Environmental Advances 9 (2022) 100294

Contents lists available at ScienceDirect

Environmental Advances

journal homepage: www.sciencedirect.com/journal/environmental-advances

Stability and performance studies of emulsion liquid membrane on pesticides removal using mixture of Fe3O4Â nanoparticles and span80

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ARTICLE INFO

Keywords:
Pickering emulsion
Abamectin
Stability
Extraction efficiency

ABSTRACT

The current study investigated the impact of nonionic surfactant span 80 in the existence of Fe_3O_4 magnetic nanoparticles on the emulsification of mixture of kerosene as petroleum based organic solvents and corn oil as a green diluent in the ratio 1:1, HCl was used as internal phase and the stability of the emulsion was carried out. The proposed Pickering emulsion liquid membrane has been exploited to investigate it is ability in the extraction of Abamectin pesticides from aqueous solution without utilizing carrier agent. Further, the effects of experimental parameters on extraction efficiency and emulsion stability such as, homogenizer speed, emulsification speed, contact time, Fe_3O_4-Span 80 ratios, HCL concentration, internal to membrane volume ratio (I/O) and pH of the external feed solution were carried out. The results showed that more than 99% of Abamectin could be extracted at 10 min contact time with a minimum breakage percent of 0.52% at the optimal conditions. The kinetic of the extraction were studied and the mass transfer coefficient was found to be for external phase (K_M) of 1.2×10^{-7}, interfacial reaction rate constant (K_F) of 5.83×10^{-8} and the overall mass transfer coefficient (K_O) of 3.91×10^{-8}. The results of recyclability of the PELM revealed that the emulsion stability and extraction efficiency was nearly unchanged after three cycles.

1. Introduction

Pesticides, one of the most toxic organic components, it is very harmful to the skin and eyes, and is easily absorbed into the liver and lungs by living tissue. This may lead to tissue degradation, protein degeneration, gastrointestinal pain and systemic consequences such as respiratory failure, neurological damage and eventual death (Belguet et al., 2019). Several techniques have been proposed to treat this effluent; Such as ozonation (Plakas et al., 2011), solvent extraction (Chang et al., 2009), adsorption (Mohamed et al., 2011) and (Rodriguez et al., 2016), membrane extraction (Ahmad and Tan 2004), biological (Corre et al., 2012) and electrochemical (Modirshahla et al., 2008). Each of the above process has its own advantages and disadvantages related to the capital and operation costs, efficiency, reliability, operability, production of sludge and toxic by-products, pre-treatment requirements and environmental impact. At the last few decades the membrane technology has been utilized in water purification as a cost effective process (Mahmoud and AL-Hemiri, 2010; Yahya et al., 2021). Among them the emulsion liquid membrane (ELM) technology has been applied due to its unique advantages. ELM combines extraction and de-extraction in single stage and limited amounts of exclusive carrier reagents can be used. The main ELM advantages are simple operation, high contact surface for mass transfer, high efficiency and capability of recovering solute at low concentration selectively (Salman and Mohammed, 2019 a; Shokri et al., 2020). The main problems in ELM are the instability of the emulsifier, low separation efficiency in long periods of time, and inefficient emulsification breaking process to separate solid waste and recycle the organic phase (Mokhtari and Pourabdollah, 2012; Panchal and Pandya, 2016). Emulsion stability can be enhanced by increasing surfactant concentration, but excessive concentration of surfactant is problematic as it leads to permeate of feed solution into emulsion drops causes emulsion breakage and make the emulsion difficult to de-emulsify. Recently emulsion stabilized by mixture of surfactant and nanoparticles has gained great attentiveness because of their prominent stability and easy de-emulsification after extraction process by means of an external magnetic force to quickly attract the particles from the emulsion(Mohammed et al ., 2020). The potential purpose of surfactants in the presence of the particles in emulsion is to

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https://doi.org/10.1016/j.envadv.2022.100294
Received 27 July 2022; Received in revised form 19 September 2022; Accepted 23 September 2022
Available online 24 September 2022

adjust wettability angle, avoid the particles flocculation in the external phase and to minimize the interfacial tension (Yuan and Williams, 2016). As the main component in the emulsion liquid membrane is the diluent should has low viscosity, low solubility in the aqueous solution, corrosiveness, great capacity for sequestration the wanted species, low cost and nontoxicity. The typically employed diluent solvents are commonly based on petroleum components like kerosene (Salman and Mohammed, 2019 b), heptane (Mesli and Belkhouche, 2018; Mohammed et al., 2020) and hexane (Bahloul et al, 2013), which are generally volatile, toxic, undegradable and flammable. These diluents cannot be decomposed normally and are not environmentally friendly (Shokri et al., 2020). Lin et al., 2016 a, considered the stability of ELM methods using magnetic Fe_3O_4 nanoparticles as surfactant for the abstraction of the 4-methoxy phenol from aqueous solution. The outcomes revealed that 0.5 wt. % Fe_3O_4 nanoparticles have a strong effect on enhancing emulsion stability with 86% removal in 2 min contact time. Mohammed and Salman (2019) studied the influence of the magnetic Fe_2O_3 nanoparticles in the existent of span 80 on the emulsion stability for the abstraction of lead ions from aqueous solutions, the outcomes exhibited that 0.3% (w/v) magnetic Fe_2O_3 nanoparticles in the existence of 2% (v/v) span 80 have a strong influence on emulsion stability given 0.3% emulsion breakage and 97.2% removal for the lead after 8 min contact time. Mohammed et al. (2020), also investigated the eradication of ciprofloxacin from aqueous solution. The outcomes exhibited that increasing the concentration of Fe_2O_3 nanoparticles up to 0.7%(w/v) in the organic phase enhanced the stability (0.06% emulsion breakage) and led to improvement in the removal efficiency of ciprofloxacin to 98.85% after 10 min contact time. The purpose of the current work is to treat the polluted water by ELM process using corn cooking oil and kerosene as solvent without using a carrier agent .The effect of internal phase concentration, emulsification speed and time, Fe_3O_4 nanoparticles and span 80 concentration, internal to organic volume ratio (I/O) and pH of feed solution on PELM extraction performance and emulsion stability were studied. The oil phase and magnetic particles reuse were studied in a repeatable PELM test.

2. Material and methods

2.1. Chemicals

The liquid membrane is composed of span 80 as surfactant and magnetic Fe_3O_4 nanoparticles (20-30 nm average diameter) coated with oleic acid as co-surfactant, Kerosene and corn oil as diluent,HCl solution (purity >35%) as the internal phase while the external phase was prepared by dissolving Abamectin pesticides in distilled water.

2.2. Preparation pickering emulsion

Certain quantities of span 80 and nano-Fe_3O_4 were dispersed into 25 mL kerosene and corn oil and homogenized by ultra-sonication speed homogenizer (SR30). 25 mL of HCl aqueous solution was added dropwise to the oil phase and the mixture was homogenized using a high speed homogenizer (SR30, USA) with a certain emulsification time.

2.3. Pickering emulsion liquid membrane experiments

A stock solution of 50 ppm Abamectin solution prepared by added some drops of methanol to Abamectin and dissolved in distilled water to obtain on Abamectin solution at pH=7 ± 0.1 (external or feed phase). The external phase was stirred in a beaker using a mechanical stirrer at 250 rpm, and the primary Pickering emulsion was added to the external phase with continuously stirring for certain time interval at room temperature. At that moment the mixture was transferred into a separator funnel for a 10 min to permit the phase separation of the aqueous external phase and emulsion phase as shown in Fig. 1. The upper emulsion phase and the lower aqueous phase was separated using separating funnel. The upper phase was broken under magnetic force and the aqueous phase was purified with magnet and filtered to get the particles. The collected particles were washed with acetone and deionized water and dried vacuum oven at 55 °C for 10 h. The washed Fe_3O_4 and the organic phase were used for preparing a new Pickering emulsion. Abamectin concentration in the aqueous solution was analyzed using (UV-Vis) spectrophotometric, at absorbance of 210 nm at different time intervals.

2.4. The PELM stability and extraction process

The PELM stability has been explored by calculating the concentration of Abamectin concentration permeable from the internal phase to the aqueous feed phase through the emulsion globules. The emulsion breakage percent (%B) was calculated using Eq. (1).

$$\%B = \frac{V_I}{V_{IO}} \times 100\% \quad (1)$$

Where V_{IO} is internal phase volume before extraction and V_I is internal phase volume which permit into aqueous external phase and it was calculated using Eq. (2).

$$V_I = V_F \frac{10^{-pH_{IF}} - 10^{-pH_F}}{10^{-pH_F} - [H_{IO}^+]} \times 100 \quad (2)$$

Where V_F the initial feed phase volume, pH_{IF} and pH_F are pH of

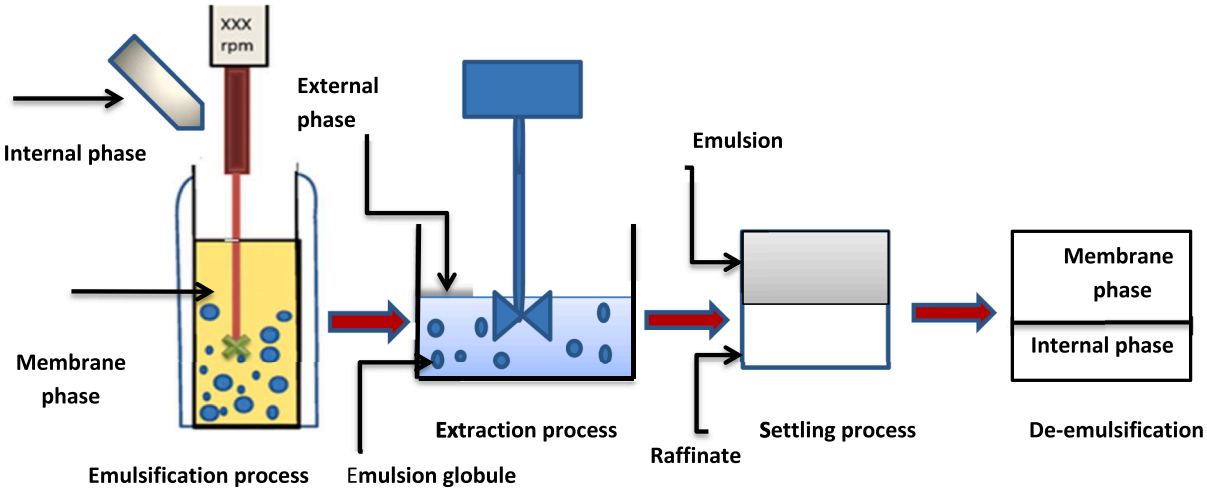

Fig. 1. Flow diagram representation of PELM process.

initial external and external phase after period time of mixing respectively, and $[H_{IO}^{+}]$ is initial concentration of H^{+} in internal phase.

The extraction efficiency of the Abamectin species from external phase was evaluated using Eq. (3).

$$E\% = \frac{C_{in} - C_t}{C_{in}} \times 100\% \quad (3)$$

Where C_{in} and C_t are initial and at a certain time period (mg/l) Abamectin concentration in the external phase, respectively. The many factors governing on the emulsion stability and extraction efficiency were explored. These factors are emulsification speed, emulsification time, span 80concentration, internal to membrane phase volume ratio (I/O), concentration of Fe_3O_4nanoparticles and pH. Unless otherwise required experiments were done with 50 ppm of Abamectin, 3% (v/v) span 80, 0.15M HCl internal phase, 1:1 kerosene to corn oil as a diluent, 1:1 (I/O), mixing speed of 250 rpm, 10 min of contact time, Fe_3O_4nanoparticles 0.2%(w/v) and external to emulsion phase 5:1 at 25°C. The results gotten for the emulsion stability from different investigation are given in Table 1

3. Effect of emulsion stability and extraction parameters

3.1. Emulsification speed

Table 1, shows the stability of the emulsion at different homogenizing speed. The outcomes showed that the greatest unstable emulsion was detected at 3000 rpm .The emulsion instability can be ascribed to the heterogeneity of the shape and size of the droplets existing in the emulsion led to the emulsion breakage occurs early while increasing the speed of the homogenizer up to 5800 rpm increased the stability of as breaking occurs at 2 h after the phase separation time due to form more droplets of smaller size that are increase homogeneity of emulsion. Silva et al., 2016, also stated that the high shear homogenizer is able to yield smaller droplets size of emulsion. However, very small emulsion droplets at 12,700 rpm emulsification speed disturb the stability of the emulsion. This manner is attributed to the rapid droplets coalescence which makes the film layer unable to overcome the impact force resultant in the emulsion breakage. The same behavior was noticed by Sulaiman et al., 2016 who identified that higher emulsification speed causes higher breakage percent because of quick coalescence of the smaller emulsion droplets. At 19,700 rpm of homogenizing speed, a high viscosity emulsion formed led to form a bigger emulsion droplet which reduces the emulsion stability. This may be due to rapidly coalescence for fine drops which leads to increases its volume causing the emulsion to break. In addition, too rapid mixing may cause the mixed surfactant to separate from the oil-water interphase. Therefore, a very high homogenizing speed is unnecessary because the emulsifier tends to be destabilizing and will break easily. The study of the extraction of Abamectin at different homogenizer speed was conducted at 3000, 5800,12,700 and 19,700 rpm and the outcomes are presented in Fig. 2, from this figure it can be noticed that the extraction percentage increased from 69% to 78% upon increasing homogenizing speed from 3000 to 5800 rpm. This trend is attributed to the reduction in the droplets size of internal phase with increasing homogenizing speed which leads to increase droplets surface area, so the rate of Abamectin transfer increases. Higher rotation speed at 12,700 rpm and 19,700 lead to increasing breakage percent to 3.57% and 6.21% respectively and decreasing the extraction efficiency to73.6% and 61% respectively.

Table 1
Effect of the different parameter on stability of PELM at 25°C.

Emulsion breakage percent(%) at 10 min contact time	Investigated parameter	
5.66	3000	Emulsification speed (rpm)
2.17	5800	
3.57	12,700	
6.21	19,700	
2.58	4	Emulsification time (min)
2.06	6	
2.17	8	
3.56	10	
2.24	1	Span 80 (v%)
1.46	3	
1.12	5	
0.66	7	
2	0.1	Fe_3O_4%(w/v)
1.46	0.2	
1.87	0.4	
4.09	0.6	
4.5	0.8	
12.7	0.01	HCl (M)
9	0.05	
1.23	0.15	
1.46	0.25	
4.71	3:1	Internal/Organic phase
2.55	2:1	
1.23	1:1	
2.38	1:2	
8.98	1:3	
19.13	2	pH
10.13	3	
0.52	5	
1.23	7	
1.78	8	

3.2. Emulsification time

The ELM stability and hence the extraction efficiency were investigated in the range 4–10 min emulsification time and the obtained outcomes are tabulated in Table 1, for the stability and Fig. 3, for the extraction efficiency respectively. Results from Table 1, showed that lowest breakage 2.06% happened at 6 min of emulsification time, while the above 6 min of emulsification time caused a decreased in the stability. For 4 min emulsification time, the breakage percent is 2.58% .This is due to the ease of droplet coalescence due to their large size. Gasser et al., 2008, noticed higher emulsion instability at the lower emulsification time. In contrast, for higher emulsification time (i.e. 8 and 10 min), the breakage gets heightened (3.17% and 3.56% respectively) due to the high internal shearing producing huge number of smaller droplets by unit volume, which is conductive to droplets diffusion into external phase (Daas and Hamdaoui, 2010). The low emulsion stability induced low extraction efficiency of Abamectin from the external solution. The Abamectin extraction percentage was nearly only 80% at 4 min emulsification time, while the removed efficiency enhanced up to 84% at 6 min homogenizing time. This is attributed to the reduction in the droplet size of internal phase and improved the homogeneity of dispersed phase. While increasing the emulsification time to 8 min and 10 min resulted in

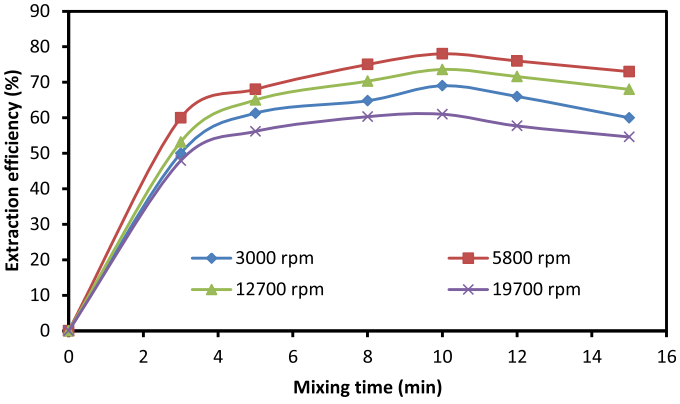

Fig. 2. Effect of homogenizer speed on Abamectin extraction efficiency "Span 80: 1(%v/v); Fe_3O_4: 0.1(%w/v); mixing speed: 250 rpm, treat ratio: 5/1; emulsification time: 8 min; (I/O): 1/1; 0.25 M HCl; external phase pH:7".

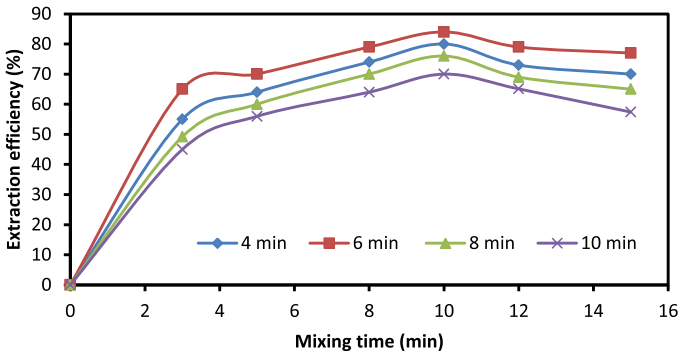

Fig. 3. Effect of emulsification time on Abamectin extraction efficiency "Span 80: 1(%v/v); Fe_3O_4: 0.1(%w/v); mixing speed:250 rpm, treat ratio: 5/1; homogenizer speed:5800 rpm;0.25 M HCL; (I/O):1/1;external phase pH:7".

a reduction in the extraction efficiency to76% and 70% respectively, essentially due to the coalescence of the internal phase droplets (Chaouchi and Hamdaoui, 2015).

3.3. Span 80 concentration

Surfactant is important parameters that influences ELM process, its organic polar compound consists of hydrophobic tail and hydrophilic head. In the absence of surfactant, it is impossible to disperse the internal aqueous phase in the oil membrane phase and so the emulsion cannot be formed. At low surfactant concentration, the membrane becomes less stable while increasing the concentration above the optimal value a thick emulsion form, which resulted in reduction in mass transfer. Experiments was carried out in the range 1% to 7% (v/v) span 80 concentration in the presence of 0.2%(w/v) Fe_3O_4 nanoparticles while keeping other parameters constant to investigate its effect on emulsion stability and extraction efficiency. The influence of surfactant concentration on the breakage percent is shown in Table 1. Though the emulsion was estimated to be stabilized with increasing span 80 concentration, while the stability becomes nearly constant beyond a critical span 80 concentration, because the oil – water interface became saturated (Gasser et al., 2008). Fig. 4, shows that enhancing the span 80 concentration from 1% to 3% increase the extraction degree of Abamectin. Above this concentration of surfactant, a reduction in the extraction efficiency decreased again. This due to that excessive surfactant concentration tends to increase the viscosity of the membrane solution which led to increase the resistance at the interface; hence the extraction degree of Abamectin was decreased. A similar results, was noticed by Valenzuela et al., 2005 in the recapture of copper ions. They establish that lower extraction produced at high surfactant concentration due to the generation of extra interfacial resistance. Therefore, 3% Span 80 concentration was chosen as the optimal extracting concentration.

3.4. Fe_3O_4 nanoparticles

PELM includes adding of nanoparticles to the membrane phase to increase the emulsion stability and reduces the amount of surfactant needed. In this study, Fe_3O_4nanoparticles improved with oleic acid were added in the range 0.1 to 0.8% (w/v) to investigate their effects on the extraction efficiency stability of emulsion. The concentration of span 80 was fixed from the previous experiments at 3%. Table 1, shows that adding 0.2% (w/v) Fe_3O_4 nanoparticles, the emulsion becomes more stable (breakage percent reduces from 2% at 0.1% (w/v) to 1.46% at 0.2% (w/v) Fe_3O_4 nanoparticles respectively). Because this ratio covered more droplets interface (Lin et al., 2016). On the other hand a higher breakage was observed with further increase in the Fe_3O_4nanoparticles concentration. Also, we can see from Fig. 5, the highest extraction efficiency 90% achieved at 0.2% (w/v) and decreased thereafter, this due to the increasing the emulsion stability by covering the emulsion interface. However, with further increasing concentration of Fe_3O_4nanoparticles beyond full coverage of the emulsion droplets, the extract efficiency reduced to nearly 53%, which is attributed to that further nanoparticle, could be spread in continuous phase and part of the particles might create aggregates on the water/oil interface, which enhances the resistance of mass transfer resistance for the transport of Abamectin. The same trend was noticed by Lin et al., 2016; Salman and Mohammed, 2019. Hence 0.2% (w/v) Fe_3O_4nanoparticles were chosen in this work.

3.5. Internal concentration

Internal phase concentration is an important condition on the emulsion stability and hence on the solute transport from feed solution to the internal phase. The influence of the concentration of hydrochloric acid in the internal phase on stability of Pickering emulsion and extraction efficiency of Abamectin in the range (0.01 – 0.25 M) at 6 min emulsification time and homogenizer speed of 5800 rpm was investigated. The results are tabulated in Table 1, and plotted in Fig. 6, for emulsion breakage and extraction efficiency respectively. Table 1, presented that with increasing HCL concentration from 0.01 to 0.15 M, the breakage percent decreases from 12.7% to 1.23% but increases when the HCl concentration is increased to 0.25 M. High breakage noticed at low HCl concentration led to because the ionic strength difference between external and internal phases is not sufficient conducting in low emulsion stability (high breakage). On the other hand, the decreases in the emulsion stability at high HCl concentration (0.25 M) may be due to the reaction of hydrochloric acid with surfactant which results in a part losing of its surfactant properties that accordingly led to emulsion

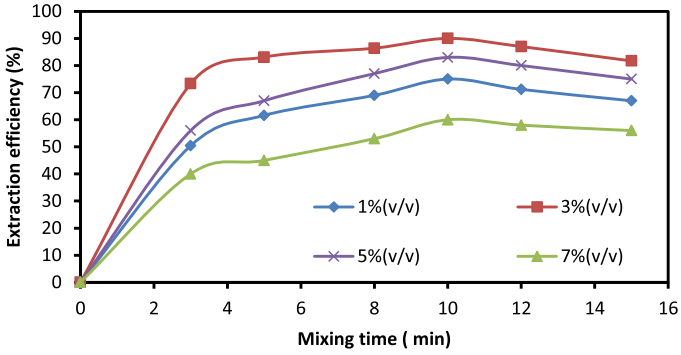

Fig. 4. Effect of surfactant concentration on Abamectin extraction efficiency "Fe_3O_4: 0.2(%w/v); mixing speed: 250 rpm, treat ratio: 5/1; emulsification time: 6 min; homogenizer speed 5800 rpm; 0.25 M HCL; (I/O): 1/1; external phase pH: 7".

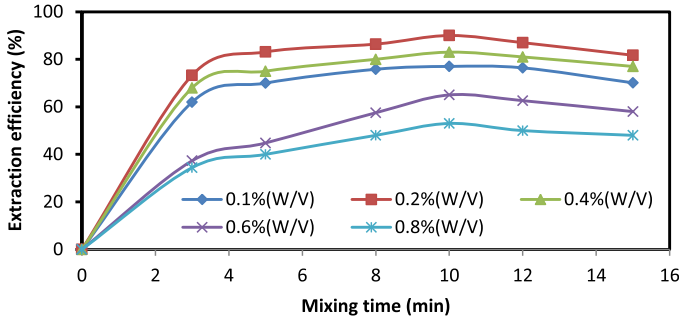

Fig. 5. Effect of Fe_3O_4 nanoparticles concentration on Abamectin extraction efficiency "Span 80: 3 (%v/v); homogenizer speed 5800 rpm; mixing speed: 250 rpm, treat ratio: 5/1; emulsification time: 6 min; 0.25 M HCl; (I/O): 1/1; external phase pH: 7".

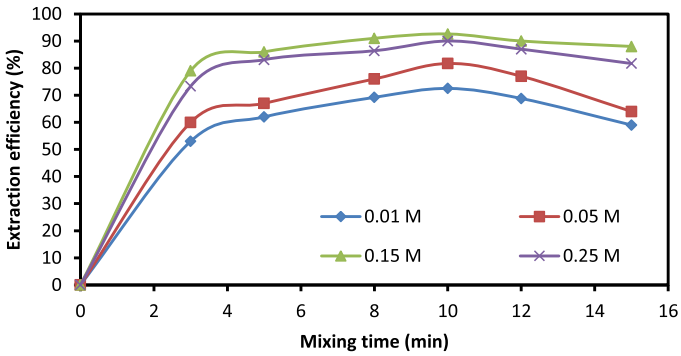

Fig. 6. Effect of HCl concentration (stripping agent) Abamectin extraction efficiency "Span 80: 3(%v/v);Fe_3O_4: 0.2 (%w/v); mixing speed: 250 rpm, treat ratio: 5/1; emulsification time: 6 min; homogenizer speed 5800 rpm, (I/O): 1/1; external phase pH: 7".

destabilization. Fig. 6 shows the influence of the concentration of hydrochloric acid in internal aqueous solution on Abamectin extraction. It can be noticed that, the extraction efficiency increased from 72.5% to 92.6% at 6 min contact time, when the HCl concentration in the internal phase increased from 0.01 to 0.15 M. This behavior is attributed to that the essential driving force in the emulsion liquid membrane is the difference in the quantity of H^+ ions between the internal and external aqueous phases. However, further increases in the concentration of HCl to 0.25 M reduced the level of Abamectin extraction to 90%. This may be due to decrease the difference of densities and increasing the emulsion viscosity. Razo –Lazcano et al., 2018, also noticed similar behavior by using hydrochloric acid as internal phase for stripping of Chlorpheniramin from aqueous solution. Therefore, 0.15M HCl was chosen as the optimum internal phase concentration.

3.6. *Effect of internal to organic phase ratio (I/O)*

The (I/O) volume ratio has a profound influence on emulsion stability and hence on extraction efficiency using ELM. Change this ratio leads to a variation in emulsion properties, and an increase in the emulsion efficiency to extract the solute (Kumbasar, 2009). From Table 1, it can be noticed that among the five different internal/oil ratios (3:1, 2:1, 1:1, 1:2, 1:3), the breakage percent of the system internal /oil ratio of 1:1 was found to be the lowest percentage of 1.23% while the highest percentage of 8.98% was found when the ratio of the internal /oil equal 1:3. When the ratio 1:1, the internal drops size distribution move towards smaller sizes, this decrease in the droplet emulsion diameter raises the interfacial contact area between the aqueous continuous phase and emulsion phase thus the extraction efficiency of Abamectin enhanced from70% to 92.6% as shown in Fig. 7. On the other hand, when the ratio above 1:1, the volume of oil phase is deficient to involve the internal phase, and this shifts the internal droplet size distribution toward large sizes and raises the viscosity of the emulsion. Increasing the droplet sizes decreases the interfacial area for contact between the membrane and the external phase thus declines the extraction efficiency. Therefore, I/O volume ratio of 1:1 was chosen as the optimal ratio.

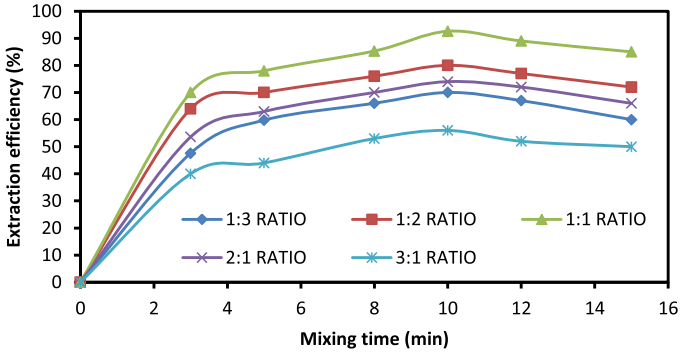

Fig. 7. Effect of (I/O) ratio on Abamectin extraction efficiency "Span 80: 3 (% v/v); Fe_3O_4: 0.2 (%w/v); mixing speed: 250 rpm, treat ratio: 5/1; emulsification time: 6 min; homogenizer speed 5800 rpm; 0.15 M HCl; external phase pH: 7".

3.7. *External pH value*

The acidity of the feed solution is another important factor in the emulsion stability and on the Abamectin extraction efficiency. Also, pH value could hasten the de-emulsification process of the Pickering emulsion droplets. In order to inspect the effects of pH value on the stability of emulsion and extraction efficiency experiments were carried out at pH value range from 2 to 8 while keeping other parameters constant. The results are tabulated in Table 1 and Fig 8, for emulsion stability and extraction efficiency respectively. It is clearly that Abamectin extraction is greatly depended on the pH. At pH of 2, the extraction efficiency was only approximately 54% after 10 min extraction time, while the breakage percent was at its highest value of 19.13%. This behavior may be due to the reduced of surfactant properties at higher H^+concentration (Sabry et al., 2007), which resulted in an emulsion destabilization and hence a reduction in the extraction efficiency. Raising the pH to 3 led to a reduction in the breakage percent 10.13% and improves the extraction efficiency to 68%. While the highest extraction efficiency of 99% and lower breakage percent of 0.52% were achieved at pH of 5. On the other hand pH above this value, the breakage percent began to increase and the extraction efficiency reduce a little. This can be attributed to the exchange reaction of cation in which protons are released.

4. Recyclability

Recycling of $\mathbf{Fe_3O_4}$nanoparticles and membrane phase is important features in PELM process from environmental protection and economic point. The emulsion were collected after the extraction process and the ability of magnetic de-emulsification was measured by applied the magnetic external field on the emulsion using a 1T cylindrical magnet for few time to separate $\mathbf{Fe_3O_4}$nanoparticles (Lin et al., 2016b). The emulsion was then allowable to separate for 60 min to aqueous internal phase and oil phase. Then the collected $\mathbf{Fe_3O_4}$ nanoparticles were cleaned with distilled water and acetone until remove oil. Then it was dried at 55 $^{\circ}\boldsymbol{C}$ for 10 hr in a vacuum oven. The obtained membrane phase and $\mathbf{Fe_3O_4}$nanoparticles are reused under optimum conditions of experimental: Homogenizer speed 5800 rpm, Emulsification time 6 min,

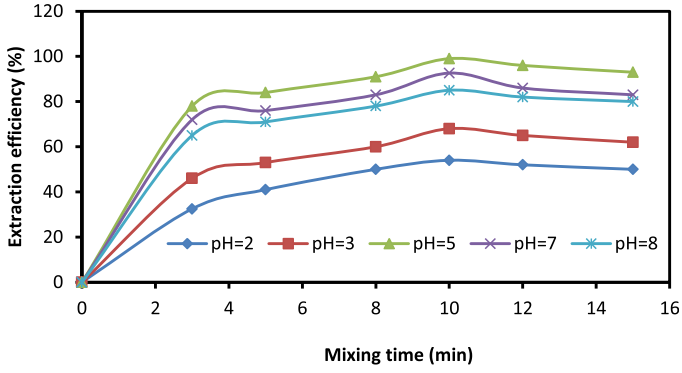

Fig. 8. Effect of external phase pH on Abamectin extraction efficiency "Span 80: 3(%v/v); Fe_3O_4: 0.2 (%w/v); mixing speed: 250 rpm, treat ratio: 5/1; emulsification time: 6 min; (I/O): 1/1; homogenizer speed 5800 rpm; 0.15 M HCl".

internal to membrane ratio 1:1, 0.15 M HCL internal phase, external to emulsion phase 5:1, 250 rpm mixing speed, 50 ppm initial concentration of Abamectin, pH=5 . The emulsion and Fe_3O_4 recyclability was successfully repeated for three cycles, the extraction percentage of Abamectin was nearly as the same. After that, the extraction efficiency began to fall and breakage percentage will be rise compared with fresh nanoparticles and oil, extraction efficiency in 10 min of contact time shown in Table 2

EVALUATION OF THE MASS TRANSFER COEFFICIENT AND THE EXTRACTION KINETICS OF ABAMECTIN COEFFICIENT

Eq. (4) was used to calculate the kinetic extraction of Abamectin using an emulsion liquid membrane (Raji et al., 2018; Kohli et al., 2019)

$$\ln\left(\frac{C_{t=t}}{C_{t=0}}\right) = -K_{obs}.\ t \tag{4}$$

Where K_{obs} is extraction rate constant (min^{-1}) *and* (t) representing extraction time (min), K_{obs} can be calculate from the slope of the straight curves produced from relationship between $\ln(\frac{C_{t=t}}{C_{t=0}})$ and (t) obtained on value of constant extraction rate $K_{obs} = 0.389\ (min^{-1})$. For the emulsion liquid membrane system, Eq. (5) represents the overall mass transfer coefficient (Kasaini et al., 1998).

$$\frac{1}{K_O} = \frac{1}{K_M} + \frac{1}{K_F} \tag{5}$$

Where K_O is overall mass transfer coefficient for PELM

K_M External phase mass transfer coefficient (m/s), Skell and Lee correlation given by Eq. (6) below were used to estimate K_M (Raji et al., 2018).

$$\frac{K_M}{\sqrt{ND}} = 2.932 \times 10^{-7} \cdot \frac{(V_I + V_M)}{(V_I + V_M + V_E)} \cdot \left(\frac{d_i}{d_{ii}}\right)^{0.548} Re^{1.371} \tag{6}$$

Where N is mixing speed of the feed phase, $d_i d_{ii}$ are diameter of impeller and mixing tank respectively, V_M, V_E, V_I are respectively, the volumes of membrane, external and internal phases.

$$Re = \frac{N\ d_i^2 \rho_E}{\mu_E} \tag{7}$$

The Re was calculated according to Eq. (7), the value obtained was 3666.29. D is the diffusivity of solute in membrane phase estimated by using the Wilke and Chang correlation given by Eq. (8), (Treybal et al .,1981), which is found equal to $2.26 \times 10^{-11} m^2/s$

$$D = \frac{117.3 \times 10^{-18} .(\varphi M_W)^{0.5}.\ T}{\mu_{O.} \phi_c^{0.6}} \tag{8}$$

Where M_w is average molecular weight of diluent (526 Kg/ Kmol) for kerosene and corn oil. The association factor of diluent (φ=1). T temperature (K). μ_o It is viscosity of organic phase (0.0387 Kg/m.s). $\varnothing_c$ It is molar volume of Abamectin ($0.862\ m^3/Kmol$), which is calculated using the Schroeder method.

K_F is the interfacial reaction rate constant (m/s) can be evaluated using Eq. (9) below.

$$K_F = \frac{K_{obs}}{A} \tag{9}$$

Where A is the specific interfacial area of emulsion estimated by Eq. (10) (Karcher et al. 2015) (Table 3).

$$A = \frac{Ai}{V} = \frac{6\alpha}{d_{32}} \tag{10}$$

5. Conclusions

The present work examines the use of Fe_3O_4nanoparticles treated with oleic acid (OA) as stabilizing agent in forming PELM for extraction of Abamectin from aqueous solution. PELM showed to be a highly e efficient process and more stable for extraction of Abamectin also can be de-emulsification easily by use external magnetic force to separate magnetic Fe_3O_4 from the emulsion. The maximum extraction percentage of 99% with minimum breakage percentage of 0.52% at 10 min, contact time were attained at the best operating condition: 5800 rpm emulsification speed, 0.2% (w/v) Fe_3O_4nanoparticles, emulsification time of 6 min and 0.15 M HCL in the internal phase. The magnetic nanoparticles and membrane phase were successfully reused to produce another Pickering emulsion to extract Abamectin for three cycles with nearly the same extraction percentage.

Table 2
Illustrate recyclability of membrane phase and $Fe_3O_4$for five cycles.

Breakage percentage%	Extraction efficiency%	Process
0.52	99	Fresh
0.88	96.4	First recycle
1.12	93.3	Second recycle
1.56	90.5	Third recycle
2.34	86.4	Fourth recycle
7.05	48.1	Five recycle

Table 3
Abamectin mass transfer coefficient in Pickering emulsion liquid membrane.

Mass transfer coefficient (m/s)	value
K_M	1.2×10^{-7}
K_F	5.83×10^{-8}
K_O	3.91×10^{-8}

CRediT authorship contribution statement

Ahmed A. Mohammed: Supervision. **Noor Q. Jaber:** Investigation, Formal analysis, Resources, Data curation, Writing – original draft, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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