetable oils as the diluent. To prepare the organic phase, 10 wt % of carrier was dissolved in vegetable oil. The compatibility study was carried out by applying the concept of liquid-liquid extraction whereby equal volume (50 ml) of the external phase and membrane phase were used. These phases were mixed thoroughly at 400 rpm for 24 hours by a magnetic stirrer. After phase separation, the external phase was then taken out to measure ACTP concentration using a UV-visible spectrophotometer. Several potential carriers and stripping agents were compared.

2.2.2. Emulsion liquid membrane preparation

Dispersing primary emulsion consist of membrane and internal phase in the external phase is how ELM system is performed. In the external phase solution, an appropriate load of ACTP solute was dissolve into deionized water and 0.1 M hydrochloric acid solution to prepare a 10 ppm of ACTP aqueous solution. Meanwhile, the membrane phase is prepared by mixing the carriers, TOA or Aliquat 336 and surfactant, Span 80 in selected commercial vegetable oil at a speed of 500 rpm. Then, the internal phase, ammonia or NaCl is added to the membrane phase at fixed concentration of 0.1 M with a 3:1 volume ratio of membrane to internal to phase. Finally, all the phases are emulsified using ultrasonic probe (USG-150) at 20W.

2.2.3. ACTP extraction

After the internal and membrane phases are prepared and mixed, it will form water/oil emulsion. Then, the emulsion was mixed into the external phase solution. Mechanical stirrer was used to circulate the emulsion at a 1:5 ratio of membrane to external phase and stirred at different speeds since the stirrer speeds are studied in this experiment [11]. The stirrer utilized four blades down impeller of 45° and diameter of 5-centimeter. Once the process is done, the solution is left for settling for 5 minutes after stirring. The ACTP ions were measured by taking sample of the external phase solution using a syringe. The experiment was performed and repeated 3 times in order to achieve higher accuracy. In this study, a UV-visible spectrophotometer is used to determine the concentration of ACTP in the solution at the wavelength (λ) of 243 nm. The extraction efficiency is calculated by the following equation:

$$\text{Extraction Efficiency, E (\%)} = \frac{C_0 - C_f}{C_0} x\ 100 \quad (1)$$

where C_0 is the ACTP initial concentration (ppm) while C_f is the ACTP final concentration at the end of extraction process [2].

2.3. Transport mechanism of ACTP

Chemical reactions (such as extraction and stripping reactions) involved during the reaction mechanism of ACTP removal have been elucidated accordingly [2]. At the external-membrane interface, ACTP chemically react with carrier as shown in Equation 2 while at the membrane-stripping interface, the complex ACTP-carrier then diffuses to the internal interface through the membrane phase by reacting with stripping agent as shown in Equation 3

$$\underbrace{(C_8H_9NO_2\text{-}H^+)_{aq}}_{\text{ACTP ion}} + \underbrace{(NR_3)_{org}}_{\text{Carrier at outer interface}} \; ? \; \underbrace{(C_8H_9NO_2\text{-}H^+NR_3)_{org}}_{\text{Complex at outer interface}} \quad (2)$$

$$\underbrace{(C_8H_9NO_2\text{-}H^+NR_3)_{org}}_{\text{Complex at inner interface}} + \underbrace{(OH^-)_{aq}}_{\text{stripping agent}} \; ? \; \underbrace{(C_8H_9NO_2)_{aq}}_{\text{ACTP ion}} + \underbrace{H_2O}_{\text{water}} + \underbrace{(NR_3)_{org}}_{\text{carrier at inner interface}} \quad (3)$$

3. Results and discussion

3.1. Diluent compatibility study

Figure 1 displays the ACTP extraction efficiency (E%) by using Aliquat 336 and TOA as carriers dissolved in sunflower, palm, and canola oils respectively. Based on Figure 1, the extraction efficiency achieved by Aliquat 336 in vegetable oils shows a higher extraction efficiency compared to vegetable oils loaded with ToA. The highest extraction efficiency achieved by Aliquat 336|Sunflower oil is 87.82 % while the highest extraction efficiency achieved by ToA|Sunflower oil is 62.23 %. When canola oil is used as the diluent for both the carriers, the extraction efficiency reduces slightly. The extraction efficiency was recorded at 85.85 % and 59.94 % by Aliquat 336 and ToA, respectively. The extraction efficiency keeps decreasing to 81.06 % for Aliquat 336-Palm oil in contrast to ToA|Palm oil where the extraction efficiency slightly increases to 60.89 %. Supposedly, when the diluents are more viscous, the extraction efficiency will be reduced. However, in this case, the extraction efficiency of ToA|Palm oil is higher than ToA|Canola oil. This might happen due to the compatibility of ToA and palm oil where the desirable effects on the extractability of solutes are less favourable resulting in lower extraction efficiency.

The properties of vegetable oils were compared and tabulated as shown in Table 1. The viscosity of sunflower oil has the lowest value followed by canola and palm oils respectively. Besides that, these vegetable oils have low dielectric constant value (~3) which makes them non-polar and immiscible in the external phase due to their aliphatic property [12]. Also, the vegetable oil-based diluent has a high flash point which enhances the safety of the overall process. It is recommended that the usage of diluent with a flashpoint of more than 100 ºC [13].

The data obtained in Figure 1 shows that extraction efficiency of Aliquat 336 and ToA as carriers by different diluents have increased following the order of palm oil < canola oil < sunflower oil and canola oil < palm oil < sunflower oil respectively. The ordering of the extraction efficiency proves that the highest extraction efficiency was achieved by sunflower oil which has the lowest viscosity compared to others. Dâas and Hamdaoui [16] showed that different in extraction efficiency may be due to different viscosity of vegetable oils and type of carrier used whereas the lower the viscosity of diluent, the better the solute separation. Besides, viscous vegetable oil increases emulsion stability however it will in turn decrease the mass transport of solute. Björkegren, Karimi [10], reported that over 99% of extraction efficiency was achieved for the removal of hexavalent chromium by using palm oil as diluent and tri-n-octyl methylammonium chloride (TOMAC) as a mobile carrier under optimum operating conditions proving that viscosity of diluent affects the extraction efficiency of ACTP as a different type of diluents used. Similar results of extraction efficiency were obtained by [15] where they used corn, sunflower and palm oils loaded with Aliquat 336 in their study. The outcomes acquired show the extraction efficiency has increased in the order of palm oil < sunflower oil < corn oil. Chang and Teng [17] studied for the extraction of copper ions by utilizing D2EHPA loaded into canola, corn, soybean, and sunflower oils also show quite similar results. According to the report, the results obtained were arranged such as soybean > corn > sunflower > canola oil. It can be observed that sunflower oil has the best extraction efficiency as diluent compared to canola and palm oil.

It is identified that sunflower oil possesses properties of low viscosity, low dielectric constant and considerable high flash point fulfilling the criteria needed for a good diluent. Thus, the most compatible vegetable oils for both Aliquat 336 and ToA in this study is sunflower oil as it gives the highest extraction efficiency compared to palm oil and canola oil. Sunflower oil is chosen and used for further study on the optimization of parameters by using Aliquat 336 and ToA as carriers.

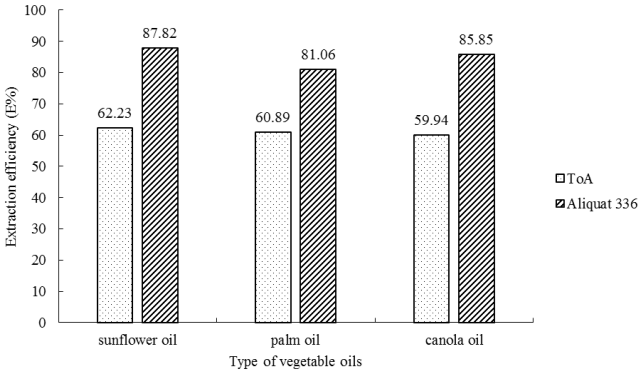

Fig. 1. Effect of vegetable oil base on the extraction efficiency (E%) of ACTP.

Table 1
Properties of vegetable oils [14, 15].

Properties	Sunflower oil	Palm oil	Canola oil
Viscosity, μ (mPa.s)	44	77	56
Dielectric Constant	~3	~3	~3
Specific gravity	0.921	0.918	0.930
Flash point, T_f (ºC)	121	174	204
Melting Point, T_m (ºC)	-15	35	-10

3.2. Emulsification time

Emulsification time is important in this optimization study as emulsification is a process of mixing two immiscible liquids [18]. Time taken for emulsification has a great influence on performance and the stability of ELM. Thus, the effect of emulsification time was investigated from 3 to 15 minutes with an interval of 3 minutes.

Based on Figure 2, the extraction efficiency recorded has continuously increased as the emulsification time increases from 3 minutes to 15 minutes. It is because, at a sufficient emulsification time, a stable and homogenized emulsion is produced. Based on the figure, the maximum extraction efficiency was recorded at 97.61 % by Aliquat 336|Ammonia. It was then followed by ToA|Ammonia at 75.31 %, ToA|NaCl at 67.38% and Aliquat 336|NaCl at 58.44%. As reported by Ahmad, Kusumastuti [19], a stable emulsion in removing cadmium by using Aliquat 336 was obtained at 15 minutes of emulsification time with the lowest membrane breakage of 0.05 %. It was concluded that the increment of extraction efficiency over 15 minutes of emulsification time is due to ample time for exposure which allowed the production of smaller aqueous internal phase droplets resulting in an enhanced homogeneity of the dispersed phase. As stated by Dâas and Hamdaoui [16], the extraction efficiency increases also due to an increase in the emulsion stability as the emulsification time increase.

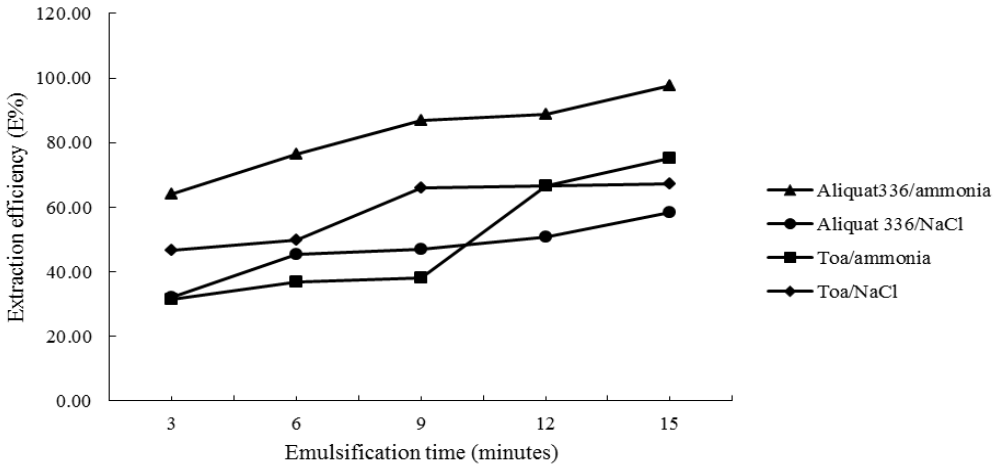

Fig. 2. ACTP extraction efficiency (E%) vs emulsification time (Experimental condition: [TOA] = 6 wt%; [Aliquat 336] = 6 wt%; [Span 80] = 6 wt%; Internal phase concentration = 0.1M; Membrane phase to Internal phase Ratio = 3:1; Diluent = sunflower oil).

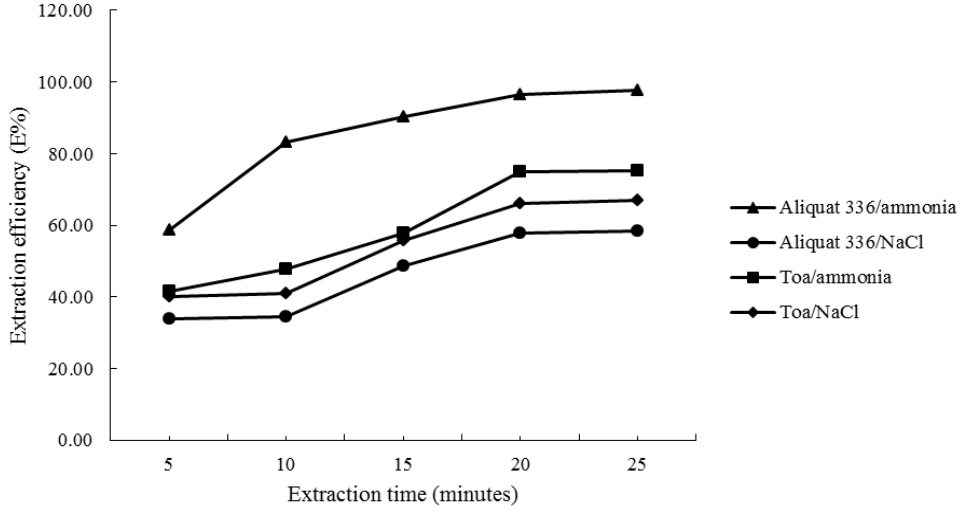

Fig. 3. ACTP extraction efficiency (E%) vs extraction time (Experimental condition: [TOA] = 6 wt%; [Aliquat 336] = 6 wt%; [Span 80] = 6 wt%; Emulsification time = 15 minutes; Internal phase concentration = 0.1M; Membrane phase to Internal phase Ratio = 3:1; Diluent = sunflower oil).

Low extraction efficiency was observed at low emulsification time at 3 minutes because of the enormous internal droplets formed which inhibits the transfer area of solute [20]. It is discovered that the lowest extraction efficiency was attained by ToA|Ammonia at 31.49 %, followed by Aliquat 336|NaCl at 31.99%, ToA|NaCl at 46.72% and Aliquat 336|Ammonia at 64.23%. The extraction efficiency is low at shorter emulsification time because it is not enough to homogenize the emulsion thus membrane solution unable to cover the internal phase completely resulting in poor extraction efficiency. Nevertheless, theoretically, lengthening the emulsification time would cause an excessive amount of fine droplets which causes facilitated coalescence and bigger emulsion. As carried out by Djenouhat, Hamdaoui [21], excessive emulsification time-triggered emulsion coalescence.

Optimal emulsification for the carriers was found to be at 15 minutes of emulsification time for all of the pairing. Therefore, 15 minutes of emulsification time was used for the subsequent studies.

3.3. Extraction time

Time taken for the emulsion to be stirred by mechanical stirrer is referred as extraction time. Optimization of extraction time is important to obtain a high extraction efficiency. The effect of extraction time to extraction efficiency was done at a time variation of 5, 10, 15, 20, and 25 minutes.

Based on Figure 3, E% increases as the extraction time increases. In other words, the greater the extraction time, the higher the extraction efficiency. The highest E% was achieved at a value of 97.61 %, 75.31 %, 66.88 % and 58.44 % for Aliquat 336|Ammonia, ToA|Ammonia, ToA|NaCl and Aliquat 336|NaCl respectively. It is noted that the extraction efficiency increases gradually with extraction time. This is because more solute will be extracted from the feed solution due to the increase in the total mass transfer area. However, further extension of the time resulted in a constant or plateau efficiency.

Similar results were reported by Zhao, Fei [22] on the residence time in the range of 5 to 35 minutes. They concluded that at 5 minutes of extraction time, the system was able to transfer about 78% of cadmium while at higher extraction efficiency of 15 minutes, more than 99% of cadmium was removed. Besides that, Djenouhat, Hamdaoui [21], found a low extraction efficiency of less than 50% was achieved in 1 minute. The efficiency increases gradually with time before reached equilibrium at 9 minutes with an efficiency of 96%. Extending the extraction process resulted in the same efficiency. Chiha, Samar [23], also found that the extraction efficiency increased along the extraction time until 7 minutes. After 7 minutes, it was found that there was no significant increase in extraction efficiency. Therefore, the optimal extraction time using mechanical stirrer for the extraction of ACTP was found at 20 minutes.

3.4. Stirring speed

The main purpose of stirring is to produce W/O/W emulsions by dispersing W/O emulsion at different speeds for various contact times. Over the times, the external aqueous solution is sampled intermittently at different

time intervals to measure how much the ACTP is extracted from W/O/W emulsion.

The stirring speed was studied to determine the best extraction efficiency based on different carriers and internals phase used. Stirring speed is considered as one of the significant parameters that can improve the transport of ACTP from one phase to another phase by minimizing the boundary layers in the aqueous and organic phase [24]. Thus, the stirring speed was investigated by varying at 100 rpm, 200 rpm, 300 rpm, 400 rpm, and 500 rpm.

Figure 4 shows the extraction efficiency based on stirring speed for each carrier and stripping agent. Based on the figure, as the stirring speed increases, the extraction efficiency increases. Aliquat 336|Ammonia increases from 96.10% to 97.73% [100 rpm to 200 rpm], Aliquat 336|NaCl increases from 63.35% to 77.83% [100 rpm to 300 rpm], ToA|Ammonia increases from 59.70% to 60.23% [100 rpm to 200 rpm] and ToA|NaCl increases from 60.52% to 63.87% [100 rpm to 200 rpm]. This is because, as the stirring speed increases, the interfacial area and mass transfer also increases. This is due to enough shear which reduce the membrane layer thickness resulting in a shorter transportation path [25]. Similar results were found by [26] for aniline removal. Increasing stirring speed can enhance mass transfer of solute thus increase the extraction efficiency.

However, further, an increase in stirring speed decrease the extraction efficiency as it is detrimental towards membrane stability. The extraction efficiency was reduced to 36.65%, 62.97%, 28.72% and 25.57% for Aliquat 336|Ammonia, Aliquat 336|NaCl, ToA|Ammonia and ToA|NaCl respectively. The decrement is because when stirring speed is increased above a critical value, it influences emulsion stability and also causes the extraction efficiency to reduce considerably [27]. In other words, excessive shear causes membrane breakage which is due to unstable emulsion and leakage of internal dispersed phase to external phase. The breakage of membrane transferred back the captured solute in the emulsion to the external phase. This phenomenon was also faced by other researchers when using excessive stirring speed. Extremely high stirring speed could induce the coalescence and breakdown of the emulsion globules. Thus, the optimum stirring speed on average is at 200 rpm where the carriers and stripping agents achieve the highest extraction efficiency.

3.5. Extraction efficiency

The optimized parameters of each study are summarized and tabulated as shown in Table 2 while Figure 5 shows the extraction efficiency achieved by the studied carriers and stripping agents using the optimized parameters that were conducted throughout the study.

Table 2
Summary of the optimized parameter in this study.

Type of Parameter	Optimized Parameters
Diluent Compatibility	Sunflower Oil
Emulsification time	15 minutes
Extraction Time	20 minutes
Stirring Speed	200 rpm

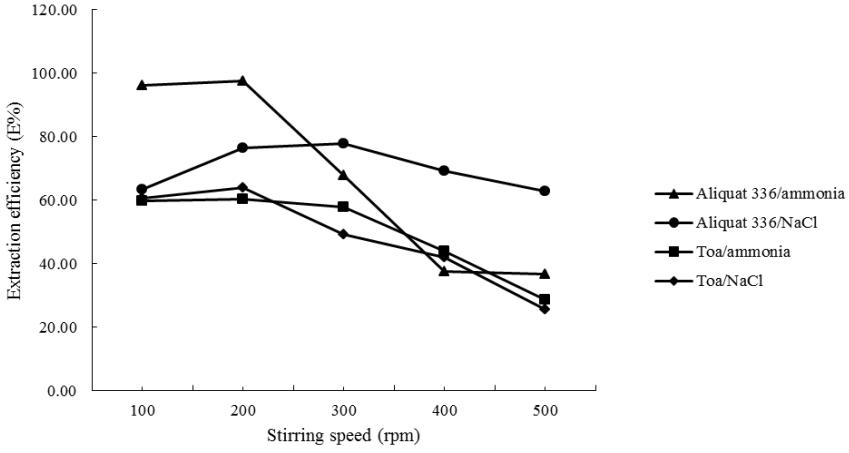

Fig. 4. ACTP extraction efficiency (E%) vs stirring speed (Experimental condition: [TOA] = 6 wt%; [Aliquat 336] = 6 wt%; [Span 80] = 6 wt%; Emulsification time = 15 minutes; Extraction time = 20 minutes; Internal phase concentration = 0.1M; Membrane phase to Internal phase Ratio = 3:1; Diluent = sunflower oil).

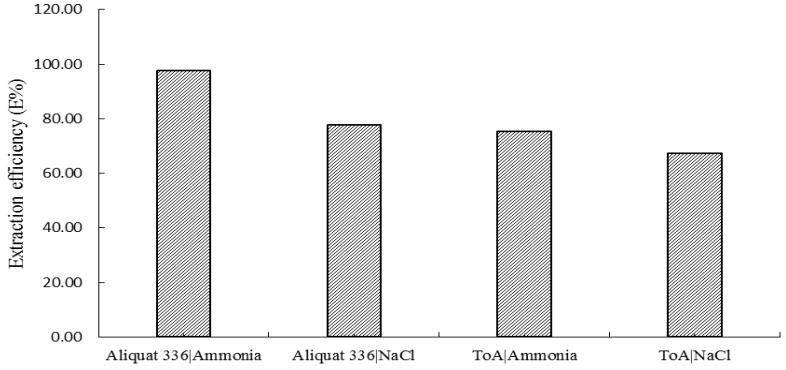

Fig. 5. The extraction efficiency (E%) based on the optimized parameters (Experimental condition: [TOA] = 6 wt%; [Aliquat 336] = 6 wt%; [Span 80] = 6 wt%; Emulsification time = 15 minutes; Extraction time = 20 minutes; Stirring speed = 200 rpm; Internal phase concentration = 0.1M; Membrane phase to Internal phase Ratio = 3:1; Diluent = sunflower oil).

The type of carriers used in this study is Aliquat 336 and ToA while the stripping agents used are Ammonia and NaCl. These carriers and stripping agents were compared to determine the best ELM formulation using vegetable oil-based diluent for ACTP extraction. Based on Figure 5, the highest extraction efficiency was attained by Aliquat 336|Ammonia with an extraction efficiency of 97.73 %, followed by Aliquat 336|NaCl at 77.83%, ToA|Ammonia at 75.31 % and ToA|NaCl at 67.38%. Aliquat 336 gives a better extraction efficiency based on the overall results of extraction time compared to ToA. The acidic solution of the external phase causes the extraction efficiency of Aliquat 336 better than ToA. This is because, in acidic solution, Aliquat 336 has low solubility as reported by Xu, Paimin [28], resulting in fewer losses of carriers into the feed phase. Thus, Aliquat 336 can achieve better extraction efficiency compared to ToA [28]. For the stripping agents, ammonia shows a convincing result compared to NaCl for the internal phase as most of the ELM system by both carriers achieve high extraction efficiency. This condition might be conceivable because of higher stripping reaction. The ACTP ion was discharged from ACTP complex by the OH^- ion of the basic internal phase solution compared to NaCl [29].

4. Conclusions

The incorporation of vegetable oils as the diluent in the formulation ELM was discovered and explored as their compatibility with each carrier was carried out in this study. Based on the result, sunflower oil which has the lowest viscosity is chosen for both Aliquat 336 and ToA as their compatibility with sunflower oils are better than canola and palm oils. The optimal operating conditions were found at 15 minutes of emulsification time, 20 minutes of extraction time and 200 rpm of stirring speed. With that, the highest extraction efficiency achieved for removal of ACTP is by using Aliquat 336 as carrier and ammonia as the internal phase. The ELM was capable to effectively remove 97.73% of ACTP from aqueous solutions.

Acknowledgments

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