Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2023.29542

295 (2023) 30–41
May

Emulsion liquid membrane for removal of pesticides from aqueous solution: emulsion stability and effect of operational parameters

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Received 20 November 2022; Accepted 4 April 2023

ABSTRACT

The removal of lambda-cyhalothrin (LCT) from an aqueous solution was investigated and evaluated by the emulsion liquid membrane (ELM) technique using Span 80 as the surfactant, *n*-hexane as the diluent, and HCl as the stripping phase. Crucial parameters influencing the stability of emulsions through breakage and extraction efficiency, such as emulsification time, surfactant concentration, contact time, emulsification speed, internal phase concentration, external phase-to-membrane volume ratio, effect of feed pH, mixing speed, and internal phase-to-membrane volume ratio were investigated. The results indicated that 94.7% of LCT could be extracted at a contact time of 8 min under ideal experimental conditions, with a low membrane breakage of 0.48%. Furthermore, the extraction kinetics were investigated and the mass transfer coefficient was estimated. Based on the obtained results, the ELM technique could be a promising alternative method to minimize environmental pollution caused by pesticides to a large extent.

Keywords: Emulsion liquid membrane; Lambda-cyhalothrin; Emulsion droplet size; Stability; Mass transfer coefficient; Extraction efficiency

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1. Introduction

The quantity and quality of crops depend on their protection from diseases and pests. Approximately 26%–40% of the global crop production is lost annually to pests, diseases, and weeds [1]. The use of pesticides promotes crop protection, which increases food productivity, improving yield of safe food products at reasonable prices. Pesticides also help farmers deliver sufficient nutritious foods throughout the year, which are necessary for the survival of humans. Pesticides are a heterogeneous group of compounds with diverse biological and physicochemical properties. The emergence of these contaminants is considered a public health concern. Therefore, they have been studied extensively worldwide; however, no final solution has been provided [2]. They are considered a major concern in various areas of the world [3]. The global production of these contaminants is approximately 3.5 million tons/y [4]. Approximately 0.1% of pesticides reach their target during application, whereas the remaining 99.9% may be released into the environment, including surface water and groundwater [5]. Furthermore, many types of contaminants are considered stable over time; consequently, pesticides can be transported through air and water to areas far away from the point source [6]. Even sporadic use of pesticides affects ecosystems because of their biomagnification and persistence [7], which threatens birds, fish, domestic animals, wildlife, and livestock [8]. Depending on their chemical structure, pesticides are classified as organochlorines, organophosphorus, carbamates, chlorophenols, and synthetic pyrethroids [9]. Approximately 29.5% of pesticides utilized annually are insecticides [10]. Lambda-cyhalothrin (LCT) is a synthetic insecticide with the same properties as natural pyrethroid pesticides [11] and is extremely toxic to aquatic life and carcinogenic to humans [12]. It is widely used in agriculture, horticulture, and public health management, consequently entering the human body via the digestive

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system and causing adverse effects on health through bioaccumulation in different organs [13]. The removal of pesticides from water sources is considered a crucial research domain because of the high concentration and recalcitrance of pesticides in wastewater [14–17]. The choice of suitable treatment methods for the removal of pesticides depends on the type of pesticide used and the efficiency of the utilized treatment [18]. Several techniques have been developed to remove pesticides from aqueous solutions. Each method has its own advantages and limitations, not only in terms of operational and capital costs but also in terms of reliability, operability, efficiency, environmental impact, pretreatment requirements, and the production of toxic and sludge by-products. These techniques include adsorption [19–27], oxidation [28], ion exchange [29], biodegradation [30,31], electrochemical processes [32], photo degradation [33,34], solvent extraction [35,36], advanced oxidation [37–42], pressure-driven membrane process [43–51], liquid membrane process [52–55], and bioremediation [56]. All methods used to remove pesticides depend on numerous factors such as the nature of the pesticide, pH, temperature, type of matrix, and cost of investment [57]. As it is a cost-effective process, membrane technology has been utilized extensively in water purification over the last few decades [49]. The emulsion liquid membrane (ELM) technology has become a favorable alternative to the usual practices currently employed for water and wastewater treatment [58]. In this process, both extraction and stripping occur during a single stage, leading to the simultaneous purification and concentration of the solute [59]. Emulsion stability is a major problem associated with ELM [59]. The instability of globules is one of the most significant challenges in the application of ELM technology. The key factors affecting emulsion stability include emulsion preparation and membrane formulation [59]. The stability of ELMs is extremely important and must be optimized before utilization [60]. A carrier agent is used in some liquid membrane systems to facilitate the transfer of solutes, resulting in additional costs [61]. In this study, an LCT aqueous solution was treated with *n*-hexane in the absence of a carrier agent. The ELM technique has been increasingly adopted for the extraction and recovery of different compounds (both organic and inorganic) from aqueous waste solutions [62,63]. Phenolic compounds [64], metal recovery [65,66], radioactive and heavy metal ions [67], biological product recovery [68], and gas separation from gaseous mixtures [69] are examples of the application of liquid membrane technology. To the best of our knowledge, no previous study has examined or evaluated the extraction efficiency of LCT using ELM.

The objective of the present study was to investigate the effects of homogenizer speed, surfactant concentration, emulsification time, extraction time, membrane-to-internal phase ratio, stripping agent concentration, treatment ratio, and agitation speed on membrane stability. In addition, the capacity of ELM to remove LCT from aqueous solutions (extraction and stripping efficiencies) was explored.

2. Materials and method

2.1. Materials

LCT, manufactured in Jordan, was purchased from a local market. The chemical structure of LCT ($C_{23}H_{19}ClF_3NO_3$) is shown in Fig. 1. Its physicochemical properties are molar mass: 449.85 g/mol, density: 1.33 g/mL, melting point: 49.2°C, relative density: 1.3, pKa at 20°C >9, vapor pressure: 1.5×10^{-9} mm Hg at 20°C, and degradation point: 275°C, and it decomposes before boiling [59,60]. Hydrochloric acid and sodium hydroxide used in this study were obtained from Thomas Beaker (India). The liquid membrane phase solution consists of a diluent and surfactant. In this study, the diluent used was *n*-hexane obtained from Thomas Beaker (India) while the non-ionic surfactant was sorbitan monooleate, commonly known as Span 80, obtained from Merck, Darmstadt, Germany (Sigma-Aldrich). All chemicals used with no additional purification. All lab tests are performed at room temperature (20°C ± 2°C).

2.2. Feed solution preparation

In the external feed phase, 100 mg/L was formulated when dissolving LCT in distilled water beaker flask by dissipating the specified amount of LCT. Subsequently, pH was then adjusted and controlled by the addition of NaOH or HCl as required. LCT concentrations were analyzed using an ultraviolet (UV)-visible spectrophotometer (PG Instruments, T80+ UV/VIS Spectrometer) at a wavelength corresponding to the highest absorbance (240 nm for LCT). Tests are conducted in triplicate, and average results were then reported.

2.3. Membrane preparation and extraction procedure

The organic membrane is assembled by mixing *n*-hexane with surfactant (Span 80) employing gentle stirring using a magnetic stirrer. An internal aqueous solution was prepared by adding a suitable amount of acid solution (HCl) to distilled water. In order to, form an emulsion, the internal aqueous solution is added dropwise into the organic membrane. phase. while mixing, using a homogenizer (MTOPS SR30) for a specified amount of time. Fig. 2 shows the schematic diagram of ELM process.

The emulsion. was dispersed into the feed aqueous solution which contains the contaminant to be extracted using a mechanical stirrer (Heidolph RZR 2021). Dispersion occurs with the formation of globules, which contain droplets of internal stripping solution entrapped within the membrane that includes the surfactant. Samples were collected from the mixture at certain time periods by a syringe. Each sample

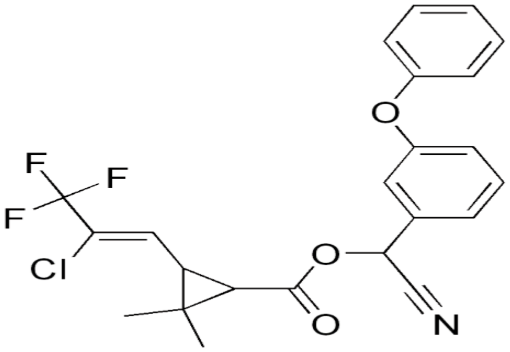

Fig. 1. Chemical formula of lambda-cyhalothrin [61].

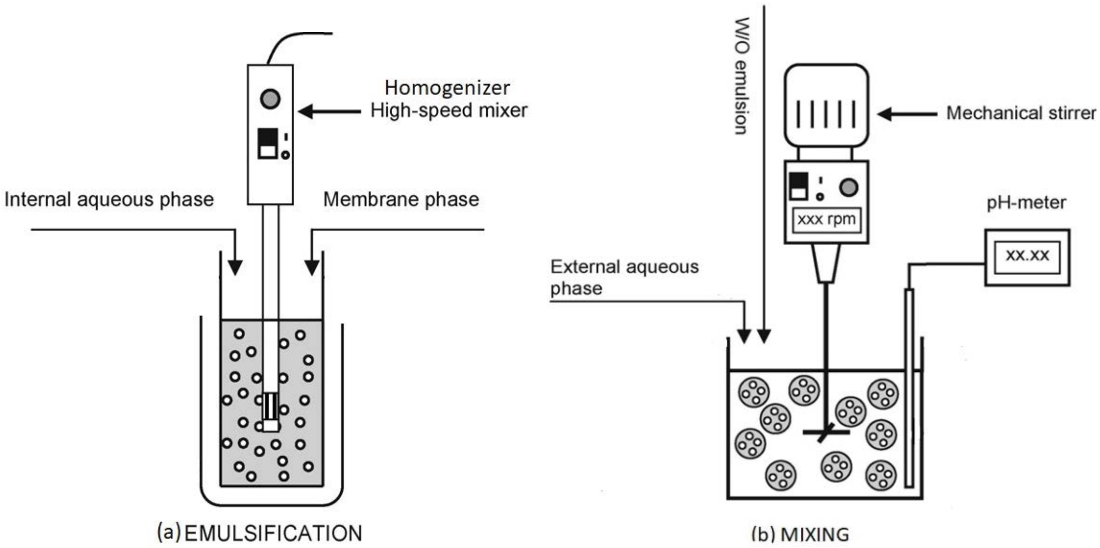

Fig. 2. Schematic diagram of emulsion liquid membrane process.

Table 1
Parameters investigated during LCT extraction

Parameter	Range
Homogenizer (emulsification) speed (rpm)	3,000; 5,800; 12,700; 19,700
Emulsification time (min)	2–15
Mixing speed (rpm)	200, 250, 300, 350
Span 80 concentration (% v/v)	1–5
Stripping agent concentration (M)	0.05–0.45
External phase-to-emulsion ratio (% v/v)	25:1, 25:2.5, 25:5, 25:7.5, 25:10
External feed phase pH	3–9
Internal phase-to-membrane ratio (% v/v)	1:3, 1:2, 1:1, 2:1, 3:1

that contained both emulsion and external phase solutions was filtered through a syringe filter having a pore size of 0.22 μm. After extraction, the emulsion was allowed to separate from the feed solution by gravity, and a demulsification process was carried out to separate both phases of the emulsion membrane, facilitating reuse of the membrane solution while the contaminant was extracted as a concentrated solution. Experiments were performed considering membrane stability. The major parameters affecting extraction include emulsification time, surfactant concentration, homogenizer speed, mixing speed, external phase-to-emulsion ratio, internal-to-membrane ratio, internal phase concentration, external feed initial concentration, and pH. The effects of these parameters were examined and the most suitable conditions for LCT extraction were determined. Demulsification by exerting centrifugal force on the emulsion was also studied to determine the stripping capacity of the LCT. The operating parameters and their corresponding ranges are tabulated in Table 1.

3. Analysis and calculations

3.1. Extraction process of LCT

The LCT concentration within the separated external phase was measured. via a UV spectrophotometer. LCT extraction efficiency ($E\%$) is then estimated by the following equation.

$$\text{Extraction efficiency}\left(E\%\right)=\frac{C_o-C}{C_o}\times 100 \quad (1)$$

where C_o represents the initial LCT concentration in the external aqueous feed solution and C represents the LCT concentration after a specified time in the feed phase aqueous solution.

3.2. Stripping

At the end of each experiment, the resulting double emulsion was allowed to be naturally separated from the feed solution by gravity, and then subjected to a demulsification process by applying centrifugal force (Hettich Instruments, EBA 200). The concentration of LCT re-extracted from the internal aqueous solution was estimated and the stripping efficiency ($S\%$) was estimated according to the following equation.

$$\text{Stripping efficiency}\left(S\%\right)=\frac{C_{f,\text{int}}}{C_o-C_{f,\text{ext}}}\times 100 \quad (2)$$

where $C_{f,\text{int}}$ represents the final LCT concentration in the internal aqueous solution, and $C_{f,\text{ext}}$ represents the final LCT concentration in the external aqueous solution.

3.3. Membrane leakage/breakage

When dispersing the emulsion into the aqueous feed, the dispersed emulsion has to be stable enough to achieve

LCT molecules extraction. Stabilization is achieved by adding a surfactant; thus, the degree of extraction for any solute is affected by the emulsion stability. Emulsion breakdown usually occurs after a period of time when the emulsion is considered unstable, causing a decrease in extraction efficiency, in addition to a significant loss of the species extracted [49].

The liquid membrane stability is considered the most essential factor affecting the solute removal efficiency. Emulsion breakage (ε) is the percentage ratio of the internal stripping phase leaked outwards into the external aqueous feed solution. It can be estimated using the following general equation:

$$\varepsilon(\%) = \frac{V_s}{V_i^o} \times 100 \tag{3}$$

where V_s represents the stripping phase (internal phase), V_i^o represents initial volume of the stripping phase, while V_s value is determined using the following equation [62]:

$$V_s = V_b^o \times \frac{10^{-\text{pHo}} - 10^{-\text{pH}}}{10^{-\text{pH}} - C_{\text{H}^+}^{\text{int}}} \tag{4}$$

where V_b^o represents the external feed phase initial volume; pH represents external feed phase pH after maintaining contact with the emulsion; pHo represents the initial external phase pH; and $C_{H^+}^{\text{int}}$ represents the initial acid concentration [H$^+$] of the internal phase solution.

4. Results and discussion

4.1. Membrane stability

Emulsion stability. is considered a crucial factor and an essential condition for a successful ELM process because low stability leads to easy breakup of the emulsion, whereas extremely high stability hinders the breakup of the emulsion via mechanical processes. Therefore, the membrane stability must be optimized before use. In this study, the effects of emulsification time, emulsification speed, surfactant concentration, internal phase concentration, internal to membrane phase volume ratio, and pH on emulsion stability were explored. The parameters associated with the breakage values are presented in Table 2.

Membrane breakup is related to extraction efficiency; a significant decline in the efficiency of separation is due to a leakage process of the already separated. contaminant, leaking from the internal towards the external phase [63]. Minimal breakage values indicate improved extraction efficiencies. The results in Table 2 and their corresponding extraction efficiencies are discussed in the subsequent sections of this paper.

4.2. Effect of emulsification speed

Emulsification speed can be considered a significant parameter that influences the emulsion stability, thereby affecting the entire extraction process. In this study, emulsification speed was considered at the range specified in Table 1, while the other parameters values are emulsification time, 10 min; LCT concentration, 100 mg/L; external-to-emulsion phase ratio, 250:50; Span 80 concentration, 4% (v/v); stripping agent concentration, 0.25 M HCl; mixing speed, 250 rpm; external phase pH, 6; and internal-to-membrane volume ratio, 1:1. The effect of homogenizer speed on the emulsion stability; Table 2; demonstrates that a minimum value of percentage breakage (2.09%) occurs at a 12,700 rpm homogenizer speed. A homogenization speed below 12,700 rpm reduced the stability and breakage percentage owing to vast droplet size, causing a coalescence

Table 2
Emulsion breakage values acquired at different experimental conditions

Parameter	Value	Ɛ (%)
Emulsification speed (rpm)	3,000	3.22
	5,800	2.71
	12,700	2.09
	19,700	5.01
Emulsification time (min)	4	3.72
	5	1.49
	7	1.84
	10	2.09
	15	4.37
Surfactant concentration (% v/v)	1	7.39
	2	4.64
	3	1.77
	4	1.49
Stirring speed (rpm)	200	4.03
	250	1.77
	300	2.85
	350	3.96
pH of feed solution	3	5.33
	4	3.28
	5	0.28
	6	1.77
	7	1.98
	8	2.15
Internal (stripping) phase concentration (M)	0.05	4.25
	0.15	2.43
	0.25	0.48
	0.35	1.71
	0.45	2.08
(Internal/membrane) phase volume ratio	3:1	10.03
	2:1	7.62
	1:1	0.48
	1:3	3.37
	1:2	5.29
External phase-to-emulsion ratio	25:1	3.36
	25:2.5	3.21
	25:5	0.48
	25:7.5	2.81
	25:10	2.64

phenomenon, during a small period of time. In addition, increasing homogenizer speed above 12,700 rpm may escalate the osmotic swelling, thus reduce the stability of the emulsion, that is, increasing breakage.

Results demonstrated in Fig. 3 indicate the effect of emulsification speed at 10 min emulsification time on extraction efficiency. When increasing emulsification speed from 3,000 rpm to 12,700 rpm, the solute removal percentage improved from 75.4% to 87.6%, along with an improved stripping efficiency (from 72.5% to 83.1%). This can be attributed to the small-sized droplet at higher emulsification speeds, leading to a substantial rise in the droplet surface area, thereby accelerating the solute mass transfer rate [64]. In contrast, a higher increase in emulsification speed till 19,700 rpm decreased both extraction and stripping efficiencies to 69.4% and 69.2%, respectively, owing to the generation of larger size emulsion droplets, consequently intensifying the coalescence phenomenon occurring simultaneously. Mohammed and Al-Khateeb [65] detected a 0.83% breakage in ELM at a homogenizer speed of 12,700 rpm during phenol extraction process. Accordingly, a 12,700 rpm was the best emulsification speed.

4.3. Effect of emulsification time

A satisfactory time of emulsification to entrap the internal stripping phase within the membrane phase should be specified to achieve the best ELM system. Emulsification times considered in this study were 4, 5, 7, 10, and 15 min, while remaining variables were set at an emulsification speed of 12,700rpm, mixing speed of 250 rpm, (external phase/emulsion) volume ratio of 250:50, LCT concentration 100 mg/L, internal-to-organic phase volume ratio of 1:1, Span80 concentration 4% (v/v), external phase pH of 6, internal (stripping) phase concentration of 0.25 M HCl. The stability of emulsions was investigated at different emulsification times over a time ranging from 4–15 min. Results presented in Table 2 indicate that the minimum value of breakage (1.49%) was observed at an emulsification time of 5 min. For values less than 5 min emulsification time, breakage value increased due to the high size of droplets, which results in droplet coalescence. Salman and Mohammed [66] observed higher emulsion breakage values at shorter emulsification times. Any additional increase over 5 min in emulsification time led to breakage escalation, reaching its maximum value at 15 min. This could be due to the high internal shear force that largely assists in developing a large number of smaller droplets per unit volume; therefore, it becomes favorable owing to droplet diffusion into the external aqueous feed solution [67]. A high percentage of breakage induces a lower extraction efficiency of LCT from aqueous solutions. Fig. 4 shows emulsification time effect on the efficiency of extraction. The LCT extraction efficiency was approximately 84.8% at 4 min emulsification time, while the extraction efficiency reached 89.3% at 5 min emulsification time owing to a decrease in size of droplets constituent of the internal phase solution, which in turn enhances dispersed phase homogeneity. In contrast, a significant decrease occurred in extraction efficiency from 89.3% to 78.8% when increasing emulsification time from 5 to 15 min, owing to the coalescence phenomenon of droplets comprising the internal aqueous phase [68]. Therefore, a (5 min) emulsification time was chosen for further studies.

4.4. Effect of surfactant concentration

Typically, a surfactant is required for an ELM system. In this study, it was added as an emulsifier. The effects of surfactant concentration on stability and extraction efficiency were explored. Experiments were performed to conclude the optimal surfactant concentration. The emulsification speed and emulsification time from the previously mentioned experiments were used, while different concentrations of surfactant were implemented (1%, 2%, 3%, and 4% v/v). The other parameters were set at an external phase-to-emulsion volume ratio of 250:50, LCT concentration of 100 mg/L, mixing speed of 250 rpm, internal phase-to-membrane phase volume ratio: 1:1, external phase pH 6, and 0.25 M internal phase concentration.

Table 2 indicates that the stability increased when increasing surfactant concentration. Nevertheless, a significant rise in surfactant concentration has major drawbacks. A considerable difficulty in emulsion breakup when completing the process and a greater resistance to solute (LCT) transfer are encountered [69]. The surfactant forms aggregates in the bulk solution when sufficient concentration is added, which is called the critical micelle concentration. These aggregates promote water transport to the external aqueous phase solution (swelling) or to the internal phase solution (breakage). A considerably high emulsion rupture occurs when the surfactant concentration is considered insufficient for the surrounding and encapsulating

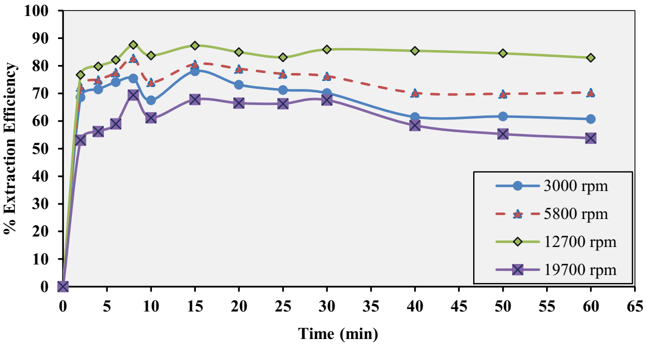

Fig. 3. Effect of emulsification speed on extraction efficiency.

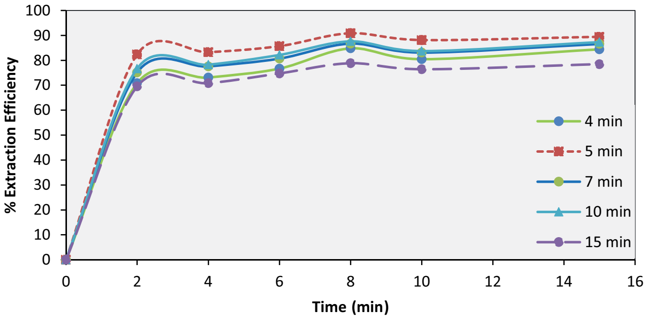

Fig. 4. Effect of emulsification time on extraction efficiency.

the internal phase molecules. Therefore, a sufficient surfactant concentration should maintain a stabilized emulsion, but if a high increase in surfactant concentration occurs, it causes a higher viscosity of emulsion, leading to a decrease in extraction. efficiency [70].

Fig. 5 displays the effects of different surfactant concentrations on extraction. efficiency. The extraction efficiency increased when increasing surfactant concentration up to 3% (v/v) concentration, where LCT extraction and stripping efficiencies reach 90.9% and 84.9%, respectively. When raising concentration from 3% to 4%, the emulsion stability improved. Conversely, LCT extracted from feed phase decreased from 90.9% to 81.4% and the stripping efficiency decreased from 84.9% to 76.5%. Previous studies have reported that the surfactant can reduce the oil and water interfacial tension, which is attributed to the adsorption occurring at the liquid.–.liquid interface, thereby maintaining emulsion stability when the solute is transferred into the membrane [62].

The membrane stability increased at 4% emulsifier concentration; however, the extraction efficiency decreased. Thus, a 3% (v/v) Span80 concentration was elected as the optimum concentration to generate a stable emulsion in addition to ensuring the highest extraction efficiency.

4.5. Effect of stirring speed

Mixing speed or stirring speed is considered a beneficial aspect of extraction for the ELM separation technique since agitation (mixing) is required to create a uniformed dispersion of the emulsion on a broad interfacial area. Higher stirring rates in the experiments led to smaller globule formation, therefore enlarging the interfacial area between the membrane and phases, consequently causing a rise in the mass transfer rates. In addition, a higher speed could cause additional swelling and, therefore, the rupture of globules. The effects of mixing speed on LCT efficiency of extraction are presented in Fig. 6. Emulsification speed and time were taken from previous experiments, along with Span 80 concentration, while other parameters remained the same: (LCT concentration, 100 mg/L; external-to-emulsion phase ratio, 250:50; stripping agent concentration, 0.25 M HCl; external phase pH, 6; and internal-to-membrane volume ratio, 1:1). The efficiency of extraction was considerably low (64.6%) at a low mixing speed (200 rpm). This could be attributed to the development of sufficiently large emulsion globules that decreases the area available for mass transfer, while maintaining a stripping efficiency of 66.09%. The calculated breakage percentage was 4.03% (Table 2) which could be because of the insufficient shear energy available for the dispersion of emulsion into the external phase therefore large globules were formed. Resulting in globules coalescing. Consequently, the occurrence of emulsion breakage. However, when increasing the speed up to 250 rpm, the shear forces affecting the emulsion globules increased, which reduced the globule's size. Therefore, when increasing stirring speed to 250 rpm, the area between internal and external phases increased and the extraction and stripping efficiencies increased significantly to 90.9% and 84.88%, respectively. Fig. 6 shows that when the agitation speed was further increased, a reduction in the extraction level occurred. The results revealed that increasing mixing speed to 250 rpm (which is considered the critical speed) to 300 rpm not only decreased the efficiency of extraction to 80.77% but also affected the emulsion stability (breakage percentage increased from 1.77% to 2.85%), thereby affecting the emulsion stability and the stripping efficiency considerably (57.18%), as reported by Davoodi-Nasab et al. [71]. It is possible that this could be the result of the excessive mixing speed being above the optimum value, which causes smaller emulsion globule size, therefore leading to the diminishing of the interfacial film, thus an occurrence of rapid coalesce of globules of the emulsion, which will eventually lead to breakage (membrane destruction) because of the high turbulence level at the membrane interface along with the partial separation of the membrane phase. Similar outcomes were recorded by Venkateswaran [72]. Therefore, a stirring speed of 250 rpm was elected as the best value in this study because it achieves an adequately stable emulsion in addition to an excellent LCT extraction efficiency.

4.6. Effect of pH in the feed solution

pH is considered an influential parameter in ion transportation by ELMs. In addition, it influences membrane stability, as low or high pH values can enhance the demulsification of emulsion droplets [73]. The effect of aqueous feed phase pH on the efficiency of extraction was investigated in the range from 3 to 8, when other previously obtained optimum conditions were used. Emulsification speed and time, 12,700 rpm and 5 min; LCT concentration, 100 mg/L; external-to-emulsion phase ratio, 250:50; Span

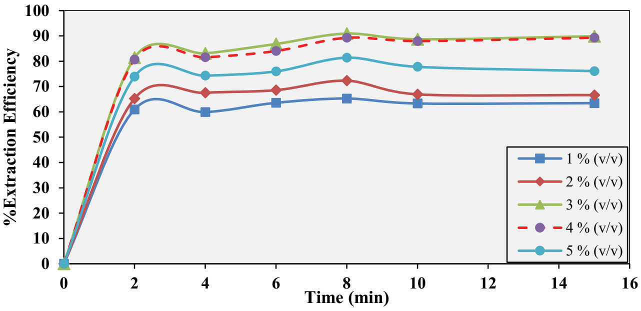

Fig. 5. Effect of surfactant concentration on. extraction efficiency.

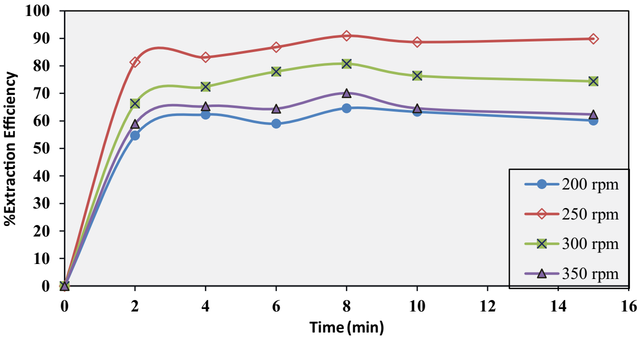

Fig. 6. Effect of mixing speed on extraction efficiency.

80 concentration, 3% (v/v); stripping agent concentration, 0.25 M HCl; mixing speed, 250 rpm; and internal-to-membrane volume ratio, 1:1. Fig. 7 shows that a highly acidic solution (pH 3), the efficiency of extraction is at its lowest value (72%), while the breakage is at its highest (5.33%), as presented in Table 2. This may be due to the higher H^+ ion concentration, which reduces the surfactant properties [74], consequently destabilizing the emulsion and decreasing the extraction efficiency. The higher H^+ initial concentration, the lower the extraction percentage. [73].

Notably, the extraction efficiency increased when the external phase pH increased to 5. Moreover, the extraction and stripping efficiencies reached maximum values of 93.06% and 84.7%, respectively, while the breakage percentage was minimal (ε = 0.28%) within a contact time of 8 min. However, for pH above 5, the efficiency decreased continuously, whereas the breakage increased gradually to 2.15%. This could be attributed to the number of protons discharged owing to the anion exchange reaction, the increase in pH can lead to the formation of other species [73].

4.7. Effect of internal. phase. concentration

The. stability of emulsion and extraction. efficiency at various HCl concentrations (0.05, 0.15, 0.25, 0.35, and 0.45 M) were investigated to achieve effective stripping at the internal phase-membrane interface. A strong acid was used as the internal stripping agent (HCl). Emulsification speed and time, 12,700 rpm and 5 min; LCT concentration, 100 mg/L; external phase pH, 5; Span 80 concentration, 3% (v/v); mixing speed, 250 rpm; external-to-emulsion phase ratio, 250:50; and internal-to-membrane volume ratio, 1:1.The effects of the internal phase concentration on emulsion stability and the efficiency of extraction are presented in Table 2 and Fig. 8. When raising the internal phase concentration from 0.05 to 0.25 M, the extraction efficiency is enhanced (77.77% to 94.75%), while the stripping percentage and breakage value changed from 80.13% and 4.25% to 91.06% and 0.48%, respectively. This could be caused by the main driving force in the ELM process, which is the H^+ ions transfer between internal and external phase solutions [74].

Further increase of acidity (above 0.25 M up to 0.45 M) caused a gradual increase in the emulsion breakage (2.08%), leading to further release of the internal constituents into the external feed aqueous phase; thus, a noticeable decline in extraction efficiency (75.62%) for 0.45 M HCl concentration. This is attributed to the reaction between the surfactant and HCl, which occurs because of the high acidity, leading to a decrease in the properties of surfactant thus destabilization of the emulsion [75].

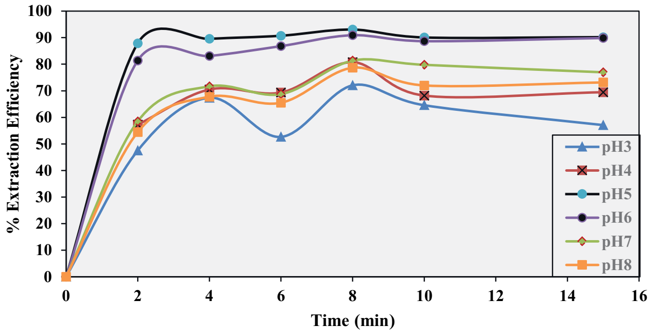

Fig. 7. Effect of the external phase pH on extraction efficiency.

In conclusion, 0.25 M HCl, which indicates the lowest breakage value with the highest extraction efficiency, was selected as the optimum concentration in this study.

4.8. Effect of internal phase-to-membrane phase volume ratio

For achieving an improved solute mass transfer rate within the membrane, and to reduce the emulsion interface thickness, an appropriate internal phase-to-membrane phase volume ratio must be met [75]. The effects of the process parameters on the membrane breakage as well as the LCT extraction and stripping efficiencies were investigated by considering the emulsification speed at 12,700 rpm, stirring speed 250 rpm, emulsification time 5min, external pH 5, internal phase concentration 0.25 M HCl, and Span 80 concentration 3% (v/v), while maintaining a volume ratio within 1:2–3:1. The effect of the internal-.to.-organic membrane volume ratio on the emulsion stability is presented in Table 2, and the profile of the extraction efficiency is presented in Fig. 9. Increasing the ratio from 1:2 to 1:1 causes an escalation in both extraction and stripping efficiencies of LCT from 74.26% and 62.41% to 94.75% and 93.58%, respectively. In contrast, the emulsion stability was preserved and enhanced when increasing the volume ratio (membrane breakage decreased from 5.29% to 0.48%). This may

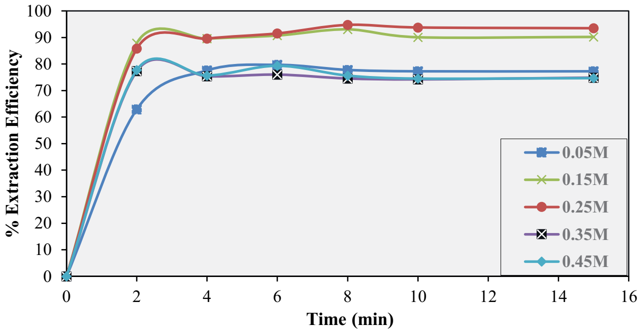

Fig. 8. Effect of the internal stripping aqueous phase concentration on extraction efficiency.

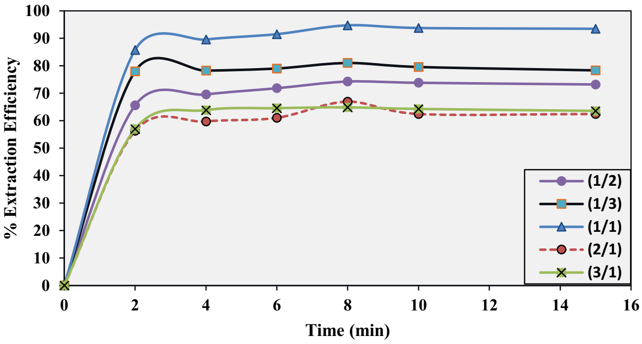

Fig. 9. Effect of volume ratio of internal aqueous phase-to-membrane phase on extraction efficiency.

be caused by the higher volume ratio, where the emulsion globules increased in size and cannot be dispersed uniformly in the feed phase [49]. However, the low extraction efficiencies for lower ratios (1:2) could be due to the low quantity of stripping agent present that strips the LCT from the membrane phase [75]. At a ratio of 3:1, the lower extraction efficiency (64.8%) could be attributed to the low organic phase volume, that is, high volume ratio, where the organic phase amount is insufficient to entirely encapsulate the stripping phase droplets; consequently, these droplets can leak out of the emulsion into the external phase solution [76]. Similar observations were reported in previous studies [62,77].

This behavior indicates that the produced emulsion is more viscous with a thicker wall that prohibits a diffusion of the stripping phase into the membrane [13]. When raising membrane volume, the membrane surface tension increases, leading to a larger droplet size, which in turn hinders the dispersion of emulsion droplets [17]. Upon raising the internal phase-to-membrane ratio up to 3:1, a notable decrease in membrane stability and a decrease in removal efficiency to 64.8% were observed. The low volume of the membrane indicates that the internal aqueous phase is not completely encapsulated, causing the stripping agent to escape from the formed globules. Previous studies have recorded similar behavior [18].

Thus, a 1:1 volume ratio of internal-to-membrane phase was considered optimal for this study.

4.9. Effect of external phase to emulsion volume ratio

Treatment ratio is expressed as the external feed phase to the organic emulsion volume ratio. It has a vital effect in establishing both effectiveness and efficiency of the ELM process [71]. An investigation of treatment ratio effect for 250:10, 250:25, 250:50, 250:75, and 250:100 ratios was conducted on the stability and extraction efficiency by altering only the volume of emulsion while maintaining a constant external phase volume, while the other parameters values are emulsification speed, 12,700 rpm; emulsification time, 5 min; LCT concentration, 100 mg/L; Span 80 concentration, 3% (v/v); stripping agent concentration, 0.25 M HCl; mixing speed, 250 rpm; external phase pH, 5; and internal-to-membrane volume ratio, 1:1.

The effect of treatment ratio on emulsion breakage is presented in Table 2, while the results of the LCT extraction are shown in Fig. 10. The results in Table 2 evidently confirm that a decrease in treatment ratio (i.e., an increase in membrane volume) increased the rate constant. A similar conclusion was drawn in previous studies [78]. A decrease in the treatment ratio above 250:50 caused an increase in emulsion coagulation. When decreasing volume ratio, the swelling phenomena developed considerably, with the crucial coalescence growth of internal droplets. The results showed that a decrease in the treatment ratio to 250:50 improved the extraction and stripping efficiencies to 94.7% and 89.2%, respectively. This could be interpreted that owing to the increase in the emulsion volume, more quantity is available, which contributes to an improved performance of LCT transport. Furthermore, a high emulsion volume tends to form a lot of globules by providing a large exchange surface area, thus increasing the transfer rate. Another reason could be the increase in the emulsion residence time, which increases the interfacial area available for the solute mass transfer [79].

For lower ratios, the fall in extraction efficiency could be a consequence of the low availability of emulsion to remove the solute [49,62]. Another reason is the broader distribution of emulsion globules, that is, an increase in the distance between globules of emulsion, which further reduce the interfacial area per unit volume of the external phase [80]. The lower stripping efficiency could be attributed to the low availability of the internal aqueous phase volume that strips the solute compared with the external feed aqueous phase. Further decreasing the volume ratio to 250:100 caused a significant decline in both the stripping and extraction efficiencies to approximately 68.7% and 64.2%, respectively. This is because of the curtailed interfacial area available for mass transfer, that is because of the difficulties in dispersing the organic emulsion due to its large volume compared to the feed phase; accordingly causing an increase in the emulsion total viscosity, and the subsequent occurrence of an inverse effect on the interfacial area [81]. In conclusion, a minimal volume of emulsion is favored for obtaining a decent internal phase droplet distribution in the external aqueous solution, thereby obtaining a better extraction efficiency [81]. Therefore, to establish a good distribution and dispersion of the emulsion into the feed phase, a 250:50 treatment ratio was selected as the optimal ratio for this study.

4.10. Evaluation of the solute (LCT) extraction kinetics and estimation of mass transfer coefficients

The extraction kinetics of LCT using the ELM method were investigated according to the procedures performed by Raji et al. [82] and Kohli et al. [83] using the following equation:

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

where t represents time in minutes and K_{obs} is the rate constant of extraction (min^{-1}), which can be estimated from the resulting straight line slope from the previous equation representing the K_{obs} value. Because the value obtained

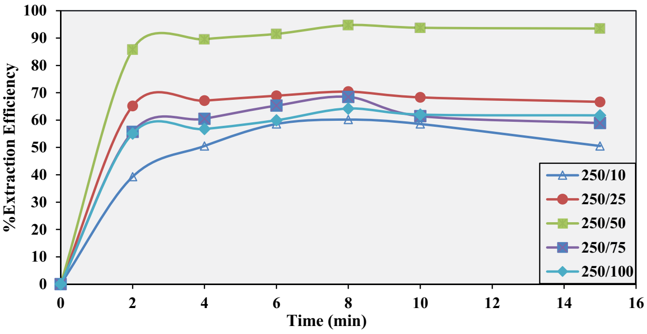

Fig. 10. Effect of the external phase-to-emulsion volume ratio on the extraction efficiency.

was positive, the extraction follows the first-order kinetics and the obtained K_{obs} value was 0.3033 min^{-1}.

The total mass transfer coefficient of the ELM system is calculated according to the following equation [84]:

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

where K_T is the total mass. transfer coefficient (m/s), K_F denotes the interfacial reaction rate constant (m/s), and K_M represents the mass transfer coefficient of the external phase (m/s), which is evaluated by the Skelland–Lee correlation [82], as specified by the following equation:

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

where N represents stirring speed (rpm); T and d represent the mixing tank and impeller diameter, respectively (m); V_i, V_e, and V_m denote volume of the internal, external, and membrane phases, respectively; D represents species diffusivity (LCT) in the membrane phase; and Re is the Reynolds number, which is calculated from Eq. (8).

$$\text{Re} = \frac{Nd^2 \rho_{\text{ext.}}}{\text{¼}_{\text{ext.}}} \tag{8}$$

where $\rho_{\text{ext.}}$ is the density (kg/m^3), $\mu_{\text{ext.}}$ is the viscosity (kg/m·s). The calculated Re value was 348,577. The D value is estimated using the Wilke and Chang correlation [85] shown in Eq. (9).

$$D = \frac{117.3 \times 10^{-8} \times \left(M \times \varnothing \right)^{0.5} \times \text{T}_{\text{emp.}}}{\text{¼}_m \times \varnothing_c^{0.6}} \tag{9}$$

where ϕ represents the solvent association factor (n-hexane = 1), M represents molecular weight of solvent (n-hexane = 86.18 kg/k·mol), Temp represents temperature (Kelvin), μ_m represents membrane viscosity 12.224 × 10^{-3} kg/m·s, and ϕ_c represents molar volume of solute; calculated using the Schroeder method [86], which is calculated as 0.399 m^3/kmol. However, the calculated D was found to be 1.67 × 10^{-10} m^2/s and the estimated K_M was 3.177 × 10^{-4} m/s.

K_F is calculated using the following equation:

$$\text{Ln}\left(\frac{C}{C_o} \right) = -A \cdot K_F \cdot t \tag{10}$$

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

$$K_F = \frac{K_{\text{obs}}}{A} \tag{11}$$

A represents the emulsion-specific interfacial area, estimated using the following equation [87]:

$$A = \frac{A_i}{V} = \frac{6\alpha}{d_{32}} \tag{12}$$

where A_i represents the emulsion droplet's interfacial area, α denotes the water volume fraction, V is the emulsion unit volume, and d_{32} represents the diameter of the emulsion droplet.

In conclusion, the calculated mass transfer coefficients are:

$K_M = 3.177 \times 10^{-4}$ m/s, $K_F = 0.24 \times 10^{-6}$ m/s, and $K_T = 2.398 \times 10^{-7}$ m/s.

5. Conclusions

This study aimed to extract LCT from an aqueous solution using an ELM with n-hexane as the diluent and Span 80 as the surfactant. The optimum experimental conditions for lower breakage percentage and higher removal percentage are 12,700 rpm emulsification speed, 3% (v/v) surfactant concentration, 5 min emulsification time, pH 5 external feed solution, 250 rpm stirring speed, 0.25 M internal (stripping) phase concentration, 1:1 internal phase-to-membrane volume ratio, 250:50 external phase-to-emulsion ratio without utilizing a carrier agent. 94.75% of LCT was successfully extracted under the optimal operating conditions with minimum breakage of (0.48%). The ELM technique represents a productive and efficient advanced separation method for the removal of LCT from an aqueous solution.

Acknowledgement

Ahmed A. Mohammed: conceptualization, project administration, supervision, writing; review and editing. Farrah Emad Al-Damluji: Investigation, methodology, data curation, analysis and writing.

Funding

The study did not receive a contribution from the commercial, public, or non-profit organizations.

References

[1] Organisation of Economic Co-operation and Development and Food and Agriculture Organization of the United Nations, OECD-FAO Agricultural Outlook 2012–2021, 2012. Available at: https://doi.org/10.1787/agr_outlook-2012-en

[2] I.A. Saleh, N. Zouari, M.A. Al-Ghouti, Removal of pesticides from water and wastewater: chemical, physical and biological treatment approaches, Environ. Technol. Innovation, 19 (2020) 101026, doi: 10.1016/j.eti.2020.101026.

[3] I.B. Gomes, L.C. Simões, M. Simões, The effects of emerging environmental contaminants on *Stenotrophomonas maltophilia* isolated from drinking water in planktonic and sessile states, Sci. Total Environ., 643 (2018) 1348–1356.

[4] W.J. Zhang, Global pesticide use: profile, trend, cost/benefit and more, Proc. Int. Acad. Ecol. Environ. Sci., 8 (2018) 1–27.

[5] D. Pimentel, Amounts of pesticides reaching target pests: environmental impacts and ethics, J. Agric. Environ. Ethics, 8 (1995) 17–29.

[6] G. Lofrano, G. Libralato, S. Meric, V. Vaiano, O. Sacco, V. Venditto, M. Guida, M. Carotenuto, 1 – Occurrence and Potential Risks of Emerging Contaminants in Water, O. Sacco, V. Vaiano, Eds., Visible Light Active Structured Photocatalysts for the Removal of Emerging Contaminants: Science and Engineering, Elsevier, Amsterdam, Netherlands, 2020, pp. 1–25. Available at: https://doi.org/10.1016/B978-0-12-818334-2.00001-8

[7] A. Sharma, V. Kumar, B. Shahzad, M. Tanveer, G.P.S. Sidhu, N. Handa, S.K. Kohli, P. Yadav, A.S. Bali, R.D. Parihar, O.I. Dar, K. Singh, S. Jasrotia, P. Bakshi, M. Ramakrishnan, S. Kumar, R. Bhardwaj, A.K. Thukral, Worldwide pesticide usage and its impacts on ecosystem, SN Appl. Sci., 1 (2019) 1446, doi: 10.1007/s42452-019-1485-1.

[8] R.W. Coppock, M.M. Dziwenka, Threats to Wildlife by Chemical and Warfare Agents, R.C. Gupta, Ed., Handbook of Toxicology of Chemical Warfare Agents, Academic Press, Boston, 2020, pp. 1077–1087.

[9] R.A. Hamza, O.T. Iorhemen, J.H. Tay, Occurrence, impacts and removal of emerging substances of concern from wastewater, Environ. Technol. Innovation, 5 (2016) 161–175.

[10] A. De, R. Bose, A. Kumar, S. Mozumdar, Worldwide Pesticide Use: Targeted Delivery of Pesticides Using Biodegradable Polymeric Nanoparticles, Springer, Berlin, 2014, pp. 5–6.

[11] L.M. He, J. Troiano, A. Wang, K. Kean Goh, Environmental Chemistry, Ecotoxicity and Fate of Lambda-Cyhalothrin. Review of Environmental Contamination and Toxicology, Vol. 195, Springer Cham Heidelberg, NY, USA, 2008.

[12] M.L. Feo, E. Eljarrat, D. Barceló, Determination of pyrethroid insecticides in environmental samples, TrAC, Trends Anal. Chem., 29 (2010) 692–705.

[13] K. Alalibo, U.A. Patricia, D.E. Ransome, Effects of lambda-cyhalothrin on the behaviour and histology of gills of *Sarotherodon melanotheron* in brackish water, Sci. Afr., 6 (2019) e00178, doi: 10.1016/j.sciaf.2019.e00178.

[14] M. Stuart, D. Lapworth, E. Crane, A. Hart, Review of risk from potential emerging contaminants in UK groundwater, Sci. Total Environ., 416 (2012) 1–21.

[15] M. Köck-Schulmeyer, M. Villagrasa, M. López de Alda, R. Céspedes-Sánchez, F. Ventura, D. Barceló, Occurrence and behaviour of pesticides in wastewater treatment plants and their environmental impact, Sci. Total Environ., 458–460 (2013) 466–476.

[16] L. Goodwin, I. Carra, P. Campo-Moreno, A. Soares, Treatment Options for Reclaiming Wastewater Produced by the Pesticide Industry, Int. J. Water Wastewater Treat., Cranfield Water Science Institute, Cranfield University, Cranfield, MK43 0AL, UK, 2017. Available at: http://dx.doi. org/10.16966/2381-5299.149

[17] N. Vela, J. Fenoll, I. Garrido, G. Pérez-Lucas, P. Flores, P. Hellín, S. Navarro, Reclamation of agro-wastewater polluted with pesticide residues using sunlight activated persulfate for agricultural reuse, Sci. Total Environ., 660 (2019) 923–930.

[18] I.A. Saleh, N. Zouari, M.A. Al-Ghouti, Removal of pesticides from water and wastewater: chemical, physical and biological treatment approaches, Environ. Technol. Innovation, 19 (2020) 101026, doi: 10.1016/j.eti.2020.101026.

[19] V.K. Gupta, B. Gupta, A. Rastogi, S. Agarwal, A. Nayak, Pesticides removal from wastewater by activated carbon prepared from waste rubber tire, Water Res., 45 (2011) 4047–4055.

[20] J. Rodriguez-Liebana, A. Lopez-Galindo, C. de Cisneros, A. Galves, M. Rozalen, R. Sanchez-Espejo, E. Caballero, A. Pena, Adsorption/desorption of fungicides in natural clays from southeastern Spain, Appl. Clay Sci., 132–133 (2016) 402–411.

[21] S. Salazar, D. Guerra, N. Yutronic, P. Jara, Removal of aromatic chlorinated pesticides from aqueous solution using β-cyclodextrin polymers decorated with Fe_3O_4 nanoparticles, Polymers (Basel), 10 (2018) 1038, doi: 10.3390/polym10091038.

[22] W. Lu, W. Chen, N. Li, M. Xu, Y. Yao, Oxidative removal of 4-nitrophenol using activated carbon fiber and hydrogen peroxide to enhance reactivity of metallophthalocyanine, Appl. Catal., B, 87 (2009) 146–151.

[23] J. Huang, C. Yan, K. Huang, Removal of p-nitrophenol by a water-compatible hypercrosslinked resin functionalized with formaldehyde carbonyl groups and XAD-4 in aqueous solution: a comparative study, J. Colloid Interface Sci., 332 (2009) 60–64.

[24] C. Corre, C. Couriol, A. Amrane, É. Dumont, Y. Andrès, P. Le Cloirec, Efficiency of biological activator formulated material (BAFM) for volatile organic compounds removal – preliminary batch culture tests with activated sludge, Environ. Technol., 33 (2012) 1671–1676.

[25] Z. Pan, S. Yu, H. Huang, J. Lang, Y. Yang, C. Lin, Treatment of high concentration pesticide wastewater by pressurized biochemical process, Asian Pac. J. Chem. Eng., (2004) 1–8.

[26] N. Modirshahla, M. Behnajady, 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, J. Hazard. Mater., 154 (2008) 778–786.

[27] V. Héquet, C. Gonzalez, P. Le Cloirec, Photochemical processes for atrazine degradation: methodological approach, Water Res., 35 (2001) 4253–4260.

[28] A. Tomašević, S. Gasic, Photochemical Processes and Their Use in Remediation of Water Containing Pesticides, 7th Congress on Plant Protection, Plant Protection Society of Serbia, Belgrade, 2015, pp. 365–369.

[29] P. Yu, Z. Chang, Y. Ma, S. Wang, H. Cao, C. Hua, H. Liu, Separation of p-nitrophenol and o-nitrophenol with three-liquid phase extraction system, Sep. Purif. Technol., 70 (2009) 199–206.

[30] S.K. Selahle, A. Mpupa, P.N. Nomngongo, A review of extraction, analytical, and advanced methods for the determination of neonicotinoid insecticides in environmental water matrices, Rev. Anal. Chem., 40 (2021) 187–203.

[31] R.O. Costa, P.S. Barcellos, M.C. Canela, Removal of pesticide residues after conventional drinking water treatment: by-products and acetylcholinesterase inhibition, Eclética Quím. J., 43 (2018) 65–73.

[32] M. Salimi, A. Esrafili, M. Gholami, A. Jonidi Jafari, R. Rezaei Kalantary, M. Farzadkia, M. Kermani, H.R. Sobhi, Contaminants of emerging concern: a review of new approach in AOP technologies, Environ. Monit. Assess., 189 (2017) 414, doi: 10.1007/s10661-017-6097-x.

[33] R. Colombo, T.C.R. Ferreira, S.A. Alves, R.L. Carneiro, M.R.V. Lanza, Application of the response surface and desirability design to the lambda-cyhalothrin degradation using photo-Fenton reaction, J. Environ. Manage., 118 (2013) 32–39.

[34] B. Van der Bruggen, K. Everaert, D. Wilms, C. Vandecasteele, Application of nanofiltration for removal of pesticides, nitrate and hardness from ground water: rejection properties and economic evaluation, J. Membr. Sci., 193 (2001) 239–248.

[35] C. Causserand, P. Aimar, J.P. Cravendi, E. Singlande, Dichloroaniline retention by nanofiltration membranes, Water Res., 39 (2005) 1594–1600.

[36] M. Nikbakht Fini, H.T. Madsen, J. Muff, The effect of water matrix, feed concentration and recovery on the rejection of pesticides using NF/RO membranes in water treatment, Sep. Purif. Technol., 215 (2019) 521–527.

[37] A. Mukherjee, R. Mehta, S. Saha, A. Bhattacharya, P.K. Biswas, R.K. Kole, Removal of multiple pesticide residues from water by low-pressure thin-film composite membrane, Appl. Water Sci., 10 (2020) 244, doi: 10.1007/s13201-020-01315-y.

[38] A.A. Yahya, K.T. Rashid, M.Y. Ghadhban, N.E. Mousa, H.S. Majdi, I.K. Salih, Q.F. Alsalhy, Removal of 4-nitrophenol from aqueous solution by using polyphenylsulfone-based blend membranes: characterization and performance, Membranes, 11 (2021) 171, doi: 10.3390/membranes11030171.

[39] R. Mehta, H. Brahmbhatt, N.K. Saha, A. Bhattacharya, Removal of substituted phenyl urea pesticides by reverse osmosis membranes: laboratory scale study for field water application, Desalination, 358 (2015) 69–75.

[40] L.S. Tan, A.L. Ahmad, S.R.A. Shukor, S.P. Yeap, Impact of solute properties and water matrix on nanofiltration of pesticides, Chem. Eng. Technol., 42 (2019) 1780–1787.

[41] F.H. Al-Ani, Q.F. Alsalhy, M. Al-Dahhan, Enhancing emulsion liquid membrane system (ELM) stability and performance for the extraction of phenol from wastewater using various nanoparticles, Desal. Water Treat., 210 (2021) 180–191.

[42] R. Romero-González, E. Pastor-Montoro, J. Luis Martínez-Vidal, A. Garrido-Frenich, Application of hollow fiber supported liquid membrane extraction to the simultaneous determination of pesticide residues in vegetables by liquid chromatography/

mass spectrometry, Rapid Commun. Mass Spectrom., 20 (2006) 2701–2708.

[43] Z. Ao, Z. Yang, J. Wang, G. Zhang, T. Ngai, Emulsion-templated liquid core-polymer shell microcapsule formation, Langmuir, 25 (2009) 2572–2574.

[44] J. Đorđević, G.T. Vladisavljević, T. Trtić-Petrović, Liquid phase membrane extraction of targeted pesticides from manufacturing wastewaters in a hollow fiber contactor with feed-stream recycles, Environ. Technol., 38 (2016) 78–84.

[45] H. Xia, Removal of Lambda-Cyhalothrin by Water Hyacinth (Eichornia Crassipes), 2nd International Conference on Bioinformatics and Biomedical Engineering, IEEE, Shanghai, China, 2008, pp. 3446–3450.

[46] A. Marican, E.F. Durán-Lara, A review on pesticide removal through different processes, Environ. Sci. Pollut. Res., 25 (2018) 2051–2064.

[47] R.A. Kumbasar, Selective extraction of chromium(VI) from multicomponent acidic solutions by emulsion liquid membranes using tributhylphosphate as carrier, J. Hazard. Mater., 15 (2010) 875–82.

[48] A. Dâas, O. Hamdaoui, Extraction of bisphenol A from aqueous solutions by emulsion liquid membrane, J. Membr. Sci., 348 (2010) 360–368.

[49] S. Laguel, M.H. Samar, Removal of Europium(III) from water by emulsion liquid membrane using Cyanex 302 as a carrier, Desal. Water Treat., 165 (2019) 269–280.

[50] A. Shorki, P. Daraei, S. Zereshki, Water decolorization using waste cooking oil: an optimized green emulsion liquid membrane by RSM, J. Water Process Eng., 33 (2020) 101021, doi: 10.1016/j.jwpe.2019.101021.

[51] M.A. Mohammed, W.O. Noori, H.A. Sabbar, Application of emulsion liquid membrane process for cationic dye extraction, Iraqi J. Chem. Petrol. Eng., 21 (2020) 39–44.

[52] S.H. Chang, Types of bulk liquid membrane and its membrane resistance in heavy metal removal and recovery from wastewater, Desal. Water Treat., 57 (2016) 19785–19793.

[53] A. Kargari, K. Abbassian, Study of phenol removal from aqueous solutions by a double emulsion (W/O/W) system stabilized with polymer, Sep. Purif. Technol., 50 (2015) 1083–1092.

[54] A. Kargari, T. Kaghazchi, B. Mardangahi, M. Soleimani, Experimental and modeling of selective separation of gold(III) ions from aqueous solutions by emulsion liquid membrane system, J. Membr. Sci., 279 (2006) 389–393.

[55] H.M. Salman, A.A. Mohammed, Removal of copper ions from aqueous solution using liquid-surfactant membrane technique, Iraqi J. Chem. Petrol. Eng., 20 (2019) 31–37.

[56] N. Rathore, A.M. Sastre, A.K. Pabby, Membrane assisted liquid extraction of actinides and remediation of nuclear waste: a review, J. Membr. Sci. Res., 2 (2016) 2–13.

[57] S. Fathi, M. Yaftian, A. Kargari, Water-in-oil emulsion liquid membrane transport of L-cysteine, Sep. Sci. Technol., 48 (2013) 105–112.

[58] S. Suahadah, K. Kamarudin, S. Najib, N. Dolmat, Carbon dioxide removal in emulsion liquid membrane containing 2-amino-2-methyl-1-propanol/monoethanolamine, J. Teknol., 75 (2015) 61–65.

[59] C.D.S. Tomlin, A World Compendium: The Pesticide Manual, 11th ed., British Crop Protection Council, Farnham, Surrey, UK, 1997, pp. 300–302.

[60] K.A. Lewis, J. Tzilivakis, D. Warner, A. Green, An international database for pesticide risk assessments and management, Hum. Ecol. Risk Assess.: Int. J., 22 (2016) 1050–1064.

[61] C. Wang, B. Cui, L. Guo, A. Wang, X. Zhao, Y. Wang, C. Sun, Z. Zeng, H. Zhi, H. Chen, G. Liu, H. Cui, Fabrication and evaluation of lambda-cyhalothrin nanosuspension by one-step melt emulsification technique, J. Nanomater., 9 (2019) 145, doi: doi: 10.3390/nano9020145.

[62] A.A. Mohammed, H.M. Selman, G. Abukhanafer, Liquid surfactant membrane for lead separation from aqueous solution: studies on emulsion stability and extraction efficiency, J. Environ. Chem. Eng., 6 (2018) 6923–6930.

[63] A. Dâas, O. Hamdaoui, Extraction of anionic dye from aqueous solutions by emulsion liquid membrane, J. Hazard. Mater., 178 (2010) 973–981.

[64] A.A. Mohammed, M.A. Atiya, M.A. Hussein, Removal of antibiotic tetracycline using nano-fluid emulsion liquid membrane: breakage, extraction and stripping studies, Colloids Surf., A, 595 (2020) 124680, doi: 10.1016/j.colsurfa.2020.124680.

[65] A.A. Mohammed, R.W. Al-Khateeb, Application of emulsion liquid membrane using green surfactant for removing phenol from aqueous solution: extraction, stability and breakage studies, J. Ecol. Eng., 23 (2022) 305–314.

[66] H.M. Salman, A.A. Mohammed, Extraction of lead ions from aqueous solution by co-stabilization mechanisms of magnetic Fe_2O_3 particles and nonionic surfactants in emulsion liquid membrane, Colloids Surf., A, 568 (2019) 301–310.

[67] S. Laki, A. Kargari, Extraction of silver ions from aqueous solutions by emulsion liquid membrane, J. Membr. Sci. Res., 2 (2016) 33–40.

[68] S. Chaouchi, O. Hamdaoui, Extraction of endocrine disrupting compound propylparaben from water by emulsion liquid membrane using trioctylphosphine oxide as carrier, J. Ind. Eng. Chem., 22 (2015) 296–305.

[69] M. Samar, D. Pareau, A. Chesne, G. Durand, Membrane liquide échangeuse de cations: application à l'extraction du nickel, Bulletin de la Société chimique de France, 129 (1992) 259–264.

[70] K. Anarakdim, G. Gutiérrez, Á. Cambiella, O. Senhadji-Kebiche, 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) 76, doi: 10.3390/membranes10040076.

[71] P. Davoodi-Nasab, A. Rahbar-Kelishami, J. Safdari, H. Abolghasemi, Evaluation of the emulsion liquid membrane performance on the removal of gadolinium from acidic solutions, J. Mol. Liq., 262 (2018) 97–103.

[72] P. Venkateswaran, Di(2-ethylhexyl) phosphoric acid-coconut oil supported liquid membrane for the separation of copper ions from copper plating wastewater, J. Environ. Sci., 19 (2007) 1446–1453.

[73] A.A. Mohammed, M.A. Atiya, M.A. Hussein, Studies on membrane stability and extraction of ciprofloxacin from aqueous solution using pickering emulsion liquid membrane stabilized by magnetic nano-Fe_2O_3, Colloids Surf., A, 585 (2020) 124044, doi: 10.1016/j.colsurfa.2019.124044.

[74] R. Sabry, A. Hafez, M. Khedr, A. El-Hassanin, Removal of lead by an emulsion liquid membrane: Part I, Desalination, 212 (2007) 165–175.

[75] A.A. Mohammed, M.A. Atiya, M.A. Hussein, Simultaneous studies of emulsion stability and extraction capacity for the removal of tetracycline from aqueous solution by liquid surfactant membrane, Chem. Eng. Res. Des., 159 (2020) 225–235.

[76] M. Djenouhat, O. Hamdaoui, M. Chiha, M.H. Samar, Ultra sonication-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 (2008) 231–238.

[77] S. Zereshki, P. Daraei, A. Shokri, Application of edible paraffin oil for cationic dye removal from water using emulsion liquid membrane, J. Hazard. Mater., 356 (2018) 1–8.

[78] A.A. Mohammed, Removal of emulsified paraffine from water: effect of bubble size and particle size on kinetic of flotation, Iraqi J. Chem. Eng., 8 (2007) 1–5.

[79] A. Kumar, A. Thakur, P.S. Panesar, A review on emulsion liquid membrane (ELM) for the treatment of various industrial effluent streams, Rev. Environ. Sci. Biotechnol., 18 (2019) 153–182.

[80] N.F.M. Naoh, N. Othman, N. Jusoh, Highly selective transport of palladium from electroplating wastewater using emulsion liquid membrane process, J. Taiwan Inst. Chem. Eng., 64 (2016) 134–141.

[81] P.S. Kulkarni, V.V. Mahajani, Application of liquid emulsion membrane (LEM) process for enrichment of molybdenum from aqueous solutions, J. Membr. Sci., 201 (2002) 123–135.

[82] M. Raji, H. Abolghasemi, J. Safdari, A. Kargari, Response surface optimization of dysprosium extraction using an emulsion liquid membrane integrated with multi-walled carbon nanotubes, Chem. Eng. Technol., 41 (2018) 1857–1870.

[83] H.P. Kohli, S. Gupta, M. Chakraborty, Stability and performance study of emulsion nanofluid membrane: a combined approach of adsorption and extraction of ethylparaben, Colloids Surf., A, 579 (2019) 123675, doi: 10.1016/j.colsurfa.2019.123675.

[84] H. Kasaini, F. Nakashio, M. Goto, Application of emulsion liquid membranes to recover cobalt ions from a dual-component sulphate solution containing nickel ions, J. Membr. Sci., 146 (1998) 159–168.

[85] R.E. Treybal, Mass – Transfer Operations, 3rd ed., McGraw-Hill Book Co., Singapore, 1981.

[86] B.E. Poling, J.M. Prausnitz, J.P. O'connell, The Properties of Gases and Liquids, McGraw-Hill, New York, 2001.

[87] V. Karcher, F. Perrechil, A. Bannwart, Interfacial energy during the emulsification of water-in-heavy crude oil emulsions, Braz. J. Chem. Eng., 32 (2015) 127–137.