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Emulsion Liquid Membrane for Pesticides Removal from Aqueous Solution: Emulsion Stability, Extraction Efficiency and Mass Transfer Studies

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Abstract

The current study investigated the stability and the extraction efficiency of emulsion liquid membrane (ELM) for Abamectin pesticide removal from aqueous solution. The stability was investigated in terms of droplet emulsion size distribution and emulsion breakage percent. The proposed ELM included a mixture of corn oil and kerosene (1:1) as a diluent, Span 80 (sorbitan monooleate) as a surfactant and hydrochloric acid (HCl) as a stripping agent without utilizing a carrier agent. Parameters such as homogenizer speed, surfactant concentration, emulsification time and internal to organic volume ratio (I/O) were evaluated. Results show that the lower droplet size of 0.9 µm and higher stable emulsion in terms of breakage percent of 1.12 % were formed at 5800 rpm of homogenizer speed, 4 v% of span 80 surfactant, 8 min of emulsification time and 1:1 (I/O) ratio while 86.4% of Abamectin pesticides were extracted under these conditions. Extraction kinetics and mass transfer study were also accomplished. The outcome of this study can be extended to the removal of other type of pesticides from water and wastewater.

Keywords: Emulsion liquid membrane, Pesticides, Stability, Extraction.

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1- Introduction

Pesticides are chemical compounds that are poor water solubility used for the control of pests. The constant population growth, changing lifestyle patterns, and technical improvement necessitate the usage of pesticides in significant quantities to meet the enormous demand for agricultural products in modern times. Because their use has resulted in soil pollution, excessive amounts of residual pesticides are now considered emergent contaminants [1]. Additionally, pesticides frequently leak from the location of their initial application into surrounding water bodies, causing secondary water contamination [2]. It is considered one of the main factors that cause death by self-poisoning. They are extremely poisonous and they spread quickly in the surroundings, creating chronic disease (World health organization) [3]. There are many traditional techniques used to sequestration of pesticides from wastewater such as, chemical oxidation [4], adsorption [5], revers osmoses membrane [6] and electrochemical process [7]. Many of these methods pose clear disadvantages, such as high energy consumption, low removal efficiency, high operation and capital cost. Membrane separation processes (MSPs) are energy-efficient and clean techniques for separating various types of liquids and gases, particularly in the chemical and petrochemical industries [8]. Among the various MSPs, liquid membranes (LMs) found much application in chemical engineering, chemistry, and environmental studies [9]. Bulk liquid membrane, emulsion liquid membrane, and supported liquid membrane are the three most common types of liquid membranes [10]. Recently, the emulsion liquid membrane has been given a considerable attention by a host of researchers for removing and recovering organic and inorganic contaminants from aqueous solutions due to its simplicity, high efficiency, easy operation, low operating cost, high flux and simultaneous extraction and stripping in one-step [11]. ELM are double water-in-oil-in–water emulsions (W/O/W) stabilized by employment of suitable surface-active agents. This system consists of organic solution (membrane phase), stripping solution (internal phase) and dispersed phase (external phase) [12]. ELMs are true double emulsions, an internal aqueous phase being spread as small droplets into oil phase, while the resulting emulsion is spread as large droplets into the external aqueous phase [13]. In spite of the various benefits, the applicability of ELM very restricted owing to several problems; one of them is emulsion instability. The term instability refers to breakage or swelling of an emulsion, which lowers the

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effectiveness of solute extraction and recovery [14, 15]. Emulsion breakage occurs during extraction process or before this process. In the ELM process, the resistance of liquid membrane for rupture during solute extraction under strong shear stress is known as emulsion stability. Membrane rupture also occurs when the pH of the external phase rises, allowing the internal phase to spill out into external phase [16].

Emulsion diameter is on of important factors affecting on emulsion stability [17]. Emulsification process and membrane composition play an essential part in emulsion stability related with the droplet size of the emulsion. Large diameter of droplet product the poor stability and low extraction efficiency [18, 19]. Surfactant concentrations, emulsification time, internal to organic volume ratio and homogenizer speed, are the main factors affecting emulsion stability. A carrier agent is utilized in various liquid membrane technologies to assist the transfer of the target species, which imposing extra cost [20]. The conventional diluents used in emulsion liquid membrane systems are primarily made up of organic solvents derived from petroleum (diluents) kerosene [12, 21] hexane [22, 23], heptane [24, 25], which are flammable, volatile, toxic, and non-biodegradable. In addition, these materials could be extremely expensive due to restricted resources. To overcome these problems, replacement of the classical petroleum-based organic diluents with greener materials such as vegetable oil-based organic diluents, which is easily obtainable and might include surface active compounds that can enhance emulsion stability [26].

To date, investigating the stability of ELM employing a combination of kerosene and corn oil in the presence of span 80 as surfactant and using this membrane to remediation of Abamectin pesticide from an aqueous solution has not been studied. Therefore, the current research aims to investigate its impact of the surfactant concentration, emulsification speed, emulsification time, internal to membrane (I/O) phase ratio on the emulsion droplets and membrane stability. Additionally, extraction efficiency of Abamectin pesticides without using extractant (carrier agent) was studied.

2- Materials and Methods

2.1. Materials

Corn oil (density=0.92g/ml, molcular wieght= 882 g/mol) obtained from a local market and kerosene (density=0.81g/ml, molcular wieght=170 g/mol) supplied from Iraq southren oil company were used as diluent and they are insoluble in water. Span 80 and hydrochloric acid (HCl 35% purity) were used as the surfactant and the internal agent respectively. The external aqueous solution was produced by mixing distilled water with the Abamectin pesticide.

2.2. Preparing the water in oil (W/O) emulsion

A high-speed homogenizer was used to prepare the emulsion in a 100 mL beaker flask. The liquid membrane phase was prepared by dissolving suitable amount of Span 80 in the diluent (corn oil and kerosene). 0.25 M HCl solution acting as internal phase, was added drop by drop to oil phase and blended with a high-speed homogenizer at a specific emulsification time. The W/O emulsion droplet diameters were measured directly after formation using the Olympus optical microscope (Nikon eclipseme 600) equipped with a digital camera (DXM1200 F). Sauter mean diameter d32 is calculated according to Eq. 1 below [19].

$$d32 = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} = 6\frac{V}{A} \quad (1)$$

Where d_i and n_i are the diameter and numbers of drops fitting to the ith class. V and A are the volume and total area of dispersed phase respectively.

2.3. Stability Study

Emulsion was added to 50 ppm Abamectin aqueous solution. A mixer was used to agitate the system at 250 rpm during 15 minutes, then samples of the aqueous solution (external phase) were taken for measurement of Abamectin concentration and pH. Membrane breakage B (%) was calculated using Eq. 2 below [27, 28].

$$B(\%) = \frac{V_I}{V_{IO}} \times 100\% \quad (2)$$

Where V_{IO}: initial volume of the internal phase and V_I: volume of internal phase that dripped into feed phase, which is evaluable using Eq. 3 below.

$$V_I = V_F \frac{10^{-pH_{IF}} - 10^{-pH_F}}{10^{-pH_F} - [H_{IO}^+]} \times 100 \quad (3)$$

Where V_F is a volume of initial feed phase, $pH_{IF}$is a pH of initial feed phase, $pH_F$is the pH of feed phase after the mixing time, while $[H_{IO}^+]$: proton concentration in internal phase.

2.4. Extraction Study

The extraction investigation was conducted by determining the removal efficiency of Abamectin from feed phase by using Eq. 4 below.

$$E\% = \frac{C_{IN} - C_{OUT}}{C_{IN}} \times 100\% \quad (4)$$

Where C_{IN}: initial concentration of Abamectin in external phase, and C_{OUT}: the post- extraction Abamectin concentration in external phase. The concentration of Abamectin in the solution was determined by a UV-visible spectrophotometer at the wave length of 210 nm. Fig. 1 represents the sequence of ELM process.

Unless otherwise stated the experimental condition of the emulsion liquid membrane as given in Table 1.

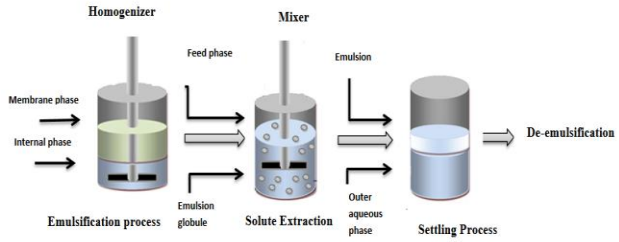

Fig. 1. Sequence of ELM Process

Table 1. Experimental Condition for ELM

External phase	
pH	7
Volume (ml)	250
Abamectin concentration (ppm)	50
External to emulsion phases ratio (treat ratio)	5:1
Organic solution	
Volume (ml)	25
Diluent	1:1 corn oil to kerosene
Span 80 (v%)	4
Emulsification time (min)	8
Homogenizer speed (rpm)	5800
Extraction speed (rpm)	250
Extraction time (min)	15
Internal phase	
Volume (ml)	25
[HCl] (M)	0.25

3- Results and Discussion

3.1. Effect of Span 80 Concentration

Surfactant is one of essential compound that is influence on stabilizing the emulsion as decrease the interfacial tension between oil and water phases. A surfactant was introduced to act as a barrier between the two miscible phases, thereby, inhibiting emulsion breaking. By changing the surfactant concentration at 2, 4, 6, and 8 (%v/v), the effect of surfactant concentration on droplet size, membrane rupture, and extraction efficiency was investigated. The results are plotted in Fig. 2 and Fig. 3 respectively, from Fig. 2 it can be seen that at low surfactant concentration 2 (%v/v), the droplet diameters of (W/O) emulsion is 1.6 µm, that is lead to high interfacial tension of oil-water because of low concentration from surfactant, the membrane interface is not completely covered leading to the difficult dispersion of emulsion droplet and occur coalescence of small droplet lead to bigger emulsion droplets formed [29]. As the concentration increased to 4 (%v/v) the droplet diameter decreased from 1.6 µm to 0.9 µm and hence breakage percent from 3.17% to 1.12% and extraction efficiency of about 86.4% was achieved compared to 71.6% with 2 (%v/v) of surfactant concentration. That because of increasing the surfactant concentration gradually reduced membrane surface tension, resulting in larger contact area [30]. Furthermore, increase in span 80 concentrations beyond 4 (%v/v) up to 8 (%v/v) led to increase droplet diameter and breakage percent from 0.9 µm to 1.36 µm and from 1.12% to 2.1% respectively. The explanation of this behavior is that the excess of surfactant adsorbed onto the surface of emulsion droplets, which led to droplets coalescence [31]. Ahmad et al., [32] noticed same behavior. Alternatively, Abamectin extraction efficiency fallen from 86.4 % to 62% with an increase in surfactant concentration from 4 v% to 8 v%. This decrease could be attributed to the high mass transfer impedance of Abamectin transport at the internal–oil contact.

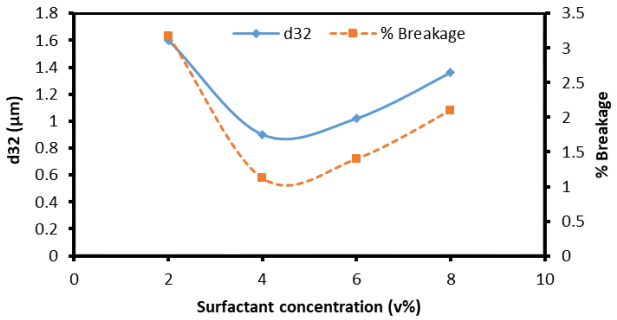

Fig. 2. Effect of Span 80 Concentration on Emulsion Diameter and Membrane Breakage (emulsification time= 8 min, I/O= 1:1, homogenizer speed= 5800 rpm, 0.25 M HCl)

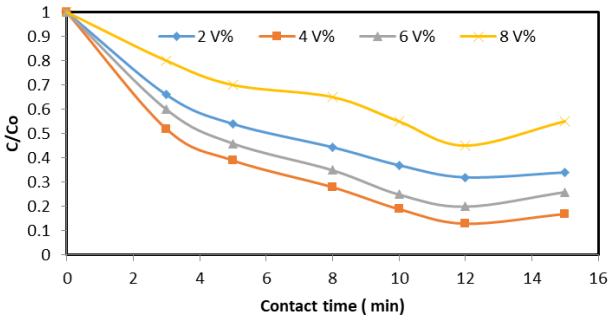

Fig. 3. Effect of Surfactant Concentration on Extraction of Abamectin (homogenizer speed= 5800 rpm, emulsification time= 8min, mixing speed of feed solution= 250 rpm, 0.25 M HCl internal phase, I/O= 1:1, pH=7)

3.2. Effect of emulsification speed

Emulsification speed represents one of essential factors having a signification effects on droplets size, emulsion stability and so on the extraction efficiency. To investigate the impact of homogenizer speed to droplet size and emulsion breakage, homogenizer speed was examined in the range from 3000 rpm to 19700 rpm. Fig. 4 shows that the sauter mean diameter (d32) and the breakage percent decreased from 2.3 µm to 0.9 µm and from 10% to 1.12% respectively as the homogenizer speed increased from 3000 to 5800 rpm. As internal phase droplets become smaller, it takes significantly longer time to coalesce, resulting in low breakage and hence good stability. The lack of homogeneity in the shape and size of the droplets in an emulsion might contribute to emulsion instability. Low energy yields low disruptive forces, for breaking up (oil/water) phases mechanically into smaller drops thus inhibiting the stirring ability to disperse oil

drops resulting in bigger emulsion drops [33]. Using high stirring speeds produce fine droplets with a greater surface area, increasing the interfacial area of the feed solution and the emulsion liquid membrane and thereby increasing membrane stability. Similar performance was also observed by Kumbasar and Tutkun [34]. Further increase of homogenizing speed at 12700 rpm, the droplets diameter and breakage percentage increased to 1.13 µm and 3.5% respectively. This behavior could be attributed to the ostwaled ripening phenomena caused by coalescence, which results in an oiling – off process, which produces emulsion breakdown. Furthermore, blending surfactant quickly may result in it separating from the water-oil interface [33]. Fig. 5 shows an optical microscopy image of emulsion at various homogenizer speeds. The efficiency of extraction improved from 56.4% to 86.4% as the homogenizer speed increased from 3000 to 5800 rpm within 12 min contact time as shown in Fig. 6. This is due to an increase in the mass transfer area which is enhanced the rate of mass transfer through extraction system. Further increase in the homogenizer speed at 12700 rpm resulted decline in the extraction efficiency owing to the rupture of the membrane, because of the quick coalescence of droplets made the film layers unable to withstand the impact force, causing the emulsion breakage. Suleiman et al., [35], observed similar behavior. At high homogenizing speed of 19700 rpm, a thick emulsion and emulsion is formed containing big emulsion droplet which reduces the emulsion stability. This might be because little drops agglomerate quickly, increasing their volume and forcing the emulsion to separate. As a result, since the emulsifier has a propensity to destabilize and break easily, high homogenizer speed is not necessary.

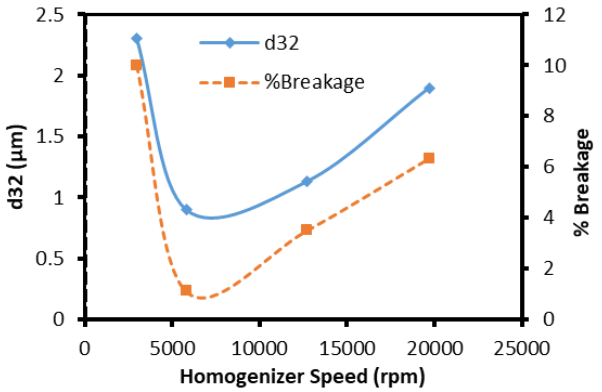

Fig. 4. Effect of Homogenizer Speed on Emulsion Diameter and Membrane Breakage (span 80= 4 v%, emulsification time =8 min , 0.25M HCl, I/O =1:1)

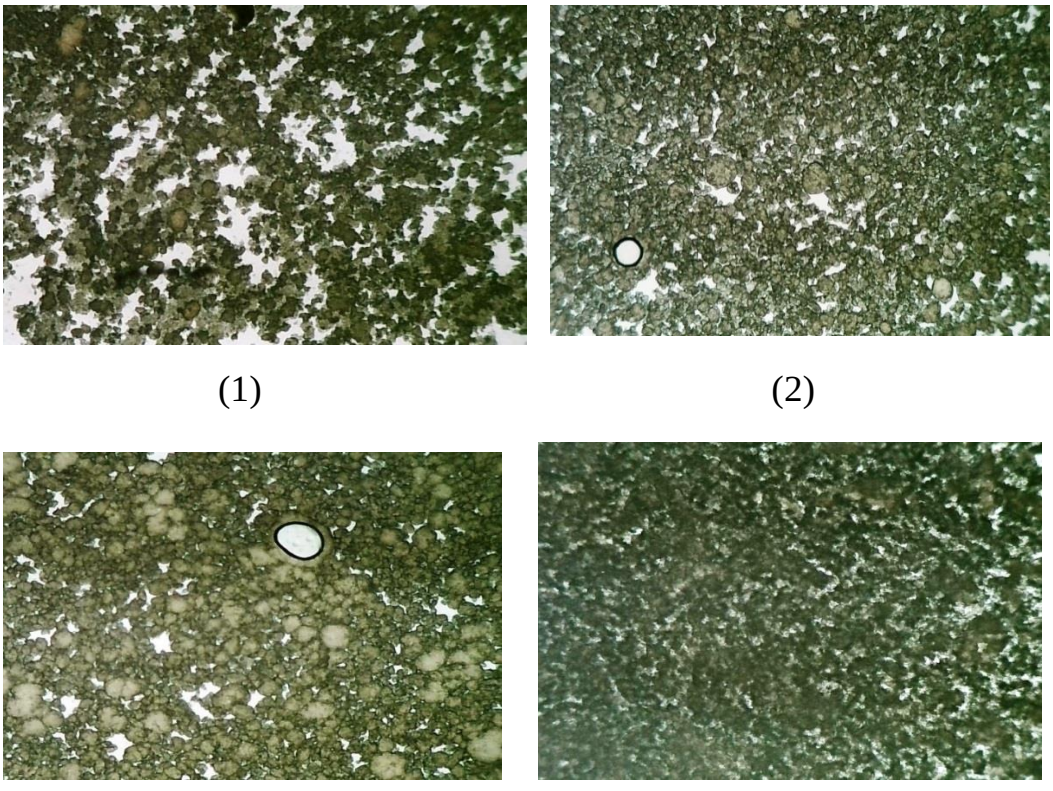

Fig. 5. Microscopic Images of the Emulsion at (1) 3000 rpm, (2) 5800 rpm, (3) 12700 rpm, (4) 19700 rpm

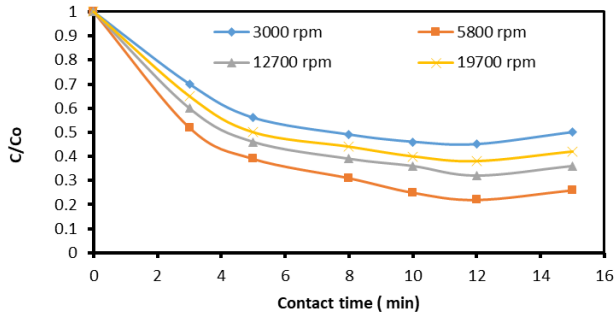

Fig. 6. Effect of Homogenizer Speed on Extraction of Abamectin (emulsification time = 8 min, mixing speed of feed solution= 250 rpm, 0.25 M HCl internal phase, I/O= 1:1, pH=7, span80 = 4 v %)

3.3. Effect of emulsification time

The effect of different emulsification time range 4 to 12 minutes on the droplet emulsion diameter, breakage percent and extraction efficiency were investigated keeping other parameters constant. As presented in Fig. 7 the lower sauter mean diameter of 0.9 µm and the lower breakage of 1.12% were obtained for an emulsification time of 8 min. For insufficient emulsification time 4 and 6 minutes, the droplet have a large size of 2.8 µm and 1.8 µm respectively and the breakage was great at 9.8% and 4.5 % for 4 and 6 minutes emulsification time respectively, this may be related to the lack of homogeneity which, resulted in droplet coalescence. Caouchi and Hamdaoui [36] and Salahshoori et al., [37] observed a higher breakage of the emulsion with the lower emulsification time. In contrast, a further increase in emulsification time above 8 min led to increase the droplet emulsion diameter and hence reduce the emulsion stability. As shown in Fig. 7 the emulsion droplets increase to 1.2 µm and 1.7 µm and so the breakage percent increased to 1.4% and 2.2% with increasing emulsification time to 10 and 12 minutes respectively. Longer emulsifying time increases the shear stress and interfacial tension due to high homogenization pressure [38]. The effect of emulsification time on the extraction efficiency was investigated and the results are plotted in Fig. 8. This figure shows that only 56 % Abamectin removal efficiency from aqueous solution at 4 min was achieved, whereas the extraction efficiency rose up to 86.4% at 8 min emulsification time due to decrease in the droplet emulsion size and so increased the stability of the emulsion and this enhanced the homogeneity of the dispersed phase. A significant decreased in the extraction efficiency from 76.5 % to 63 % as the emulsification time increased from 10 min to 12 min particularly due to the coalescence of the internal phase droplets. On other hand, for the emulsification time less than 8 min, the extraction efficiency dropped to 65 % and 56 % at 6 min and 4 min emulsification time respectively. This reduction in the extraction efficiency, mainly due to the coalescence of the internal phase droplets. Based on these results 8 min of emulsification time was considered for all experiments.

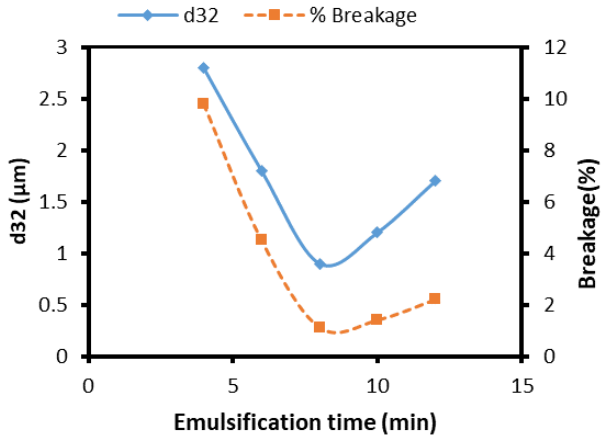

Fig. 7. Effect of Emulsification Time on Emulsion Diameter and Membrane Breakage (span 80 = 4 v%, I/O= 1:1, 0.25M HCl, homogenizer speed =5800 rpm)

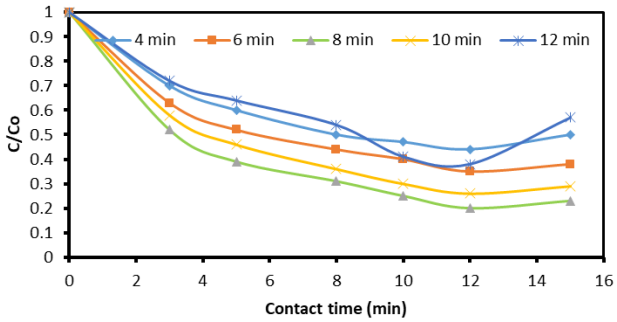

Fig. 8. Effect of Emulsification Time on Extraction of Abamectin (homogenizer speed= 5800 rpm, span80 concentration = 4 v%, mixing speed of feed solution = 250 rpm, 0.25M HCl internal phase, I/O= 1:1, pH=7)

3.4. Effect of internal to membrane phase ratio (I/O)

Volume ratio of internal aqueous phase to membrane phase has a significant effect on emulsion droplet diameter, breakage percent and hence on the extraction efficiency in the emulsion liquid membranes. The influence exerted by the ratio of the internal phase to the membrane phase on the sauter mean diameter, stability and extraction efficiency were studied at five different volume ratios (1:3, 1:2, 1:1, 2:1, 3:1). The results are presented in Fig. 9 for emulsion droplet diameter and breakage percent, while the effect of internal to membrane phase volume ratio on the extraction of the Abamectin is plotted in Fig. 10. From Fig. 9 it can be seen that the lower droplet diameter (0.9 µm) and higher emulsion stability in term of lower breakage percent (1.12 %) were obtained at equal ratio of the internal to membrane phases. Decreasing the volume ratio of the internal to membrane phase from 1:2 to 1:3 led to increasing the droplet diameter and breakage percent from 1.5 µm to 1.8 µm and from 6% to 8% respectively. This behavior is due to too much membrane solution led to produce thicker and more viscous emulsion wall which obstructs the internal phase from diffusing in. Similar trend was observed by Mohammed et al., [25]. On other hand, a high volume ratio could not encapsulate the

internal phase droplets, thus producing 1.3 µm and 2.1 µm droplet diameters at 2:1 and 3:1 volume ratio respectively and increasing the breakage percent to 5.3 % and 13 % respectively. Therefore, this resulted in the formation of a thinner membrane layer that adversely impacted the membrane stability. From Fig. 10 it can be seen that the maximum extraction efficiency was reached within phase ratio of 1:1. While the extraction efficiency dropped to 64 % and 51 % with decreasing the volume ratio to 1:2 and 1:3 respectively. This decrease in the extraction efficiency is due to less stripping agent available to re-extract the solute. Conversely increasing the volume of the internal to membrane phase above 1:1 results in a noticeable decline in the extraction efficiency from 86.4 % at equal volume to 77.2 % and 60 % at volume ratio of 2:1 and 3:1 respectively. This may be due to an increase of the droplets diameter, which in turn decreases the interfacial contact area between the feed solution and the emulsion and thereby decreases the extraction efficiency. In addition, the volume of membrane solution is not enough for enclosing all the stripping solution at higher volume ratio [39]. The same trend was observed by Daas and Hamdaoui [40]. Therefore, the value of 1/1 volume ratio of internal phase to membrane phase has been selected.

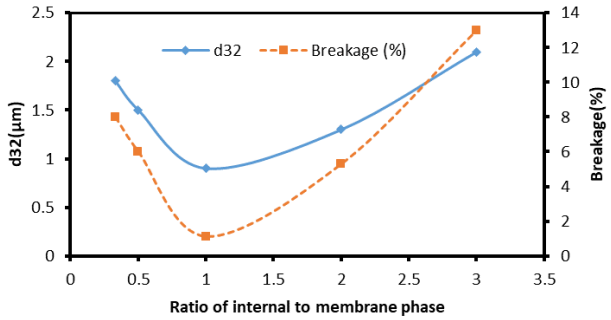

Fig. 9. Effect of I/O Phase Ratio on Emulsion Diameter and Membrane Breakage (span 80 = 4 v%, 0.25M HCl, emulsification time =8min. homogenizer speed =5800 rpm)

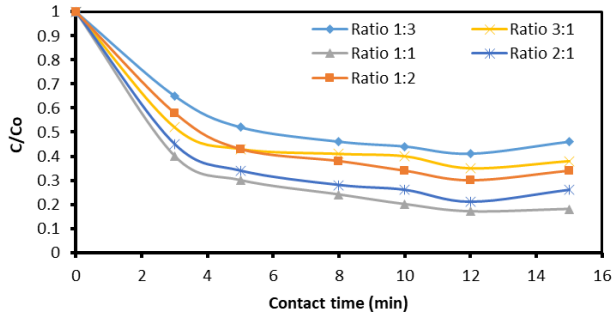

Fig. 10. Effect of I/O Phase Ratio on Extraction of Abamectin (homogenizer speed =5800 rpm, emulsification time= 8 min, mixing speed of feed solution =250 rpm, 0.25M HCl internal phase, pH=7, span 80 = 4 v %)

4- Estimation of the Abamectin Extraction Kinetics and Mass Transfer Coefficient

Abamectin kinetic extraction by ELM process was estimated in Eq. 5 as a first order rate [41, 42].

$$\ln\left(\frac{C_{t=t}}{C_{t=0}}\right) = -K_{obs}.t \quad (5)$$

Where K_{obs}: extraction rate constant (min^{-1}), t: indicating the extraction time (min), The slope of the straight line formed by $\ln(\frac{C_{t=t}}{C_{t=0}})$ and t, obtained on value of $K_{obs} = 0.236\ (min^{-1})$.

Eq. 6 represents the overall mass transfer coefficient for the ELM system [43].

$$\frac{1}{K_o} = \frac{1}{K_m} + \frac{1}{K_f} \quad (6)$$

Where K_o: represents the ELM overall mass transfer coefficient, K_m: represents mass transfer coefficient of external phase (m/s) was estimate by Eq. 7 below [41].

$$\frac{K_m}{\sqrt{ND}} = 2.932 \times 10^{-7} . \frac{(V_I+V_M)}{(V_I+V_M+V_E)} . \left(\frac{d_i}{d_{ii}}\right)^{0.548} Re^{1.371} \quad (7)$$

Feed phase mixing speed is N, diameters of mixing tank and impeller respectively are d_{ii}, d_i , volumes of external, internal and membrane phases respectively are V_E , V_I , V_M .

$$Re = \frac{N\, d_i^2 \rho_E}{\mu_E} \quad (8)$$

Re, was computed using Eq. 8, and the result is (3666.29). D: solute diffusivity in the organic phase and calculated by Eq. 9 below [44], which is found equal to $2.1\times 10^{-11} m^2/s$.

$$D = \frac{117.3 \times 10^{-18} .(\varphi M_w)^{0.5}. T}{\mu_{o.}\, \emptyset_c^{0.6}} \quad (9)$$

Where M_w: average diluent molecular weight (526 Kg/ Kmol), φ: diluent association factor (1). T: ambient temperature (298 K). μ_o: organic phase viscosity (0.0417 Kg/m.s). $\emptyset_c$: Abamectin molar volume ($0.862 m^3$/Kmol), K_f: interfacial reaction rate constant (m/s) estimated by using Eq. 10 below.

$$\ln\left(\frac{C_{t=t}}{C_{t=0}}\right) = -A\, K_f.t \quad (10)$$

On comparing Eq. 10 with Eq. 5, K_f can be identified through Eq. 11.

$$K_f = \frac{K_{obs}}{A} \quad (11)$$

Where A: emulsion specific interfacial area, calculated using Eq. 12 [45].

$$A = \frac{Ai}{V} = \frac{6\alpha}{d_{32}} \quad (12)$$

The calculated values of K_f, K_m and K_o are tabulated in Table 2 below.

Table 2. Values of K_f, K_m and K_o

Mass transfer coefficient (m/s)	Value
K_m	1.15×10^{-7}
K_f	3.54×10^{-8}
K_o	2.71×10^{-8}

5- Conclusions

In this work, the feasibility of using a mixture of green organic solvent (Corn oil) and petroleum based organic solvent (Kerosene) in the volume ratio 1:1 as diluent in emulsion liquid membrane for the removal of Abamectin pesticides from wastewater was investigated. The effect of various parameters on droplet emulsion diameter, emulsion breakage and hence on the Abamectin extraction has examined and results showed that increasing the homogenizer speed from 3000 rpm to 5800 rpm decreased the sauter mean diameter and the breakage percent from 2.3 µm to 0.9 µm and 10% to 1.12% respectively. While increasing the speed above this value resulted in an increase in the sauter mean diameter up to 1.13 µm and 1.9 µm and the breakage percent to 3.5% and 6.3% for 12700 rpm and 19700 rpm respectively. This has an adverse effect on Abamectin extraction efficiency. The effect of emulsification time showed that with increasing time from 4 min to 8min, the emulsion stability increased as the sauter mean diameter and the emulsion breakage decreased from 2.8 µm to 0.9 µm and 9.8% to 1.12% respectively. Increasing span 80 from 2 v% to 4 v% enhanced the emulsion stability and hence extraction efficiency. While concentration above 4 v% had adverse effect on extraction efficiency, mainly due to the increasing of viscosity of the membrane and lead to mass transfer resistance. The effect of internal to organic volume ratio showed that with increasing the ratio up to 1:1, the emulsion breakage and droplet diameter decreased and the extraction efficiency enhanced while further increased in this ratio, the stability of emulsion decreased and hence Abamectin extraction efficiency decreased. Finally, lower emulsion droplet diameter 0.9 µm and breakage percent of 1.12 % and higher extraction efficiency 86.4% from the aqueous solution in optimal operational condition, 5800 rpm homogenizer speed, 4 v% Span 80 concentration, 8 min emulsification time and 1:1 internal to organic volume ratio. It can be calculated that emulsion liquid membrane using a mixture of green and petroleum based organic diluents could be a promising option for pesticides removal from aqueous solution.

References

[1] S.Yavari, A. Malakahmad, N.B. Sapari, and S. Yavari, "Sorption-desorption mechanisms of imazapic and imazapyr herbicides on biochars produced from agricultural wastes", *Journal of Environmental Chemical Engineering*, 4(4), 3981-3989, 2016, https://doi.org/10.1016/j.jece.2016.09.003

[2] J.O. Ighalo, A.A. Adelodun, A.G. Adeniyi, and C.A. Igwegbe, "Modelling the Effect of sorbate –sorbent Interphase on the Adsorption of pesticideses and Herbicides by Historical Data Design", *Iranian Journal of Energy and Environment*, 11(4), 253-259, 2020, https://dx.doi.org/10.5829/ijee.2020.11.04.02

[3] A. Belguet, S. Dahamna, A. Abdessemed, K. Ouffroukh, and A. Guendouz, "Determination of abamectin pesticide residues in green pepper and courgette growing under greenhouse conditions (Eastern of Algeria –setif)", *EurAsian Journal of BioSciences*, 13(2),1741–1745, 2019.

[4] W. Lu, W. Chen, N. Li, M. Xu, and Y. Yao, "oxidative removal of 4-nitrophenol using activated carbon fiber and hydrogen peroxide to enhance reactivity of metallophthalocyanine", *Applied Catalysis B: Environmental*,87(3–4),146–151,2009, https://doi.org/10.1016/j.apcatb.2008.08.024

[5] J.A. Rodriguez-Liebana, A. Lopez-Galindo, C. Jiménez de Cisneros, A. Galves, M. Rozalen, R. Sanchez-Espejo, E.Caballero, and A. Pena, "Adsorption/desorption of fungicides in natural clays from southeastren Spain", *Applied Clay Science*, 132-133, 402–411, 2016, https://doi.org/10.1016/j.clay.2016.07.006

[6] A. Mukherjee, R. Mehta, S. Saha, A. Bhattacharya, P. K. Biswas,and R. K. Kole, "Removal of multiple pesticide residues from water by low-pressure thin-film composite membrane", *Applied Water Science*. 10,1–8, 2020, https://doi.org/10.1007/s13201-020-01315-y

[7] N. Modirshahla, M.A. Behnajady, and S. Mohammadi-Aghdam, "Investigation of the effect of different electrodes and their connections on the removal efficiency of 4-nitrophenol from aqueous solution by electrocoagulation", *Journal of Hazardous Materials*. 154 (1-3), 778–786, 2008, https://doi.org/10.1016/j.jhazmat.2007.10.120

[8] M.Takht Ravanchi, T. Kaghazchi, and A.Kargari, "Application of membrane separation processes in petrochemical industry: a review", *Desalination*, 235(1-3),199–244, 2009, https://doi.org/10.1016/j.desal.2007.10.042

[9] P. Kaghazchi, T. Jacob, , H.Wang, W.Chen, and T. E. Madey," First-principles studies on adsorbate-induced faceting of Re (11 $\bar{2}$1)", *Physical Review B - Condensed Matter and Materials Physics*, 79(13),1–4, 2009, https://doi.org/10.1103/PhysRevB.79.132107

[10] H. E. Mahmoud, and A. A. AL-Hemiri, "Minimization of toxic ions in wastewater using emulsion liquid membrane technique", *Iraqi Journal of chemical and petroleum engineering*, V.11, No.1, 11- 19, 2010.

[11] A. A. Mohammed, and R. W. Al-Khateeb, "Application of Emulsion Liquid Membrane Using Green Surfactant for Removing Phenol from Aqueous Solution: Extraction, Stability and Breakage Studies", *Journal of Ecological Engineering*, 23(1), 305–314, 2022, https://doi.org/10.12911/22998993/143970

[12] H. M.Salman, and A. A. Mohammed," Removal of copper ions from aqueous solution using liquid surfactant membrane technique", *Iraqi Journal of chemical and petroleum engineering*, V.20 , No.3 ,31 – 37, 2019, https://doi.org/10.31699/IJCPE.2019.3.5

[13] K. Anarakdim, G. Gutiérrez, Á.Cambiella, O.Senhadji-Kebiche, and M.Matos, "The effect of emulsifiers on the emulsion stability and extraction efficiency of Cr(Vi) using emulsion liquid membranes (ELMS) formulated with a green solvent", *Membranes*. 10, 2020, https://doi.org/10.3390/membranes10040076

[14] A. L. Ahmad, A. Kusumastuti, C. J.C. Derek, and B. Ooi, "Emulsion liquid membrane for heavy metal removal: an overview on emulsion stabilization and destabilization", *Chemical Engineering Journal*, 171(3) 870–882, 2011, https://doi.org/10.1016/j.cej.2011.05.102

[15] R. M. Pfeiffer, "Leakage and swell in emulsion liquid membranes: experimental studies and corrected computational methods",*Colorado School of Mines ProQuest Dissertations Publishing,* 13884892, 2019.

[16] M. A. Hussein, A. A. Mohammed, and M. A. Atiya, "Application of emulsion and Pickering emulsion liquid membrane technique for wastewater treatment: an overview", *Environmental Science and Pollution Research*, (Vol. 26, Issue 36, pp. 36184–36204). Springer, 2019, https://doi.org/10.1007/s11356-019-06652-3

[17] Y. Wan, and X. Zhang," Swelling determination of W/O/W emulsion liquid membranes", *Journal of Membrane Science*, 196185–201, 2002, https://doi.org/10.1016/S0376-7388(01)00554-3

[18] A. L. Ahmad, , N. D. Zaulkiflee, A. Kusumastuti, and M. M. H. S Buddin,"Removal of Acetaminophen from Aqueous Solution by Emulsion Liquid Membrane: Emulsion Stability Study", *Industrial and Engineering Chemistry Research*, 58(2), 713–719, 2019, https://doi.org/10.1021/acs.iecr.8b03562

[19] N. D. Zaulkiflee, A. L. Ahmad, J. Sugumaran, and N. F. C. Lah, "Stability Study of Emulsion Liquid Membrane via Emulsion Size and Membrane Breakage on Acetaminophen Removal from Aqueous Solution Using TOA", *ACS Omega*, 5(37), 23892–23897, 2020, https://doi.org/10.1021/acsomega.0c03142

[20] A. Shokri, P. Daraei, and S. Zereshki, "Water decolorization using waste cooking oil: An optimized green emulsion liquid membrane by RSM", *Journal of water process engineering*, 33, 101021, 2020, https://doi.org/10.1016/j.jwpe.2019.101021

[21] N. S. Majeed and M. A. Mohammed, "Phenol Removal from Aqueous Solution Using Emulsion Liquid Membrane Process: Batch Experimental Studies" *Association of Arab Universities Journal of Engineering Sciences*, *24*(3), 135-149, 2017.

[22] L. Bahloul, F.Ismail, and M.E. H. Samar, "Extraction and de-extraction of cationic dye using an emulsified liquid membrane in an aqueous solution", *Energy procedia Journal*, 36, 1232-1240, 2013, https://doi.org/10.1016/j.egypro.2013.07.139

[23] M. A. Mohammed, W. O. Noori, and H. A. Sabbar,"Application of Emulsion Liquid Membrane Process for Cationic Dye Extraction". *Iraqi Journal of Chemical and Petroleum Engineering*, *21*(3), 39–44, 2020, https://doi.org/10.31699/IJCPE.2020.3.5

[24] M. Mesli, and N. E. Belkhouche, "Emulsion ionic liquid membrane for recovery process of lead. Comparative study of experimental and response surface design", *Chemical Engineering Research and Design*. 129,160–169, 2018, https://doi.org/10.1016/j.cherd.2017.11.011

[25] A. A. Mohammed, M. A. Atiya, and M. A. Hussein, "Simultaneous studies of emulsion stability and extraction capacity for the removal of tetracycline from aqueous solution by liquid surfactant membrane", *Chemical Engineering Research and Design*, 159,225–235, 2020, https://doi.org/10.1016/j.cherd.2020.04.023

[26] N. Jusoh, N.F.M. Noah, and N. Othman, "Double emulsion (water-in-oil-in-water) system in succinic acid extraction - a stability study", *Chemical Engineering Transactions*, 63-523–528, 2018, https://doi.org/10.3303/CET1863088

[27] R. Sabry, A.Hafez, M. Khedr, and A. El-Hassanin, "Removal of lead by an emulsion liquid membrane: part I", *Desalination.* 212, 165–175, 2007, https://doi.org/10.1016/j.desal.2006.11.006

[28] A. A. Mohammed, H. M .Selman, and G.Abukhanafer, "Liquid surfactant membrane for lead separation from aqueous solution: Studies on emulsion stability and extraction efficiency".*Journal of Environmental Chemical Engineering*, 6,6923–6930, 2018, https://doi.org/10.1016/j.jece.2018.10.021

[29] Zaulkiflee, N. D., Shah Buddin, M. M. H., and Ahmad, A. L. (2018). Extraction of Acetaminophen from Aqueous Solution by Emulsion Liquid Membrane Using Taylor-Couette Column. International Journal of Engineering, 31(8), 1413-1420.

[30] H. R. Mortaheb, M. H. Amini, F. Sadeghian, B. Mokhtarani, and H. Daneshyar, "Study on a new surfactant for removal of phenol from wastewater by emulsion liquid membrane", *Journal of Hazardous Materials*, 160-582-588, 2008, https://doi.org/10.1016/j.jhazmat.2008.03.095

[31] B. Abismail, J.P. Canselier, A.M. Wihelm, H. Delmas, and C.Gourdon, "Emulsification by ultrasound: drop size distribution and stability", *Ultrasonics Sonochemistry*, 6(1-2), 75 -83, 1999, https://doi.org/10.1016/S1350-4177(98)00027-3

[32] A. L. Ahmad, A. Kusumastuti, C. J. C.Derek ,and B. S.Ooi, "Emulsion liquid membrane for cadmium removal: Studies on emulsion diameter and stability", *Desalination*, 287, 30–34, 2012, https://doi.org/10.1016/j.desal.2011.11.002

[33] M. B. Rosly, N . Jusoh, N. Othman, H. A.Rahman, R. N. R. Sulaiman, and N. F. M. Noah, "Stability of emulsion liquid membrane using bifunctional diluent and blended nonionic surfactant for phenol removal", *Chemical Engineering and Processing - Process Intensification*, 148, 107790, 2020, https://doi.org/10.1016/j.cep.2019.107790

[34] R. A. Kumbasar, and O.Tutkun, "Separation of cobalt and nickel from acidic leach solutions by emulsion liquid membranes using Alamine 300 (TOA) as a mobile carrier", *Desalination*. 224, 201–208, 2008, https://doi.org/10.1016/j.desal.2007.04.088

[35] R. N. R. Suleiman, and N. Othman, N.A.S. Amin, "Recovery of ionized nanosilver by emulsion liquid membrane process and parameters optimization using response surface methodology", *Desalination and Water Treatment*, 57(8) - 3339-3349, 2016, https://doi.org/10.1080/19443994.2014.985724

[36] S. Chaouchi, and O. Hamdaoui, "Acetaminophen extraction by emulsion liquid membrane using Aliquat 336 as extractant", *Separation and Purification Technology*, 129 - 32– 40, 2014, https://doi.org/10.1016/j.seppur.2014.03.021

[37] I. Salahshoori, A. Seyfaee, A. Babapoor, and I. Cacciohi , "Recovery of manganese ions from aqueous solutions with cyanex 272 using emulsion liquid membrane technique: A design experment study", *Journal of sustainable metallurgy*,7(3), 1074–1090, 2021, https://doi.org/10.1007/s40831-021-00396-6

[38] Z. Y. Ooi, N. Othman, M. Mohamed, and R. Rashid, "Removal performance of lignin compound from simulated pulping wastewater using emulsion liquid membrane process", *International Journal of Global* 2014, https://doi.org/10.1504/IJGW.2014.061021

[39] R. S. Juang, and K. H. Lin, "Ultrasound assisted production of W/O emulsion in liquid surfactant membrane processes", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 238(1-3),43-49, 2004, https://doi.org/10.1016/j.colsurfa.2004.02.028

[40] A. Daas, and O. Hamdaoui ,"Extraction of bisphenol Afrom aqueous solutions by emulsion liquid membrane",*Journal of Membrane science*, 348(1-2), 360-368, 2010, https://doi.org/10.1016/j.jhazmat.2010.02.033

[41] M. Raji, M. E. M. Mekhzoum, D. Rodrigue, A.Qaiss el kacem,and R.Bouhfid, "Effect of silane functionalization on properties of polypropylene/clay nanocomposites",*Composites Part B: Engineering.* 146,106–115, 2018, https://doi.org/10.1016/j.compositesb.2018.04.013

[42] H. P.Kohli, S. Gupta, and M.Chakraborty, "Stability and performance study of emulsion nanofluid membrane: A combined approach of adsorption and extraction of Ethylparaben",*Colloids and Surfaces A: Physicochemical and Engineering Aspects*,579, 123675, 2019, https://doi.org/10.1016/j.colsurfa.2019.123675

[43] H. Kasaini, F. Nakashio, and M. Goto, "Application of emulsion liquid membranes to recover cobalt ions from a dual component sulphate solution containing nickel ions", *Journal of Membrane Science*, 146, 159–168 ,1998, https://doi.org/10.1016/S0376-7388(98)00105-7

[44] R. E. Treybal, "Mass – Transfer Operations, third ed., McGraw - Hill Book Company", *Malaysia*. ISBN-0-07-065176-0, 1980.

[45] V. Karcher, F. Perrechil, and A. Bannwart, "Interfacial energy during the emulsification of water-in-heavy crude oil emulsions", *Brazilian Journal of Chemical Engineering*,32, 127–137, 2015, https://doi.org/10.1590/0104-6632.20150321s00002696

غشاء سائل مستحلب لإزالة المبيدات من المحلول المائي: ثبات المستحلب، كفاءة الاستخلاص ودراسات نقل الكتلة

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الخلاصة

بحثت الدراسة الحالية في استقرار وكفاءة استخلاص الغشاء السائل المستحلب لإزالة مبيد أبامكتين من المحلول المائي. تم فحص الثبات من حيث توزيع حجم مستحلب القطيرات ونسبة تكسر المستحلب. تضمن ELM المقترح خليطًا من زيت الذرة والكيروسين (١: ١) كمادة مخففة، Span 80 كمادة خافضة للتوتر السطحي وحمض الهيدروكلوريك كعامل نزع دون استخدام عامل ناقل. تم تقييم معاملات مثل سرعة المجانسة وتركيز الفاعل بالسطح ووقت الاستحلاب ونسبة الحجم الداخلي إلى العضوي .(I / O) أظهرت النتائج أن حجم القطرة الأدنى ٠,٩ ميكرومتر والمستحلب المستقر الأعلى من حيث نسبة الكسر ١,١٢٪ تشكلت عند ٥٨٠٠ دورة في الدقيقة من سرعة الخلط، و ٤ فولت من الامتداد ٨٠ السطحي، و ٨ دقائق من وقت الاستحلاب و ١: ١ (I / O) بينما تم استخلاص ٨٦,٤٪ من مبيدات الأبامكتين تحت هذه الظروف. كما تم إنجاز حركيات الاستخراج ودراسة النقل الجماعي. يمكن أن تمتد نتائج هذه الدراسة إلى إزالة أنواع أخرى من المبيدات من المياه ومياه الصرف الصحي.

الكلمات الدالة: مستحلب سائل غشاء، مبيدات حشرية، استقرار، اِستِخلاص.