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Chlorpyrifos Removal from Aqueous Solutions by Emulsion Liquid Membrane: Stability, Extraction, and Stripping Studies

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ABSTRACT

The current paper focuses on assessing key parameters affecting the extraction of Chlorpyrifos as well as emulsion stability using the emulsion liquid membrane technology. Five parameters affecting the extraction have been studied: homogenizer speed, emulsification time, agitating time, surfactant concentration, and stripping phase concentration taking into consideration the emulsion breaking. Experiments proved that using the resulting optimum values will maximize both extraction and stripping efficiencies (93.8% and 94.7% respectively), while minimizing the emulsion breakage (increasing the stability of emulsion) to 0.73% with no need to employ a carrier agent. A 10 min agitating time, 3% (v/v) Span 80 as a surfactant, 12700-rpm homogenizer speed, 0.25 M HCl as an internal phase concentration, and 5 min emulsification time are chosen to be the optimum parameters' values. A study of extraction kinetics and estimation of mass transfer coefficient was also accomplished (3.89×10^{-9} m/s). The conclusions of this work can be extended to the removal of other types of pesticides from water.

Keywords: emulsion liquid membrane, chlorpyrifos, emulsion droplet size, stability, mass transfer coefficient, extraction efficiency.

INTRODUCTION

Pesticides are commonly employed in agricultural industry for controlling a wide range of harmful organisms, which destroy the produce. Pesticides are undeniably beneficial to agricultural crops, even though as a result, lower levels of certain residues may continue being in harvest posing a risk of chronic toxicity and in some cases acute toxicity for humans (Osman et al. 2014). Pesticides are categorized as organophosphorus, organochlorines, chlorophenols, carbamates, and synthetic pyrethroids based on their chemical structure. (Marican and Durán-Lara 2018). Organophosphates (OPs) are esters of pentavalent phosphorous acid, displaying an extensive spectrum of toxicity in living beings. Chlorpyrifos (CP) is a category of organophosphorus pesticides (OP), that find many applications as insecticide, acaricide and termiticide (Akhtar et al. 2009, Nandhini et al. 2021). Chlorpyrifos (CP), an organophosphorus insecticide (OP), commonly consumed in public health and agriculture, has a high octanol water partition coefficient (K_{ow} = 4.70) (Osman et al. 2014). The aqueous hydrolysis DT50 and photolysis of CP are up to 72 d and 29.6, respectively (Zhu et al. 2021). The characteristics of extensive use of CP are long-range transport potential, high lipophilicity, bioaccumulation, and extension of CP half-life leading to slow degradation and high toxicity (Nandhini et al. 2021). Concentrations of CP detected in both surface and groundwater ranged between 0.13 µg/L to 0.24 µg/L (Qurie et al. 2016). A number of conventional and physical-chemical methods, such as biotreatment, Fenton oxidation, titanium dioxide catalytic, powdered activated carbon, reverse osmosis, and filtration have been established for the elimination of organic pollutants including pesticides (Costa et al. 2018). These techniques are engrossed in pesticides dissolving in aqueous solutions (Osman et al. 2014). Hence, the integration of conventional water treatment with advanced technologies has attracted a lot of

attention (Dâas et al. 2014). Liquid membrane processes have recently received a lot of attention as an advanced extraction technique, and are considered an attractive alternative treatment for the elimination of organic contaminants existing in waterbodies. Liquid membrane extraction, commonly known as emulsion liquid membrane (ELM), was presented as a substitute technique for liquid-liquid extraction by solid polymeric membrane (Jusoh et al. 2016, Muthusaravanan et al. 2019). Comparing with membrane separation technique, the ELM process allows selective solute targeted to pass through a liquid membrane, mostly with adding carrier components (Hu et al. 2020). A carrier agent is used in some liquid membrane systems to facilitate the transfer of solutes, resulting in additional costs (Shorki et al. 2020). The mechanism of ELM is based on the diffusion of solutes passing through a liquid membrane where the membrane is an organic phase (Othman et al. 2017). The ELM process entails the following basic stages: (i) emulsification, (ii) dispersion and extraction, (iii) settling, and (iv) demulsification, i.e. breaking the resulted emulsion. For the emulsification step, preparing the emulsion by emulsifying both the organic membrane phase and the internal phase. Then dispersing the prepared emulsion into the external feed phase that contains the contaminant. Afterward, a settling process by gravity takes place in order to separate the emulsion from external solution. Finally, the membrane phase is recovered by employing a demulsification process (Jusoh et al. 2016). The chief advantages of the emulsion liquid membrane technique are: (1) contaminant (solute) high rate of diffusion through the membrane, (2) owing to the small sized droplets, availability of high interfacial area for solute mass transfer at the internal water-oil interface, (3) ability to treat an assortment of compounds and elements in industrial setting at higher speeds along with a extraordinary level of effectiveness, while utilizing various solutes (contaminants) volume concentration, and (4) simultaneous performance of both extraction and stripping at external interface and the internal interface respectively in the same system (Sabry et al. 2007).

Achieving a maximum solute extraction efficiency is always the coveted target for a liquid membrane system. However, the main obstacle in the EML method is maintaining the emulsion stability, meaning the emulsion instability that causes a breakdown and releases the internal phase of the emulsion droplet. Membrane breakage (instability) has heavily affected the efficiency of the ELM system (Buddin et al 2019). There are three main phenomena that could lead to emulsion instability: swelling, coalescence, and membrane breakage or rupture (Chakraborty et al. 2010). It is usually ruled by rupturing of the emulsion followed by leaking of the internal phase, causing a significant decrease in the stripping phase volume (Ho et al., 1992). This usually propels the driving force for mass transfer; while reducing the concentration gradient which increases the external aqueous feed concentration meanwhile a lowering of the extraction efficiency occurs (Mohammed et al. 2020a). This instability could be caused by the formulation of emulsion and the emulsification condition (Djenouhat et al. 2008).

In this paper, chlorpyrifos extraction from contaminated water employing emulsion liquid membrane (ELM) was studied. The influence of emulsification speed, agitation time, surfactant concentration, emulsification time, and internal phase concentration on the stability of the prepared W/O emulsion was investigated to determine the best conditions for attaining minimal membrane breakage in the emulsion system while reaching maximum extraction efficiency.

MATERIALS AND EXPERIMENTAL

Chemicals and equipment

Analytical reagent-grade chemicals, along with distilled water were employed in this work. Chemicals used are chlorpyrifos (CP), purchased from the local market (Om Agro Chemicals, India). The chemical formula of CP (O, O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate) ($C_9H_{11}Cl_3NO_3PS$) is shown in Figure 1. Molar mass (350.6 g/mol), Density (1.4 g/cm^3), melting point: (41.5-42.5) °C, vapor pressure: 1.87 X 10^{-5} mmHg at 25 °C, Decomposition at 160 °C (Sheikhi et al. 2021, ur Rahman et al. 2021). Both hydrochloric acid (HCl) and sodium hydroxide are acquired from Thomas beaker, India. The liquid membrane phase consists of a surfactant and a diluent, the nonionic surfactant engaged was sorbitan monooleate, commonly recognized as Span 80, which was obtained from Merck; Darmstadt; Germany (Sigma Aldrich); while n-hexane (diluent) was obtained from Thomas beaker (India). All laboratory tests were carried out at room

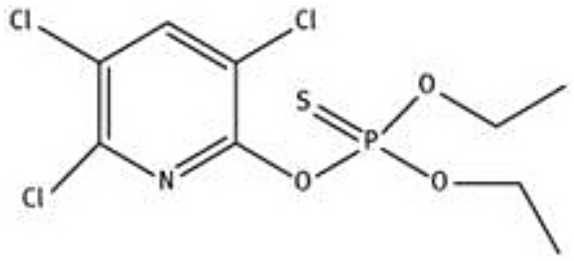

Figure 1. Chemical structure of chlorpyrifos (Díaz et al. 2020)

temperature of (20 ± 2) °C. The equipment used in this research are homogenizer (Mtops, SR 30), compact digital mixer system (Heidolph, RZR 2021), quartz cells, UV Spectrophotometer (ThermoSpectronic, USA), centrifuge (Isolab), pH meter (ATC) and a magnetic stirrer with temperature controller (Isolab).

Experimental work

The experimental structure was confined into two main sections. The first one is the ELM formulation, and determining the membrane stability via diverse operating parameters. The second section concerns investigating the ELM performance on the extraction of chlorpyrifos (CP) from simulated solution (feed phase). For the first part, a water-in-oil emulsion was formed by the addition of internal phase (HCl) dropwise into the membrane phase (Span 80 and n-hexane) while using a homogenizer (high speed mixer) for a specified time. The membrane phase was formed via dissolving a specific amount of surfactant (Span 80) in n-hexane by gently stirring via magnetic stirrer. While the internal aqueous solution was formed by taking the required amount of acid solution (HCl) in the allocated amount of distilled water. The emulsion is poured to external aqueous solution while mixing continuously, causing globule formation. Each globule is made of droplets of stripping solution encased in the membrane solution that contains the surfactant. A flow diagram of ELM process is outlined in Figure 2. Samples were taken from the mixture at certain time intervals using syringes and pH values were recorded. By the completion of each experiment, the resulting double emulsion is allowed to be naturally separated from feed solution due to gravitational force, then a demulsification process was achieved by applying centrifugal force on the emulsion to segregate the phases making up the emulsion resulting in the capability of reusing membrane solution while the contaminant

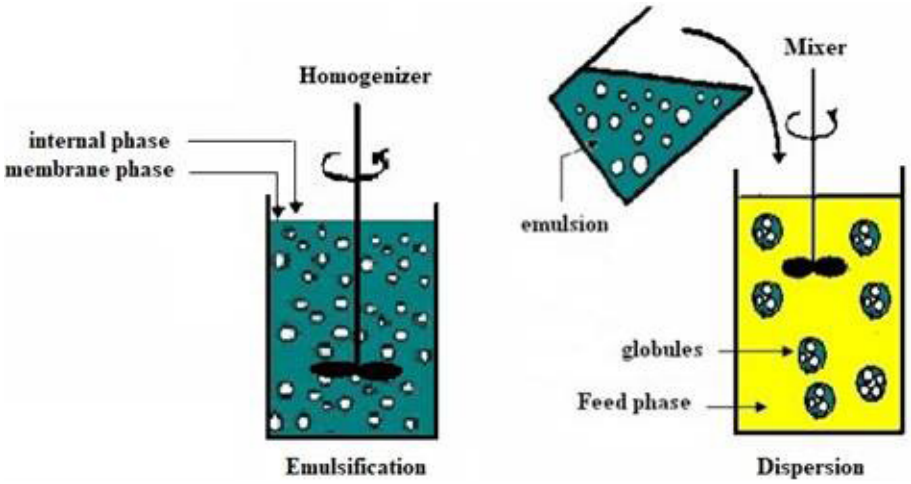

Figure 2. Flow diagram of batch process ELM

Table 1. Parameter investigated in Chlorpyrifos extraction

Parameter	Range
Homogenizer(emulsification)speed (rpm)	3000, 5800, 12700, 19700
Emulsified time, min	5, 10, 15, 20
Span 80 concentration, % v/v	1, 2, 3, 4
Mixing time, min	2, 5, 10, 15, 20
Stripping agent concentration (HCl), molar	0.05, 0.15, 0.25, 0.35, 0.45

would be extracted as a concentrated solution. Samples are filtered using syringe filters (pore diameter 0.22 μm). CP concentration in the separated external phase and in filtered samples is measured using an ultraviolet spectrophotometer (UV) corresponding to a 290 nm wavelength to evaluate the stripping and extraction capacity of Chlorpyrifos. The operating parameters with their corresponding ranges are listed in Table 1. All experiments are conducted in batch configuration, which is easier to operate and study.

ANALYSIS AND CALCULATIONS

Extraction process of CP

The CP concentration in the separated external phase is measured which by ultraviolet spectrophotometer (UV). Afterwards the extraction percentage of CP was calculated from the following equation:

$$Extraction\ Efficiency\ (E\ \%) = \frac{\mathrm{Co} - \mathrm{C}}{\mathrm{Co}} \cdot 100 \quad (1)$$

where: C_0 – represents the initial CP concentration in the external feed phase;
C – represents the CP concentration after a specific amount of time in the external feed solution.

Stripping

The resulting double emulsion was allowed to be naturally separated from feed solution due to gravity force, then a demulsification process was achieved by applying centrifugal force on the emulsion. The CP concentration extracted from internal phase was measured, and the stripping efficiency was then calculated according to the following equation:

$$Stripping\ (\mathrm{S}\%) = \frac{\mathrm{C}_{f,int}}{\mathrm{Co} - \mathrm{C}_{f,ext}} \cdot 100 \quad (2)$$

where: $\mathrm{C}_{f,int}$ – represents the final CP concentration in the internal phase;
$\mathrm{C}_{f,ext}$ – represents the final CP concentration external phase.

Membrane leakage/breakage

When dispersing emulsion into the aqueous feed phase, the emulsion has to be stable enough to extract the CP molecules into the emulsion droplets. Usually stabilization is achieved by the surfactant added thus the degree of extraction efficiency for any solute is mainly affected by the emulsion stability. Breakdown of emulsion usually occurs after a period of time when the emulsion is considered unstable causing a gradual lowering of removal efficiency along with a significant loss of extracted species (Laguel et al. 2019). The liquid membrane stability is considered the most essential factor affecting the solute removal efficiency. Using a tracer (H^+ ion) with a specific concentration within the internal aqueous phase solution. Breakage is the result of tracer transfer from internal-to-external phase solutions. Any alteration in pH value (i.e., H^+ ions leaking) of the feed phase results from the emulsion breakage (rupture) because of the excretion of the HCl from internal towards external aqueous phase. The emulsion rupture or breakage (ε) signifies the percentage ratio of the internal aqueous phase volume escaped (leaked) to the external feed aqueous phase using the following general equation:

$$\varepsilon(\%) = \frac{Vs}{V_i^{\circ}} \cdot 100 \quad (3)$$

where: Vs – represents the leaked volume of the stripping phase (internal phase);
V_i° – represents the initial volume of the internal stripping phase.
Vs was computed using the following equation (Mohammed et al. 2018).

$$Vs = V_b^{\circ} \cdot \frac{10^{-\mathrm{pHo}} - 10^{-\mathrm{pH}}}{10^{-\mathrm{pH}} - \mathrm{C}_{\mathrm{H^+}}^{\mathrm{int}}} \quad (4)$$

where: V_b° – represents the external feed phase initial volume;
pH – represents external feed phase pH after being in contact with the emulsion;
pHo – represents the initial external phase pH;
$\mathrm{C}_{\mathrm{H+}}^{\mathrm{int}}$ – represents the initial acid concentration [H^+] of the internal phase solution.

RESULTS AND DISCUSSION

Effect of homogenizer speed

Emulsification speed can be considered a significant parameter that influences the emulsion stability, thereby affecting the entire extraction process (Mohammed et al. 2020b). The stability of emulsion is a vital factor in ELM process;

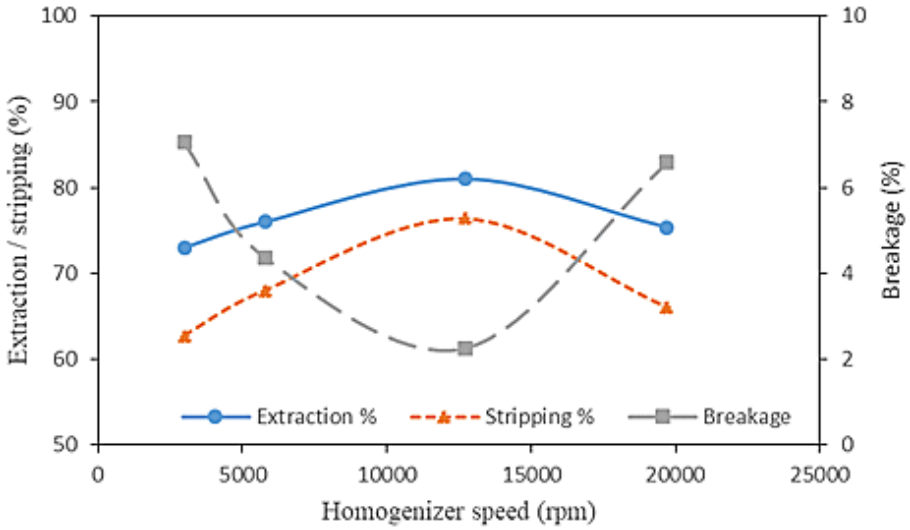

Figure 3. Effect of homogenizing speed on extraction efficiency and membrane breakage for 15 min mixing time (CP: 100 mg/L, 0.25M HCl, emulsification time 10 min, Span 80: 4% (v/v), diluent: hexane)

low values lead to break up of the emulsion while extremely high stability of emulsion causes the emulsion to be impossible to breakdown via mechanical method. Homogenizer speed was investigated using values stated above in Table 1. Figure 3 displays the effect of homogenizing speed on removal efficiency and emulsion breakage.

The results displayed in Figure 3 show that when the speed is increased from 3000 rpm to 12700 rpm, the emulsion stability increases as the breakage drops, which gives a minimum breakage value of 2.2% while the extraction and stripping efficiencies increase from 73.1% and 62.7% to 81.8% and 76.4% respectively. This occurs as a result of instigating smaller sized droplets when employing higher speeds where the sauter mean diameter lessened from 17.2 µm at 3000 rpm to 6.45 µm at 12700 rpm, which leads to increasing the interfacial surface area for droplets thus increases the mass transfer rate. At higher homogenizer speed (19700 rpm), a decrease in the emulsion stability occurs (breakage: 6.58%) also the efficiency of extraction decreases to 75.37%. Speed lower than 12700 rpm leads to a decrease in stability , i.e. for 3000 rpm homogenizer speed, an increase in breakage percentage to 7.05% occurs, this is because of the bigger droplet diameter, and the coalescence phenomenon that transpire in a short amount of time (Mohammed 2007, Salman and Mohammed 2019). Consequently, a speed of 12700 rpm is nominated as the optimum homogenizer speed. Table 2 below shows the extraction percentage, emulsion breakage, and the sauter mean diameter at varying homogenizer speeds.

Table 2. Extraction percentage, breakage, and Sauter mean diameter at various emulsification speeds

	Homogenizer speed (rpm)			
	3000	5800	12700	19700
Extraction efficiency, %	73.09	76.61	81.8	75.37
Breakage, %	7.05	4.36	2.24	6.58
D32, µm	17.2	11.6	6.45	8.75

Effect of emulsification time

To produce a stable emulsion, it is crucial to provide appropriate time to surround the internal phase into the organic oil phase. The emulsion stability was examined within a range of 5–20 min. emulsification times as stated in Table 1. Figure 4 shows that the highest efficiency of extraction and stripping; 87.9% and 78.9% respectively; occurred at 5 min. emulsification time, in accordance it offers the highest stability along with a lowest breakage value (2.07%) and a Sauter mean diameter of 4.85 µm. When increasing emulsification time (10, 15, and 20 min.), the breakage percentage increases whereas extraction efficiency decreased. At 20 min. emulsification time, the breakage increases up to 10.27%, whereas a decrease in extraction efficiency was registered at 74.6%. This happens due to the occurrence of high internal shear, therefore leading to a massive quantity of emulsion globules by unit volume, in return, it facilitates its diffusion into the feed aqueous phase (Laki et al. 2016). Hence, the optimum emulsification time of 5 min. was considered for this study.

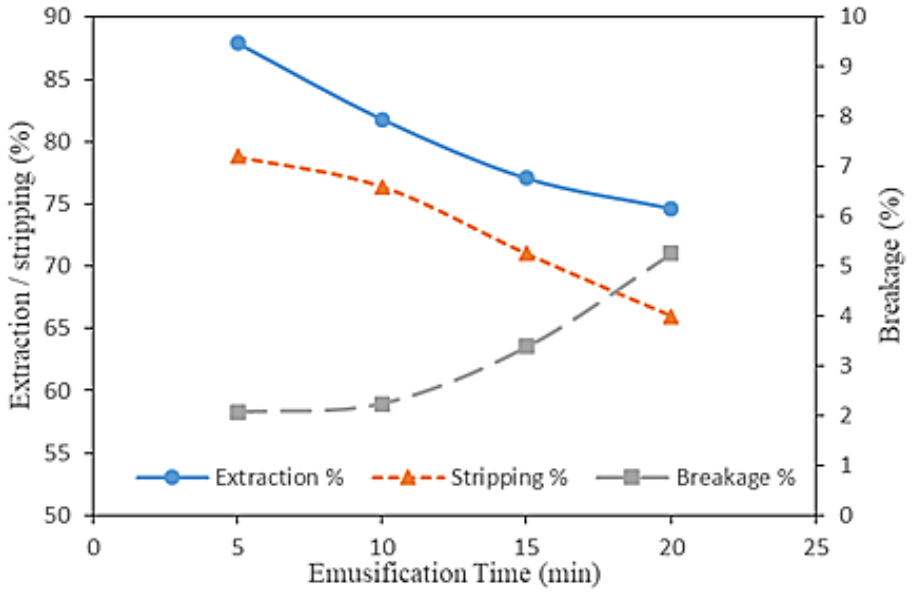

Figure 4. Effect of emulsification time on extraction, stripping, and membrane breakage for 15 min mixing time (CP: 100 mg/L; emulsification speed: 12700 rpm; Span 80: 4% (v/v); internal phase concentration 0.25M HCl; diluent: hexane)

Effect of surfactant concentration

Surfactant plays a major part in establishing the emulsion stabiliy since it diminishes the tension between the immiscible phases. A span 80 surfactant was added as an emulsifier that serves as a shielding barrier between the external and internal phases, therefore forfending an emulsion breakage. Numerous surfactant concentrations (1, 2, 3, and 4 % (v/v)) were used to investigate the influence of surfactant concentration on the stability of emulsion. Figure 5 shows extraction, stripping percentage, and membrane breakage with different surfactant concentrations. It was analyzed that the stability rises slightly when increasing Span 80 concentration until 3% (breakage = 0.82%). With increasing the concentration of surfactant, further surfactant is being absorbed within the interphase between the internal aqueous phase and the oil membrane phase, hence improving the adsorption layer strength therefore increasing stability. In addition, the surfactant concentration increase heightens emulsion stability as a result of the interfacial tension reduction

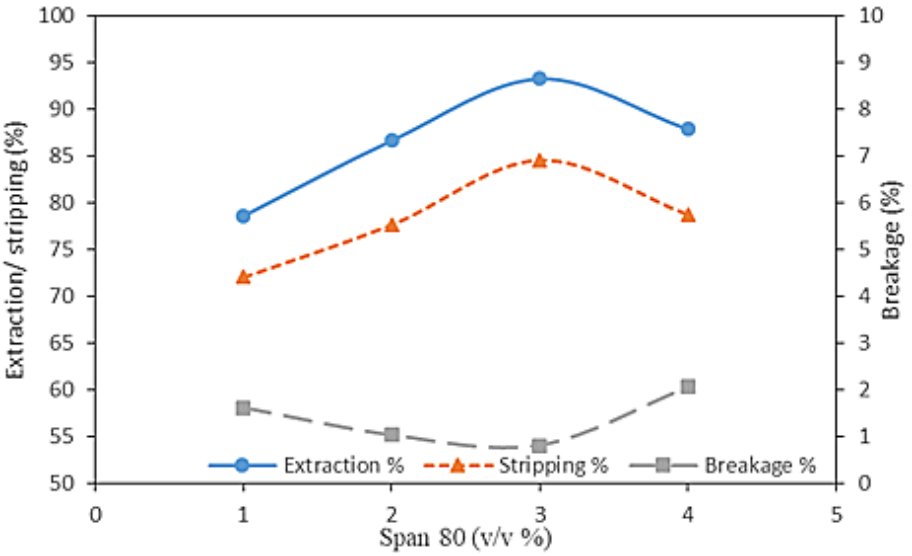

Figure 5. Effect of surfactant concentration on extraction, stripping, and membrane breakage for 15 min mixing time (CP: 100 mg/L; emulsification time: 5 min; emulsification speed: 12700 rpm; 0.25M HCl; diluent: hexane)

between oil and water phases. While extraction and stripping efficiency gradually increase to reach maximum values of 93.3% and 84.6% respectively. However, additional increase in Span 80 concentration (4%) causes a significant lowering in extraction efficieny (87.9%) whereas the breakage increases sharply to (2.07%) resulting in formation of unstable emulsion. This could be because of the decrease of interfacial tension, causing a formation of more fine droplets. Also, the excess of surfactant concentration over its critical micelle concentration (cmc) leads to forming aggregates of surfactant within the membrane phase, promoting water transport between the aqueous phases and causing swelling and breakage (Ahmad et al. 2012). It was also reported that the resulted emulsion instability when increasing surfactant concentration could be because of the Ostwald ripening of the emulsion droplets, which in effect increases both swelling and leakage (Mohammed and Al-Khateeb 2022). An optimum value of 3% surfactant concentration was selected for further experiments.

Effect of internal (stripping) phase concentration

In order to improve the stability of emulsion and lower the amount of the internal solution released into the external phase, and since extraction process at the external-membrane interface is necessary; a re-extraction process is essential at the internal-membrane interface in order to remove the CP entirely. A stripping agent (HCl) was employed as the internal aqueous phase to re-extract (strip) CP. Stripping agent concentration ranged from 0.05 to 0.45 M. When raising HCl concentration accordingly, breakage percentages diminished while extraction efficiencies improved from 4.3% and 72.5% to 0.82% and 93.3%, respectively as shown in Fig. 6. This could be attributed to the chief driving force in the emulsion liquid membrane system which is the amount of $[H^+]$ ions variation between two aqueous phases (Sabry et al. 2007). Furthermore, when the internal phase acidity is being raised above 0.25 M, it causes a partial increase in breakage, leading to additional release of the enclosed internal constituent outwards into the external aquous phase ensuring an extraction efficiency decline. It could be attributed to the reaction between the surfactant and HCl that occurs due to the relatively high acidity achieving a significant drop in the surfactant properties which lead to a de-stabilization of emulsion (Mohammed 2007). In conclusion, a 0.25M of HCl which achieves higher extraction efficiency along with lower breakage percentage and was selected for this work.

Effect of mixing time

Mixing time is a necessary factor in the ELM process. It can be specified as the time required to achieve maximum extraction of CP. Mixing time, also known as contact time, is defined as the period of time in which the external feed phase stays in direct contact with the emulsion while continuously stirring (Benderrag et al. 2022, Ahmad et al. 2021). Figure 7 shows the

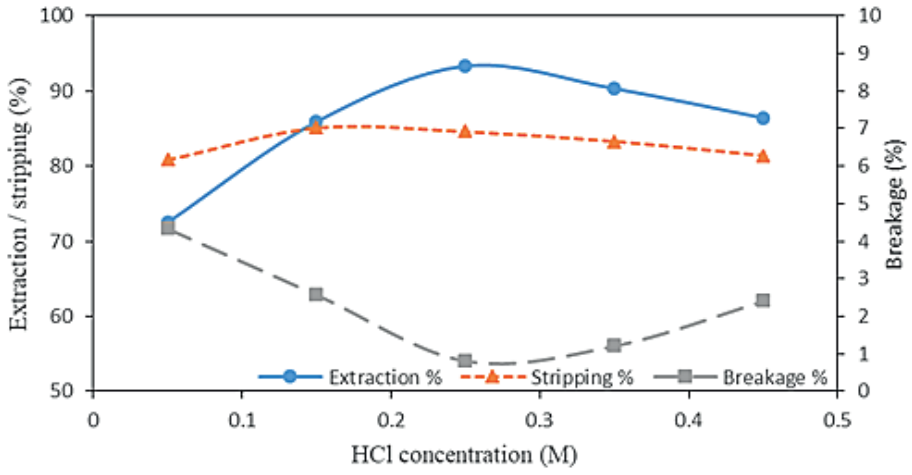

Figure 6. Effect of internal phase concentration on extraction, stripping, and membrane breakage for 15 min mixing time (CP: 100 mg/L; emulsification speed: 12700 rpm; emulsification time: 5 min; Span 80: 3% (v/v); diluent: hexane)

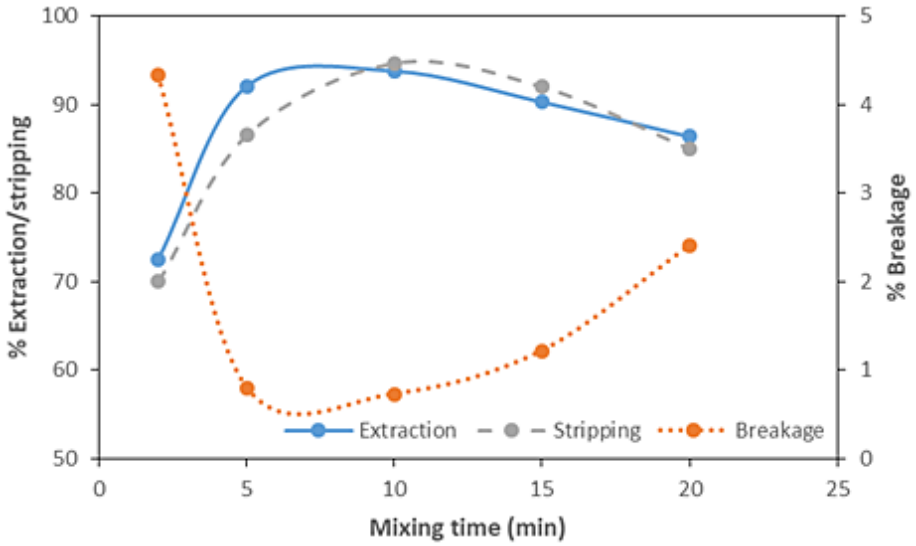

Figure 7. Effect of mixing time on membrane breakage, extraction and stripping efficiencies (CP: 100 mg/L; emulsification time: 5 min; emulsification speed: 12700 rpm; 0.25M HCl; Span 80: 3% (v/v); diluent: hexane)

effect of mixing time on emulsion breakage, extraction and stripping percentage for times ranging from 2 min to 20 min. Upon increasing mixing time, CP extraction and stripping efficiency keep increasing reaching an optimum level of 93.8% and 94.7% respectively at 10 min. while the breakage percentage is reduced to a minimum (0.73%). Longer contact time will cause the movement of internal phase solution towards the feed solution due to the increase of emulsion breakage (Salman and Mohammed 2019, Mohammed 2007); therefore, the extracted molecules revert backward to the feed phase, hence decreasing extraction and stripping efficiencies. Therefore, a 10 min. mixing time was chosen as the optimal period to extract CP.

Evaluation of the solute (CP) extraction kinetics and estimation of mass transfer coefficient

Extraction kinetics of CP using the ELM method were investigated in accordance with the approach performed by (Kohli et al. 2019, Raji et al. 2018), using the first order rate Eq.:

$$Ln\left(\frac{C}{Co}\right) = -K_{obs} \cdot t \tag{5}$$

where: t – represents time in minutes;
K_{obs} – is the rate constant of extraction (min^{-1}), which can be evaluated from the slope of the resulting line from the previous equation representing the K_{obs} value. Because the value obtained was positive, the extraction process follows the first-order kinetics. K_{obs} value obtained was 0.2173 min^{-1}.

Total mass transfer coefficient for the ELM system is shown in the following equation (Kasaini et al. 1998):

$$\frac{1}{K_T} = \frac{1}{K_F} + \frac{1}{K_M} \tag{6}$$

where: K_T – represents total mass transfer coefficient (m/s);
K_F – represents interfacial reaction rate constant (m/s);
K_M – represents mass transfer coefficient of the external phase (m/s), estimated by Skelland–Lee correlation (Kohli et al. 2019) correlation given in the following equation:

$$\frac{K_M}{\sqrt{ND}} = 2.932 * 10^{-7} \cdot \cdot \left(\frac{\mathrm{Vi} + \mathrm{Vm}}{Vi + Vm + Ve}\right) Re^{1.371} \left(\frac{\mathrm{d}}{T}\right)^{0.548} \tag{7}$$

where: N – represents mixing speed (rpm);
T and d – represent the mixing tank and impeller diameter, respectively (m);
Vi, Ve, and Vm – denote the internal, external, and membrane phase volumes, respectively;
D – represents species diffusivity (CP) in the organic membrane phase, determined using Wilke–Chang correlation (Treybal 1981) shown in Eq. (9).

$$Re = \frac{\mathrm{N}\ \mathrm{d}^2 \rho_{ext.}}{\mu_{\mathrm{ext.}}} \quad (8)$$

where: $\rho_{ext.}$ – the density (kg/m^3);
$\mu_{ext.}$ – the viscosity (kg/m.s);
Re – value calculated was equal to 348577.

$$D = \frac{117.3 \cdot 10^{-8} \cdot (M \cdot \emptyset)^{0.5} \cdot T_{emp.}}{\mu_m \cdot \emptyset_c^{0.6}} \quad (9)$$

where: M – solvent molecular weight (n-hexane = 86.18 kg/ kmol);
T – temperature in kelvin;
ϕ – solvent association factor (n-hexane = 1);
μ_m – membrane viscosity 12.224×10^{-3} kg/m.s;
ϕ_c – molar volume of the CP, evaluated using Schroeder method (Poling et al. 2001), ϕ_c calculated is 0.399 m^3/kmol. The calculated D was found to be 6.79×10^{-10} m^2/s. K_M obtained was 2.6×10^{-4} m/s.

K_F is calculated through the following equation:

$$Ln\left(\frac{C}{Co}\right) = -A \cdot K_F \cdot t \quad (10)$$

K_F could be calculated by comparing Eqs. (10) and (5):

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

where: A – represents emulsion-specific interfacial area, calculated from the following equation (Karcher et al. 2015):

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

where: A_i – the interfacial area of the emulsion droplet;
V – the unit volume of the emulsion;
α – represents the water volume fraction;
$\mathrm{d_{32}}$ – represents the diameter of the emulsion droplet.

In conclusion, the calculated mass transfer coefficients are:

$$\mathrm{K_M} = 2.6 \times 10^{-4}\ \mathrm{m/s} \quad (13)$$

$$\mathrm{K_F} = 3.89 \times 10^{-9}\ \mathrm{m/s} \quad (14)$$

$$\mathrm{K_T} = 3.89 \times 10^{-9}\ \mathrm{m/s} \quad (15)$$

CONCLUSIONS

The present study investigates the stability of ELM while evaluating extraction and stripping efficiencies of the emulsion for chlorpyrifos pesticide removal from aqueous wastewater. A minimum emulsion breakage of 0.73% and the highest removal percentage of 93.8% and 94.7% stripping efficiency within 10 min contact time were achieved at the optimum experimental conditions, which are: emulsification speed, 12700 rpm; emulsification time, 5 min; surfactant concentration, 3% (v/v); and internal (stripping) phase concentration, 0.25M; with no requirement of an additional carrier. With mass transfer coefficients (K_M, K_F, and K_T) values of 2.6×10^{-4} m/s, 3.89×10^{-9} m/s, and 3.89×10^{-9} m/s respectively.

Generally, it can be concluded that the emulsion liquid membrane represents a productive, efficient, and suitable advanced separation method for the treatment of wastewater contaminated with pesticides. It could be a promising alternative technique to minimize environmental pollution caused by pesticides to large extent.

REFERENCES

1. Ahmad A.L., Kusumastuti A., Derek C.J.C., Ooi B.S. 2012. Emulsion liquid membrane for cadmium removal: Studies on emulsion diameter and stability. Desalination, 287, 30–34. https://doi.org/10.1016/j.desal.2011.11.002
2. Ahmad A.L., Mohd Harun M.H.Z., Akmal Jasni M.K., Zaulkiflee N.D. 2021. Removal of Ibuprofen at Low Concentration Using a Newly Formulated Emulsion Liquid Membrane. Membranes (Basel), 11(10), 740. https://doi.org/10.3390/membranes11100740.
3. Akhtar N., Srivastava M. K., Raizada R.B. 2009. Assessment of chlorpyrifos toxicity on certain organs in rat, Rattus norvegicus. J Environ Biol, 30(6), 1047-1053.
4. Benderrag A., Djellali M., Haddou B., Daaou M., Bounaceur B. 2022. Experimental design and RSM on the recovery of Ni (II) ions by ELM using TX-100 as a biodegradable surfactant. Environ Technol., 3, 386-401. https://doi.org/10.1080/09593330.2020.1791967
5. Buddin M.M.H.S., Salizan Ahmad N.D.S.M.N., Elha A.L., Rashidi A.R. 2019. Water-in-oil-in-water (W/O/W) emulsion instability in emulsion liquid membrane: membrane breakage. Journal of Physics, 1349-012106. https://doi.org/10.1088/1742-6596/1349/1/012106

6. Chakraborty M., Bhattacharya C., Datta, S. 2010. Emulsion Liquid Membranes: Definitions and Classification, Theories, Module Design, Applications, New Directions and Perspectives. In Liquid Membranes Principles and Applications in Chemical Separations and Wastewater Treatment, Kislik, V.S. Elsevier Science: Amsterdam, 141−199.
7. Costa R.O., Barcellos Canela P.S. 2018. Removal of pesticide residues after conventional drinking water treatment: byproducts and acetylcholinesterase inhibition. Eclética Química Journal, 43(2), 65-73. https://doi.org/10.26850/1678-4618eqj.v43.2.2018.p65-73
8. Dâas A., Hamdaoui O. 2014. Removal of non-steroidal anti-inflammatory drugs ibuprofen and ketoprofen from water by emulsion liquid membrane. Environ. Sci. Pollut. Res, 21, 2154–2164. https://doi.org/10.1007/s11356-013-2140-9
9. Díaz S.S., Al-Zubaidi H., Ross-Obare A.C., Obare S.O. 2020. Chemical reduction of chlorpyrifos driven by flavin mononucleotide functionalized titanium (IV) dioxide. Physical Sciences Reviews, 5, 11. https://doi.org/10.1515/psr-2020-0007
10. Djenouhat M., Hamdaoui O., Chiha M., Samar M.H. 2008. Ultrasonication-Assisted Preparation of Water-in-Oil Emulsions And Application to the Removal Of Cationic Dyes From Water By Emulsion Liquid Membrane: Part 2: Permeation and Stripping. Sep. Purif. Technol, 63, 231−238. https://doi.org/10.1016/j.seppur.2008.05.005
11. Ho W.S., Kamalesh K.S. 1992. Electrostatic Pseudo-Liquid- Membrane. In Membrane Handbook. Chapman & Hall, New York, 867−884.
12. Hu J., Zou D., Chen J., Li D. 2020. A novel synergistic extraction system for the recovery of scandium (III) by Cyanex272 and Cyanex923 in sulfuric acid medium. Sep Purif Technol, 233, 115977. https://doi.org/10.1016/j.seppur.2019.115977
13. Jusoh N., Othman N., Nasruddin N.A. 2016. Emulsion liquid membrane technology in organic acid purification. Malaysian Journal of Analytical Sciences, 20(2), 436-443. ↰ https://doi.org/10.17576/mjas-2016-2002-28
14. Karcher V., Perrechil F., Bannwart A. 2015. Interfacial energy during the emulsification of water-in-heavy crude oil emulsions, Braz. J. Chem. Eng., 32, 127-137. https://doi.org/10.1590/0104-6632.20150321s00002696
15. Kasaini H., Nakashio F., Goto M. 1998. Application of emulsion liquid membranes to recover cobalt ions from a dual-component sulphate solution containing nickel ions. J. Memb. Sci., 146, 159–168. https://doi.org/10.1016/S0376-7388(98)00105-7.
16. Kohli H.P., Gupta S., Chakraborty M. 2019. Stability and performance study of emulsion nanofluid membrane: a combined approach of adsorption and extraction of Ethylparaben. Colloids Surf. A Physicochem. Eng. Asp., 579, 123675. https://doi.org/10.1016/j.colsurfa.2019.123675
17. Laguel S., Samar M.H. 2019. Removal of Europium (III) from water by emulsion liquid membrane using Cyanex 302 as a carrier. Desalination and Water Treatment, 165, 269–280. https://doi.org/10.5004/dwt.2019.24551
18. Laki S., Kargari, A. 2016. Extraction of silver ions from aqueous solutions by emulsion liquid membrane. J. Membr. Sci. Res. 2, 33–40. https://doi.org/10.22079/JMSR.2016.15876
19. Marican A., Durán-Lara E.F. 2018. A review on pesticide removal through different processes. Environmental Science and Pollution Research, 25(3), 2051-2064. ↰ https://doi.org/10.1007/s11356-017-0796-2
20. Mohammed A.A., Al-Khateeb R.W. 2022. Application of Emulsion Liquid Membrane Using Green Surfactant for Removing Phenol from Aqueous Solution: Extraction, Stability and Breakage Studies. J. Ecol. Eng., 23(1), 305–314. https://doi.org/10.12911/22998993/143970
21. Mohammed A.A., Atiya M.A., Hussein M.A. 2020a. 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. https://doi.org/10.1016/j.cherd.2020.04.023
22. Mohammed A.A., Selman H.M., Abukhanafer G. 2018. Liquid surfactant membrane for lead separation from aqueous solution: Studies on emulsion stability and extraction efficiency, Journal of Environmental Chemical Engineering 6, 6923-6930. https://doi.org/10.1016/j.jece.2018.10.021
23. Mohammed A.A. 2007. Removal of Emulsified Paraffine from Water: Effect of Bubble Size and Particle Size on Kinetic of Flotation. Iraqi J. of Chem. Eng., (8)3, 1-5.
24. Mohammed M.A., Noori W.O., Sabbar H.A. 2020b. Application of Emulsion Liquid Membrane Process for Cationic Dye Extraction. Iraqi Journal of Chemical and Petroleum Engineering, 21(3), 39-44. https://doi.org/10.31699/IJCPE.2020.3.5
25. Muthusaravanan S., Priyadharshini S.V., Sivarajasekar N., Subashini R., Sivamani S., Dharaskar S., Dhakal N. 2019. Optimization and extraction of pharmaceutical micro-pollutant-norfloxacin using green emulsion liquid membranes. Desalination and water treatment, 156, 238-244. ↰ https://doi.org/10.5004/dwt.2019.23833
26. Nandhini A.R., Muthukumar H., Gummadi S.N. 2021. Chlorpyrifos in environment and foods: A critical review of detection methods and degradation pathways. Environmental Science: Processes & Impacts, 23, 1255-1277. https://doi.org/10.1039/D1EM00178G

27. Osman K.A., Al-Humaid A.I., Al-Redhaiman K.N., El-Mergawi R.A. 2014. Safety methods for chlorpyrifos removal from date fruits and its relation with sugars, phenolics and antioxidant capacity of fruits. Journal of food science and technology, 51(9), 1762-1772. https://doi.org/10.1007/s13197-012-0693-0
28. Othman N., Noah N.F.M., Shu L.Y., Ooi Z.Y., Jusoh N., Idroas M., Goto M. 2017. Easy removing of phenol from wastewater using vegetable oil-based organic solvent in emulsion liquid membrane process. Chinese Journal of Chemical Engineering, 25(1), 45-52. https://doi.org/10.1016/j.cjche.2016.06.002
29. Poling B.E., Prausnitz J.M., O'Connell J.P. 2001. The Properties of Gases and Liquids. Mcgraw-hill New York.
30. Qurie M., Khamis M., Ayyad I., Scrano L., Lelario F., Bufo S.A., Karaman R. 2016. Removal of chlorpyrifos using micelle–clay complex and advanced treatment technology. Desalination and Water Treatment, 57(33), 15687-15696. https://doi.org/10.1080/19443994.2015.1096836
31. Raji M., Abolghasemi H., Safdari J., Kargari A. 2018. Response surface optimization of dysprosium extraction using an emulsion liquid membrane integrated with multi-walled carbon nanotubes. Chem. Eng. Technol., 41, 1857–1870. https://doi.org/10.1002/ceat.201700351.
32. Sabry R., Hafez A., Khedr M., El-Hassanin A. 2007. Removal of lead by an emulsion liquid membrane: Part I. Desalination, 212(1-3), 165-175. https://doi.org/10.1016/j.desal.2006.11.006
33. Salman H.M., Mohammed A.A. 2019. Removal of Copper Ions from Aqueous Solution Using Liquid-Surfactant Membrane Technique. Iraqi Journal of Chemical and Petroleum Engineering 20(3), 31-37. https://doi.org/10.31699/IJCPE.2019.3.5
34. Sheikhi S., Dehghanzadeh R., Maryamabadi A., Aslani H. 2021. Chlorpyrifos removal from aqueous solution through sequential use of coagulation and advanced oxidation processes: By-products, degradation pathways, and toxicity assessment. Environmental Technology & Innovation, 23, 101564. https://doi.org/10.1016/j.eti.2021.101564
35. Shorki A., Daraei P., Zereshki S. 2020. Water decolorization using waste cooking oil: An optimized green emulsion liquid membrane by RSM. J. water process engineering, 33, 101021. https://doi.org/10.1016/j.jwpe.2019.101021
36. Treybal R.E. 1981. Mass-Transfer Operations, 3rd ed., McGraw-Hill Book Co, Singapore.
37. Ubaid ur Rahman H., Asghar W., Nazir W., Sandhu M.A., Ahmed A., Khalid N. 2021. A comprehensive review on chlorpyrifos toxicity with special reference to endocrine disruption: Evidence of mechanisms, exposures and mitigation strategies. Science of The Total Environment, 755, 142649. https://doi.org/10.1016/j.scitotenv.2020.142649
38. Zhu H., Yu X., Xu Y., Yan B., Bañuelos G., Shutes B., Wen Z. 2021. Removal of chlorpyrifos and its hydrolytic metabolite in microcosm-scale constructed wetlands under soda saline-alkaline condition: Mass balance and intensification strategies. Science of The Total Environment, 777, 145956. https://doi.org/10.1016/j.scitotenv.2021.145956