

# Performance Evaluation of Emulsion Liquid Membrane on Chlorpyrifos Pesticide Removal: Stability, Mass Transfer Coefficient, and Extraction Efficiency Studies

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## ABSTRACT

Emulsion Liquid Membrane (ELM) is an emerging technology that removes contaminants from water and industrial wastewater. This study investigated the stability and extraction efficiency of ELM for the removal of Chlorpyrifos Pesticide (CP) from wastewater. The stability was studied in terms of emulsion breakage. The proposed ELM included n-hexane as a diluent, span-80 as a surfactant, and hydrochloric acid (HCl) as a stripping agent. Parameters such as mixing speed, aqueous feed solution pH, internal-to-organic membrane volume ratio, and external-to-emulsion volume ratio were investigated. A minimum emulsion breakage of 0.66% coupled with a maximum chlorpyrifos extraction and stripping efficiency were achieved at 96.1% and 95.7% at best-operating conditions of 250/50 external-to-emulsion volume ratio, external feed solution pH 6, 250rpm mixing speed, and 1:1 internal-to-membrane volume ratio at 10min contact time without utilizing a carrier agent. A study of extraction kinetics and estimation of mass transfer coefficient was also conducted ( $3.89 \times 10^{-9}$  m/s). The results of this work can be extended to the removal of other types of pesticides from wastewater.

*Keywords-emulsion liquid membrane; chlorpyrifos; stability; mass transfer coefficient; extraction efficiency*

## I. INTRODUCTION

Emerging Contaminants (ECs) such as synthetic dyes, cosmetics, pharmaceuticals (antibiotics, hormones, and others), and pesticides are considered major issues in many parts of the world [1]. The final fate of pesticides after use has different pathways: (1) soil top layer accumulation, where pesticides may be adsorbed and deposited, (2) degradation on both the plant surface and the soil, (3) plant organs translocation, and (4) dissolution-transport of contaminants from soil and plant surfaces into water runoff causing water resource contamination [2, 3]. Chlorpyrifos (CP) is a broad-spectrum organophosphorus insecticide (OP) and has a high value of octanol-water partition coefficient  $K_{ow} = 4.70$  [4]. Exposure to chlorpyrifos can produce nausea, diarrhea, salivation, vomiting, tremor, and convulsion symptoms [5-7]. Chlorpyrifos is banned in many countries, nevertheless, monitoring still has to be carried out. The liquid membrane extraction, commonly known as Emulsion Liquid Membrane (ELM), was presented as a

substitute technique for separation by a polymeric membrane as well as liquid-liquid extraction [8, 9]. The mechanism of ELM depends on the diffusion of the solute (contaminant), passing through an organic liquid membrane [10]. The main advantages of ELM are: (1) high diffusion rate of the contaminant through the membrane, (2) high interfacial area for solute mass transfer at the internal water-oil interface due to the small-sized droplets, (3) ability to treat an assortment of compounds and elements in an industrial setting at higher speeds along with an extraordinary level of effectiveness for various solute (contaminants) volume concentrations, and (4) simultaneous performance of both extraction and stripping at the external and the internal interfaces of a system, respectively [11, 12]. Despite the promising features of ELM, its instability has impeded widespread applications on a larger scale. The stability of an emulsion is defined as liquid membrane resistance to high shear stress during solute extraction. The best stability level is essential in the ELM process [13], as it is produced using the appropriate surfactant to overcome the

difficulties of an ELM system on a practical industrialized level [14].

This study investigated chlorpyrifos extraction from contaminated water using ELMs to propose a novel method for pesticide extraction. The influences of stirring speed, internal aqueous phase-organic phase volume ratio, external feed phase pH, external phase-emulsion volume ratio, and contact time were studied to determine the best conditions to achieve minimal membrane breakage in the emulsion system and reach maximum removal efficiency.

## II. MATERIALS AND METHODS

### A. Chemicals and Equipment

This study used analytical reagent-grade chemicals. The CP used was purchased from the local market (Om Agro Chemicals, India). The chemical formula of CP ( $C_9H_{11}Cl_3NO_3PS$ ) can be seen in [19]. CP has a molar mass of 350.6g/mol, 1.4g/cm<sup>3</sup> density,  $1.87 \times 10^{-5}$ mmHg vapor pressure at 25°C, 41.5-42.5°C melting point, and decomposition at 160°C [15, 16]. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were acquired from Thomas beaker in India. The organic membrane consists of a diluent and a surfactant. The nonionic surfactant was sorbitan monooleate, commonly recognized as Span80, obtained from Merck, Darmstadt, Germany (Sigma Aldrich); n-hexane was used as a diluent, obtained from Thomas beaker, India, which was selected because of the higher rate of transport of solute than heptane and kerosene [17, 18]. All laboratory tests were carried out at a room temperature of  $20 \pm 2^\circ\text{C}$ , using Mtops SR 30 homogenizer, Heidolph RZR 2021 compact digital mixer system, quartz cells, PG instruments T80+ UV/VIS spectrometer, Isolab centrifuge machine, ATC pH meter, and an Isolab magnetic stirrer with a temperature controller.

### B. Experimental Work

The membrane phase was produced by dissolving a specific amount of surfactant (Span 80) in n-hexane by gently stirring via a magnetic stirrer. The emulsion was established by adding the internal phase (HCl) dropwise to the organic membrane phase (Span 80 and n-hexane as a solvent) while using a homogenizer. The resulting emulsion was then added to the external phase while mixing continuously. Dispersion occurs in the shape of globule formation, where each globule is made of stripping solution droplets encased in the membrane solution. Samples were withdrawn from the mixture at certain time intervals of 1, 2, 4, 6, 8, 10, 15, and 20min. The sample containing both the emulsion and the external phase was filtered (pore size 0.22µm diameter). After extraction, a separation of the emulsion from the feed solution was carried out by gravity, and a demulsification process was carried out by applying a centrifugal force to the emulsion (4000rpm for 30min) to segregate the phases, while the contaminant would be extracted as a concentrated solution. The CP concentration in the separated external phase and the filtered samples was measured periodically using an ultraviolet spectrophotometer (UV). Figure 1 shows the ELM process.

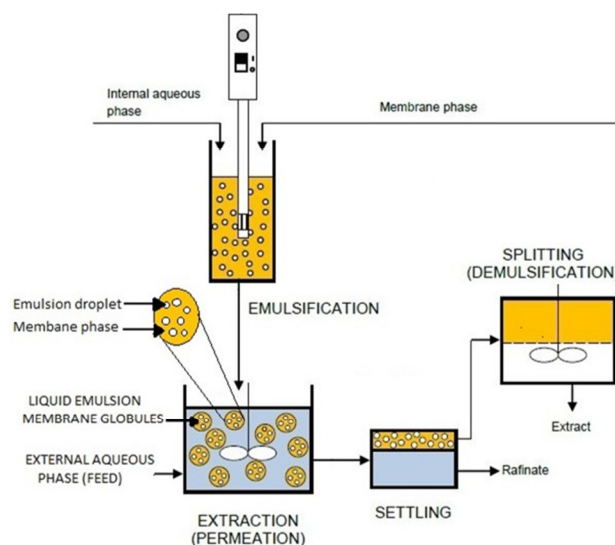


Fig. 1. Flow diagram of batch process ELM.

## III. ANALYSIS AND CALCULATIONS

### A. Extraction Process of CP

The CP concentration in the separated phase solution was measured by the ultraviolet spectrophotometer having 290nm UV wavelength. Subsequently, the percentage of CP extraction was calculated using [20]:

$$\text{Extraction Efficiency (E \%)} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where  $C_0$  and  $C$  represent the initial CP concentration and the CP concentration after a specified time interval, respectively.

### B. Stripping

The resulting emulsion was allowed to be naturally separated from the feed solution by gravity, then a demulsification process was achieved by applying centrifugal force on the emulsion. The CP concentration extracted from the internal aqueous solution was measured, and the stripping efficiency was then estimated according to [20]:

$$\text{Stripping (S\%)} = \frac{C_{f,int}}{C_0 - C_{f,ext}} * 100 \quad (2)$$

where  $C_{f,int}$  and  $C_{f,ext}$  represent the final CP concentration in the internal and external phases, respectively.

### C. Membrane Leakage/Breakage

Stabilization is achieved by adding the surfactant, thus the extraction efficiency of any solute is mainly affected by emulsion stability [21]. The breakdown of the emulsion usually occurs after a period when the emulsion is considered unstable, causing a gradual lowering of the removal efficiency along with a significant loss of extracted species [22]. The stability of the liquid membrane is considered the most essential factor affecting the efficiency of solute removal [23]. The tracer method ( $H^+$  ion of the internal phase) was used to evaluate the stability because this tracer is easily detectable by a pH meter. Breakage is the result of tracer transfer from internal-to-external phase solutions. Any alteration in the pH of the feed

phase (i.e. leaking  $H^+$  ions) results from the emulsion breaking (rupture) because of the excretion of the HCl from the internal to the external aqueous phase. The emulsion rupture or breakage ( $\varepsilon$ ) signifies the internal aqueous phase volume leaked to the external feed aqueous phase ratio using [20]:

$$\varepsilon(\%) = \frac{V_s}{V_i} * 100 \quad (3)$$

where  $V_s$  represents the leaked volume of the stripping phase (internal phase) and  $V_i$  represents the initial volume of the internal stripping phase.  $V_s$  was computed using [24]:

$$V_s = V_b^\circ * \frac{10^{-pH_o} - 10^{-pH}}{10^{-pH} - C_{H^+}^{int}} \quad (4)$$

where  $V_b^\circ$  is the external feed phase initial volume,  $pH$  is the external feed pH having been in contact with the organic emulsion,  $pH_o$  is the initial external phase pH, and  $C_{H^+}^{int}$  is the initial acid concentration ( $H^+$ ) of the internal phase solution.

#### IV. RESULTS AND DISCUSSION

##### A. Effect of Internal to Membrane Phase Volume Ratio

The volume ratio of the internal to organic membrane phase must be satisfied to achieve a better transfer rate of the solute within the organic membrane and reduce emulsion interface thickness [25]. The appropriate amount of volume ratio improves solute transport through the organic membrane. Different internal-membrane phase ratios (1:3, 1:2, 1:1, 2:1, 3:1) were selected to study their influence on emulsion stability, in addition to the CP removal efficiency. Figure 2 shows the profiles of emulsion breakage percentage and extraction and stripping efficiency. Increasing the ratio from 1:3 to 1:1, i.e. equalizing membrane phase with internal phase volume, caused a decrease in breakage from 2.44% to 0.82% and increased the extraction and stripping efficiencies of CP to a maximum of 90.3% and 86.2%, respectively. This could be because at a lower volume ratio (1:3), an abundance of oil phase volume led to the creation of a thicker interface and more viscous emulsion that hindered internal phase diffusion into the membrane [20].

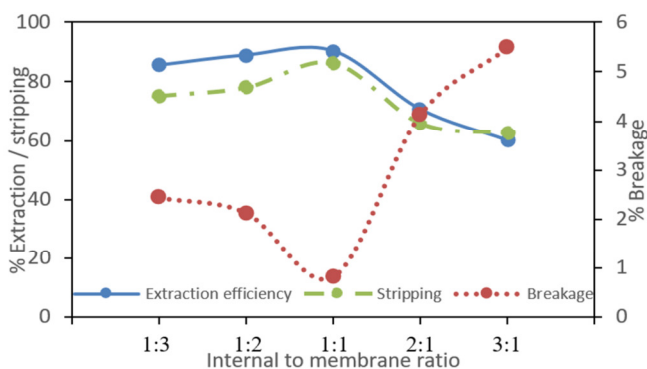


Fig. 2. Effect of internal-to-membrane ratio on membrane breakage percentage, extraction, and stripping efficiencies (stirring speed: 300rpm for 5min, external pH = 7, external to emulsion phase volume ratio: 10/1).

Additionally, at low volume ratios, the lowering in extraction efficiency due to a smaller amount of the internal

phase (stripping agent) extracted the solute from the organic membrane phase. A further increase in ratio from 1:1 to 3:1, i.e. increasing the volume of the internal phase related to the organic membrane phase, caused an evident waning in stability. Breakage elevated to 5.48%, while extraction and stripping efficiencies reduced to 61.1% and 62.7%, respectively. This decrease in efficiency occurred because of the insufficient membrane volume that caused a partial entrapment of the internal droplet, hence, droplets tended to leak out of the bubble towards the aqueous feed phase [26]. Similar results were recorded in [27]. Therefore, a 1:1 volume ratio of internal to organic membrane phase was designated and considered the best ratio to achieve the highest extraction efficiency.

##### B. Effect of External to Emulsion Volume Ratio

Experiments were carried out for the following ratios: 250/10, 250/25, 250/50, 250/75, and 250/100, by altering the emulsion volume only while maintaining a fixed volume of external feed aqueous phase. Figure 3 displays the extraction, stripping efficiency, and emulsion breakage percent for different treatment ratios.

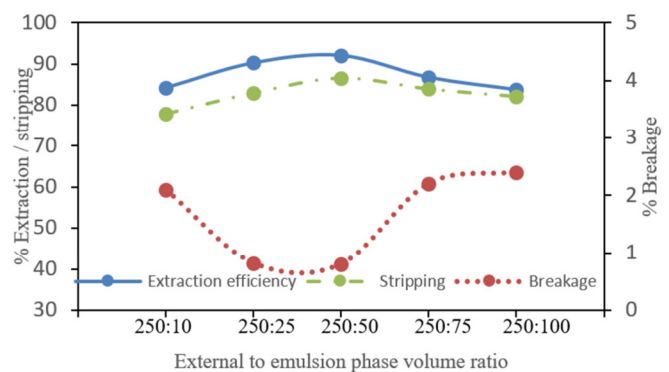


Fig. 3. Effect of external-to-emulsion phase ratio on membrane breakage percentage, extraction, and stripping efficiencies (stirring speed: 300rpm for 5min, internal to membrane ratio: 1/1, external phase pH = 7).

The results show that a decrease in the treatment ratio to 250/50 improved extraction efficiency and decreased breakage from 84.3% and 2.1% to 92.1% and 0.8%, respectively. With decreasing the ratio, the swelling phenomena develop and become fast, and also an occurrence of substantial internal droplets coalescence that will eventually grow in size [20]. This could be explained that due to the volume increase of emulsion, more quantity would be available to add to the progress of CP transport. Furthermore, a big volume of the emulsion favors an enormous number of globules formation in providing a vast surface area for exchange, thus an enhanced rate of solute transfer. Another possible reason could be because of the increase in emulsion holdup that further increases the interfacial area for a better rate of mass transfer [28]. Further decreasing the volume ratio to 250/100 causes a substantial reduction in extraction efficiency to 83.9%. This could be due to the limited interfacial area available for the solute mass transfer rate, owing to the challenges in dispersing the emulsion into the aqueous feed solution due to the emulsion's large

volume that increases its total viscosity causing an adverse effect on the interfacial area [29]. As a result, the 250/50 treatment ratio was chosen as the best ratio.

### C. Effect of Mixing Time

Mixing time can be specified as the time required to achieve maximum extraction and is a necessary factor in the ELM process [30]. Mixing time, also known as contact time, is defined as the period in which the external feed phase stays in direct contact with the emulsion while continuously stirring [31, 32]. Figure 4 shows the effect of mixing time on emulsion breakage and the percentages of extraction and stripping for times ranging from 2 to 20 minutes. When increasing mixing time, CP extraction and stripping efficiency keep increasing, reaching an optimal level at 10min of 93.8% and 94.7%, respectively, while the breakage percentage is reduced to a minimum of 0.73%. Longer contact time would cause the internal phase solution to move toward the feed solution due to the increased emulsion breakage [33, 34]. Therefore, the extracted molecules revert backward to the feed phase, decreasing extraction and stripping efficiencies. Therefore, a mixing time of 10 minutes was chosen as the optimal period to extract CP.

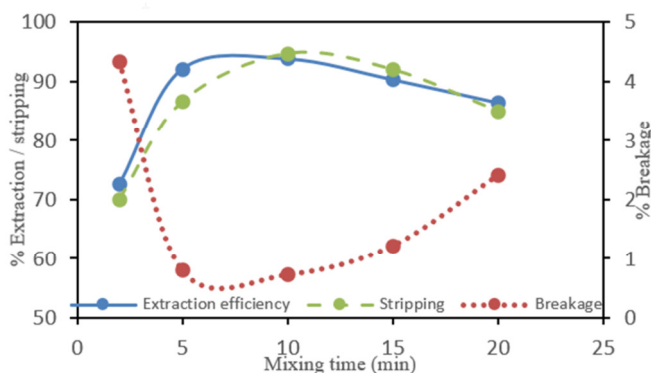


Fig. 4. Effect of mixing time on membrane breakage, and extraction and stripping efficiencies (stirring speed: 300rpm, external phase pH = 7, feed phase to emulsion ratio: 5/1, internal to organic membrane ratio: 1/1).

### D. Effect of External Phase pH

The pH of the external phase is a significant factor for extraction purposes [35]. Additionally, pH also influences membrane stability, considering that it can accelerate the emulsion demulsification process. The tests were carried out at different pH values in basic, neutral, and acidic mediums ranging from pH 3 to 8. Figure 5 presents the effects of external feed pH on extraction percentage, stripping efficiency, and organic emulsion breakage. CP extraction and stripping efficiency are exceedingly influenced by the external phase pH. For a highly acidic solution of pH=3, the extraction and stripping efficiencies were 62.72% and 85%, respectively, while the emulsion breakage was found to be at its peak at 7.41%. This could be attributed to the higher H<sup>+</sup> ion concentrations which reduce the surfactant properties [12], causing a de-stabilization process that leads to a drop in CP extraction efficiency. The higher the initial concentration of H<sup>+</sup>, the lower the extraction efficiency is [36]. When increasing pH

towards a neutral medium (pH=6), increase in both extraction and stripping efficiency occurs, reaching maximum values of 95.3% and 97.2%, respectively, while the breakage percentage is reduced to 0.69% within 10min of stirring time. However, the CP extraction efficiency decreases continuously when further increasing pH, while the breakage increases gradually at 82.8% and 1.89%, respectively, for pH=8. This could be explained by the released protons as the result of an anion exchange reaction [37]. Also, due to the increase in pH, a formation of other species occurs [36]. Therefore, it was appropriate to maintain the pH of the external feed phase at 6.

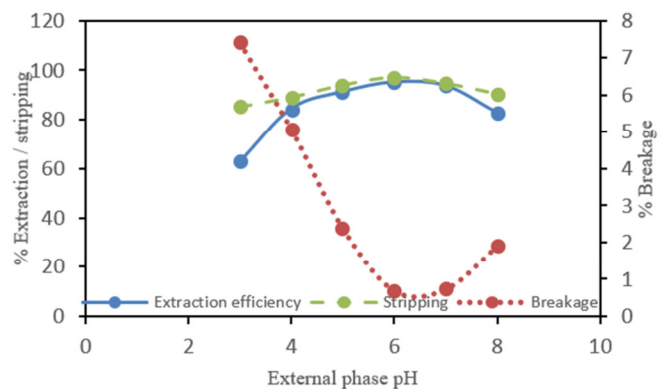


Fig. 5. Effect of external phase pH on membrane breakage, extraction, and stripping efficiency (stirring speed: 300rpm for 10min, feed phase to emulsion ratio: 5/1, internal to organic membrane ratio: 1/1).

### E. Effect of Stirring Speed

A set of experiments was conducted to study the effect of different mixing speeds (200, 250, 300, and 350rpm) on extraction efficiency, stripping efficiency, and membrane breakage, while the other parameters were: mixing time: 10 min, external phase pH=6, external phase to emulsion volume ratio: 5/1, and internal to organic membrane phase ratio: 1/1. Figure 6 displays the experimental results. At lower mixing speeds (200rpm), a minimum membrane breakage value was recorded (0.81%) due to the insufficient shear that resulted from the impeller dispersing emulsion. This could be because lower stirring speeds cause the formation of large globules, increasing the membrane thickness. Although low values of membrane breakage were noted, slow stirring speeds do not usually improve the extraction and stripping efficiencies (89.39% and 93.6%, respectively, for 200rpm stirring speed), since large globules of emulsion minimize the available area for mass transfer [38]. However, using high mixing speeds (over 250rpm) was not beneficial neither to emulsion stability nor to extraction efficiency (2.63% and 84.84%, respectively, for 350rpm). Figure 6 proves that increasing speed above 250rpm leads to the deterioration of the organic membrane. Elevated levels of membrane leakage are predicted at higher mixing speeds since the emulsion can not bear the excessive shear delivered by impellers in addition to the contactor wall [39], causing an easy rupture of the membrane wall, discharging the already extracted solute into the feed phase. As the emulsion was produced from a viscous component, the stability of the emulsion was sustained at 250rpm stirring speed

because of the rigid membrane wall. At 250rpm stirring speed, 0.66% membrane breakage, 96.1% extraction percentage, and 95.7% stripping efficiency were registered. Thus, 250rpm was considered the critical speed of stirring.

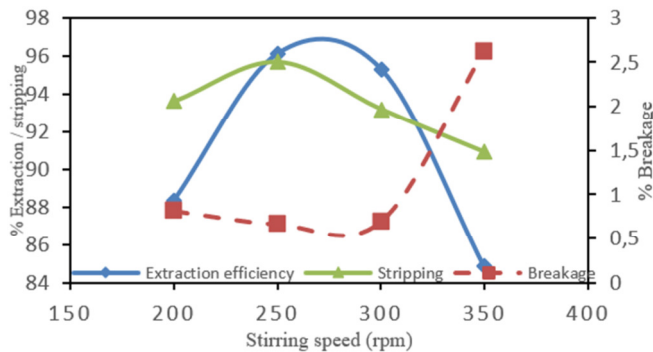


Fig. 6. Effect of stirring speed on membrane breakage, extraction and stripping efficiencies for 10min (external phase pH = 6, external to organic emulsion volume ratio: 5/1, and internal to membrane volume ratio: 1/1).

#### F. F. Evaluation of the Solute (CP) Extraction Kinetics and Estimation of Mass Transfer Coefficient

The extraction kinetics of CP using the ELM method were investigated following the approach in [40, 41], using the first-order equation:

$$\ln\left(\frac{C}{C_0}\right) = -K_{obs} \cdot t \quad (5)$$

where  $t$  represents time in minutes, and  $K_{obs}$  is the rate constant of extraction ( $\text{min}^{-1}$ ), which can be evaluated from the slope of the resulting line from the previous equation representing the  $K_{obs}$  value. Because the obtained value was positive, the extraction process follows the first-order kinetics. The obtained  $K_{obs}$  value was  $0.2173\text{min}^{-1}$ . The total mass transfer coefficient for the ELM system was found by [42]:

$$\frac{1}{K_T} = \frac{1}{K_F} + \frac{1}{K_M} \quad (6)$$

where  $K_T$  is the total mass transfer coefficient (m/s),  $K_F$  is the interfacial reaction rate constant (m/s), and  $K_M$  represents the mass transfer coefficient of the external phase (m/s), estimated by the Skelland-Lee correlation [40] given by:

$$\frac{K_M}{\sqrt{ND}} = 2.932 \cdot 10^{-7} \left( \frac{V_i + V_m}{V_i + V_m + V_e} \right) Re^{1.371} \left( \frac{d}{T} \right)^{0.548} \quad (7)$$

where  $N$  is mixing speed (rpm),  $T$  and  $d$  are the mixing tank and impeller diameter (m), respectively,  $V_i$ ,  $V_e$ , and  $V_m$  denote the internal, external, and membrane phase volumes, and  $D$  represents the species diffusivity (CP) in the organic membrane phase, determined using Wilke-Chang correlation [43] shown in (9).

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

where  $\rho_{ext.}$  is the density ( $\text{kg/m}^3$ ) and  $\mu_{ext.}$  is the viscosity ( $\text{kg/m}\cdot\text{s}$ ). The calculated  $Re$  value was equal to 348577.

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

where  $M$  is the solvent molecular weight (n-hexane=86.18 kg/Kmol),  $Temp$  is the temperature in kelvin,  $\phi$  is the solvent association factor (n-hexane=1),  $\mu_m$  is the membrane viscosity ( $12.224 \times 10^{-3} \text{Kg/m}\cdot\text{s}$ ), and  $\phi_c$  is the molar volume of the CP evaluated using Schroeder method [44]. The  $\phi_c$  was  $0.399 \text{m}^3/\text{kmol}$ ,  $D$  was  $6.79 \times 10^{-10} \text{m}^2/\text{s}$ , and  $K_M$  was  $2.6 \times 10^{-4} \text{m/s}$ .  $K_F$  was calculated through:

$$\ln\left(\frac{C}{C_0}\right) = -A \cdot K_F \cdot t \quad (10)$$

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

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

where  $A$  represents the emulsion-specific interfacial area, given by [45]:

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

where  $A_i$  is the interfacial area of the emulsion droplet,  $V$  is the unit volume of the emulsion,  $\alpha$  represents the water volume fraction, and  $d_{32}$  represents the diameter of the emulsion droplet. Finally, the calculated mass transfer coefficients were:  $K_M = 2.6 \times 10^{-4} \text{m/s}$ ,  $K_F = 3.89 \times 10^{-9} \text{m/s}$ , and  $K_T = 3.89 \times 10^{-9} \text{m/s}$ .

#### V. CONCLUSIONS

This study investigated the stability and extraction efficiency of ELM for removing chlorpyrifos pesticide from wastewater. A minimum emulsion breakage of 0.66% along with the highest removal percentage of 96.1% and 95.7% stripping efficiencies were achieved at the best operating experimental conditions, which were: internal-to-membrane volume ratio: 1:1, external feed solution pH: 6, stirring speed: 250rpm, external phase-to-emulsion ratio: 250:50 at 10min contact time, no requirement of an additional carrier, and the mass transfer coefficients  $K_M$ ,  $K_F$ , and  $K_T$  had values of  $2.6 \times 10^{-4} \text{m/s}$ ,  $3.89 \times 10^{-9} \text{m/s}$ , and  $3.89 \times 10^{-9} \text{m/s}$ , respectively. In general, it can be concluded that ELM is a productive, efficient, and suitable advanced separation method for the treatment of wastewater contaminated with pesticides.

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