



## Enhancing emulsion liquid membrane system (ELM) stability and performance for the extraction of phenol from wastewater using various nanoparticles

Faris H. Al-Ani<sup>a,b,\*</sup>, Qusay F. Alsalhy<sup>c,\*</sup>, Muthanna Al-Dahhan<sup>a</sup>

<sup>a</sup>Department of Chemical and Biochemical Engineering, Missouri University of Science and Technology, Rolla, MO 65409, USA, Tel. +964-7901730181; emails: 40027@uotechnology.edu.iq/farishamodi@yahoo.com (F.H. Al-Ani), aldahanm@mst.edu (M. Al-Dahhan)

<sup>b</sup>Civil Engineering Department, University of Technology, Alsinaa Street 52, Baghdad, Iraq

<sup>c</sup>Membrane Technology Research Unit, Chemical Engineering Department, University of Technology, Alsinaa Street 52, Baghdad, Iraq, emails: qusay\_alsalhy@yahoo.com/qusay.f.abdulhameed@uotechnology.edu.iq (Q.F. Alsalhy)

Received 19 March 2020; Accepted 7 September 2020

### ABSTRACT

Emulsion liquid membrane (ELM) technology has recently garnered attention as an efficient alternative for separating pollutants, but it faces the problem of instability during the application, as well as emulsion breaking. With this in mind MgO, Al<sub>2</sub>O<sub>3</sub>, and three magnetic Fe<sub>2</sub>O<sub>3</sub> nanoparticles (of different sizes) were utilized to fabricate a new Pickering ELM system (PELM). The extraction efficiency of phenol from aqueous solution by PELM was studied with different NPs types and with different phenol concentrations (1,000; 500; 100; and 50 ppm). It was found that the type of NPs and concentration of phenol in aqueous solution have a significant impact on the phenol extraction efficiency. By utilizing different NPs as the emulsifier, the extraction efficiency of phenol from a feed solution of 100 ppm phenol was between 91% and 97% after 12 min of contact with different PELM.

*Keywords:* Pickering emulsion liquid membrane; Emulsion stability; Phenol extraction; Nanoparticles; Wastewater treatment

### 1. Introduction

Some of the most problematic industrial and refinery wastes and pervasive water pollutants present in the environment are phenolic compounds that are generated by various industrial activities and refineries; these, are classified as hazardous substances even at low concentrations and are difficult to grade biologically [1]. Because they have applications in many industries, the removal of these compounds has attracted a great deal of environmental interest [2]. Phenols have many negative effects on humans, such as gastrointestinal irritation, tissue erosion, skin and eyes corrosion, protein degeneration, respiratory distress, neurological effects, and even death [3]. Some organizations, such as the United States Environmental Protection Agency

(USEPA) and the European Union have included 11 phenolic compounds as priority pollutants in industrial and municipal wastewater that should be removed from the environment. The EPA-defined human health water quality criteria value for phenols is 10 mg/L [4,5].

There are various methods for removing phenols from wastewater [6,7], with the most applicable being biological treatment [8], chemical oxidation [9], activated carbon adsorption, and liquid membranes [10–12]. In contrast to using liquid membranes, biological treatment is not suitable when there is a high concentration of phenols; chemical oxidation requires a large amount of oxidizing agent, with a risk of incomplete oxidation that will result in a more toxic product; and activated carbon adsorption processes are expensive and difficult to regenerate due to the

\* Corresponding authors.

chemisorption of phenols and the degradation of carbon [9,13]. These problems can be overcome by the use of a liquid membrane, which is simple when compared to the other methods and which makes complete removal of the pollutants possible [14].

Liquid membranes are choosy permeable materials that convey certain solutes from an aqueous solution to an internal phase of emulsion [15]. Among the various types of liquid membranes, emulsion liquid membrane (ELM) processes are gaining acceptance because ELM has a high interfacial area for extraction, comparatively low cost, non-dependence on equilibrium considerations, and can be prepared using relatively simple materials and equipment [16,17].

Liquid membranes (LM) are comprised of three phases: the feed phase, the membrane phase, and the stripping phase [18]. ELM consists of the dispersions of two immiscible liquid phases together, stabilized by a suitable emulsifier (surfactant). The extraction and stripping processes are achieved in one stage [19,20], thus resulting in a compact, economical system. There are two types of emulsions: water droplets dispersed in oil, designated (W/O), and oil droplets dispersed in water, designated (O/W). An important class of emulsions is the double emulsions, known also as the “emulsions of emulsions”. The most common double emulsions are W/O/W emulsions which are thermodynamically unstable with a strong tendency for coalescence, flocculation, and creaming. They have an increasing number of applications due to their ability to entrap water-soluble materials [21]. The oil phase (membrane) acts as a barrier and traps the aqueous stripping agent inside the membrane. Then, the resulting milky emulsion disperses into the external phase with mild agitation to extract the solutes [13]. The emulsion splits into teeny globules with size of  $\sim 2,000 \mu\text{m}$ . Within each globule are plenty of very small droplets of the internal phase with size of between 0.2 and  $10 \mu\text{m}$ . The wide surface area created in this operation causes a rapid rate of extraction of pollutants/solutes from the feed liquid [22]. After a suitable time of contact between the feed phase and the emulsion, the mixing is stopped, and this results in the extraction of the emulsion from the viscous feed phase. Then, the separation of both phases can be achieved. The oil phase acts as a membrane in a system because it prevents the two water phases from homogenizing with each other (i.e., the continuous water phase and the internal water phase of the emulsion) [22]. Transfer of the solute from the feed phase into the receiving phase across the membrane phase can be regarded as a mass transfer process [23]. Separation is not limited by the conditions of equilibrium since it acts using non-equilibrium mass transfer characteristics [24].

The success of process depends on the emulsion's stability and the transport of the solute across the membrane [25], which works because membranes can operate for an extended period without compromising the quality of the separation [24]. The use of ELM has been limited due to the instability of emulsions which are governed by emulsion breakage and swelling, resulting in a reduction of the overall removal efficiency [15,26,27].

Although the formation and stability of multiple emulsions has been the subject of a many papers [28], most research has been directed at reducing these limitations by applying more surfactants to the membrane phase, changing

the materials used for support, testing new extractants [24], adding a stabilizer [12,29,30], or adding an electrolyte to the aqueous solution [31]. Other parameters reported in the literature that can influence stability include the stripping agent concentration, volume ratio, stirring speed, pH, and temperature [32]. However, enhanced stability of ELM has often also been accompanied by a decrease in the removal and extraction efficiency and rate [33]. Thus, the emulsion stability and efficiency can be assumed to be controlled by the inherent membrane properties and the operating parameters [14].

Pickering emulsions (particle-stabilized emulsions) have received attentions due to their notable stability. Many researchers are interested in emulsions stabilized by solid particles due to their irreversible adsorption, low cost, and low toxicity [34]. The solid particles irreversibly adsorb at the oil–water interface phase and can provide a steric impediment between the droplets of the emulsion, prohibiting coalescence, and collisions among droplets.

Recently Lin et al. [15] used oleic acid-coated nano- $\text{Fe}_3\text{O}_4$  particles as an emulsifier to stabilize Pickering emulsions, in order to eliminate 4 MP from wastewater due to the ease of breaking of the emulsion using a magnetic force. Mohammed et al. [35] used magnetic  $\text{Fe}_2\text{O}_3$  nanoparticles to prepare a Pickering emulsion liquid membrane system for the removal of benzoic acid from an aqueous solution. Hussein et al. [36] reviewed and described the ELM and PELM techniques, preparation methods, characteristics, stabilization methods and de-stabilization, and various parameters that could impact ELM stability, extraction, and recovery.

The impact of span 80 on the kerosene as an organic phase in the presence of magnetic  $\text{Fe}_2\text{O}_3$  particles and the stability of the formed emulsions were carried out by Salman and Mohammed [37] to investigate its ability in the extraction of lead (Pb) from aqueous solutions. PELM consists of an *n*-heptane as the diluent, nano- $\text{Fe}_2\text{O}_3$  particles as a stabilizing agent was used by Mohammed et al. [38] to remove ciprofloxacin (CIP) from wastewater. The research comprises simultaneous studies of emulsion stability and extraction efficiency through various parameters. The results confirm that PELM is a very effective technique to extract more than 98% of CIP without significant emulsion breakage after a contact time of 10 min.

Nanoparticles are very effective emulsion stabilizers because they essentially encounter irreversible adsorption at liquid–liquid interfaces (i.e., the energy of adsorption is about 100–10,000 times the thermal energy) [39]. Therefore, nanoparticles have been successfully used to stabilize emulsion liquid membranes. For the time being, by speedily attracting the particle emulsifier from the droplet interface using an external magnetic field, the magnetic emulsion can be readily demulsified [40].

The objective of this study was to apply ELMs to extract phenols from liquid waste in batch reactor processes using optimum operating conditions. Then, the optimized ELM system was further employed to treat wastewaters containing a toxic substance (e.g., phenols) by using various types of nanomaterial and nonionic surfactants (span 80) on the emulsification of kerosene to maintain and enhance the stability, without compromising the extraction efficiency, of the Pickering emulsion liquid membrane.

## 2. Experimental

### 2.1. Materials

Sorbitan monooleate (span 80) was used as emulsion stabilizer agent and low-odor kerosene (Sigma-Aldrich, St. Louis, Missouri, USA) was used as a diluent. The internal phase NaOH solution was prepared from chemical pure grade compounds (Merck Co., Massachusetts 1803, USA). Magnetic ferric oxide nanoparticles ( $\text{Fe}_2\text{O}_3$ ) of three different sizes were obtained from Alfa Aesar (Ward Hill, MA, USA), as well as aluminum oxide (Alfa Aesar) and magnesium oxide (Sigma-Aldrich, St. Louis, Missouri, USA). The phenol aqueous solution was prepared by dissolving the phenols in deionized water. The 1,000 ppm concentration of phenols was diluted to 3, 6, 12, 25, 50, and 100 ppm to obtain the calibration curve.

### 2.2. Experimental procedures

The ELM process for the treatment of phenols is shown in Fig. 1. A water-in-oil-in-water (W/O/W) emulsion system was chosen which consisted of the external, membrane, and internal phases. The W/O was prepared containing an internal stripping agent and membrane phase solution. The emulsion ratio of the inner receiving phase to the immiscible liquid membrane phase was (W1: O = 1/3 v/v); this was selected as the best value ratio, according to Mohammed et al. [41]. The membrane phase consisted of kerosene and span 80 with different nanoparticles as the stabilizer. Certain quantities of nanoparticles and span 80

were dispersed into 30 mL kerosene and mixed in a glass cylinder batch reactor using an ultra-high-speed (Turrax IKA-T25, 79219 Staufen, Germany) homogenizer to ensure the complete dispersion and homogeneity of the membrane phase solution. During this process, 10 mL of NaOH solution was added drop wise into the batch reactor and was mixed with the organic phase (O), and the mixture was homogenized at 7,000 rpm for 10 min to obtain a white emulsion. The optimum emulsification speed was selected to be 7,000 rpm because a higher speed provides enhanced dispersion of the internal phase in the membrane phase, thus producing better emulsion stability with lower leakage [41]. The emulsion was then dispersed into the feed phase in a mixing contactor at ratio of (1:12) and was continuously stirred at a low rotational speed by an overhead digital stirrer (IKA, model: RW20) with a stirring speed of 300 rpm for 25 min, during which numerous small globules of emulsion formed, eventually leading to a double emulsion W/O/W and to extraction of the phenol from the external feed phase. The external phase ratio necessitates that a small volume of emulsion is desirable, to make the process less expensive. Therefore, the ratio of the ELM to the external feed was selected as 1/12. Fig. 2 shows the transport mechanism of phenols during the ELM extraction process. A phenol in the external water phase diffuses to the O/W2 interface and reacts with the oil phase to form an oil soluble complex. The oil soluble complex then transfers through the oil membrane to reach the interface of the internal W1/O, and instantaneously reacts with NaOH to produce a water insoluble salt as depicted in the reaction below [39]:

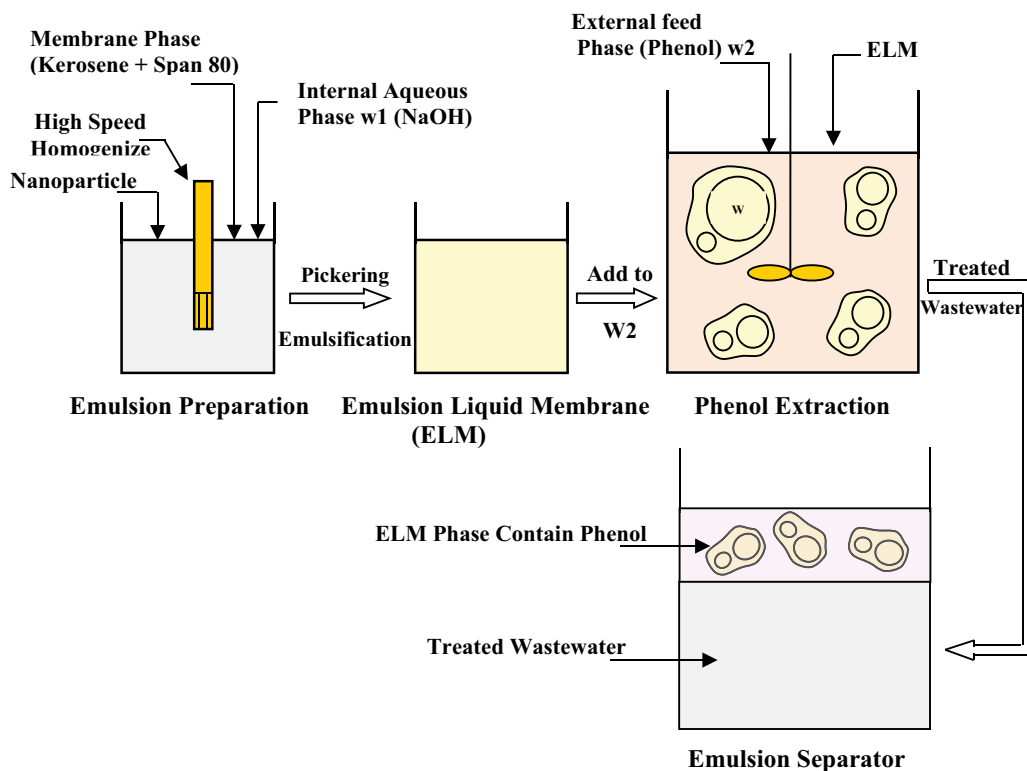


Fig. 1. Schematic diagram of the phenol extraction experiments.

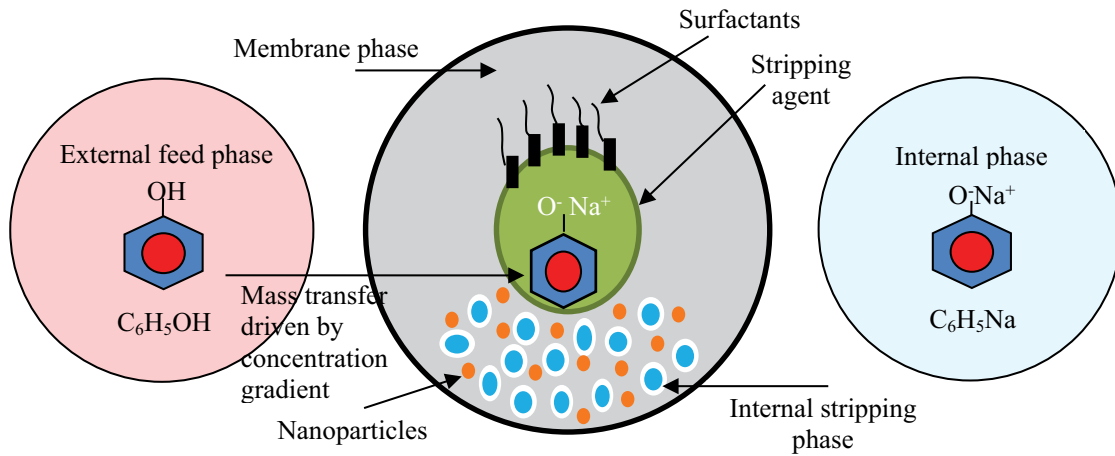
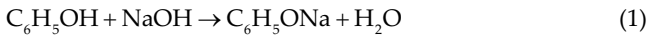


Fig. 2. Schematic diagram of the transport mechanism of phenol during ELMs process.



$C_6H_5ONa$  cannot transfer back through the liquid membrane into the feed phase due to the insolubility of  $C_6H_5ONa$  in the oil phase. Accordingly, phenols are electically separated from the external to internal phase.

Many samples were collected from the agitated solution at various times, and then separated from the emulsion phase using a 0.2  $\mu m$  nylon syringe filter (Simsii, Inc., USA). The concentration of phenols in the aqueous external phase was determined by a spectrophotometer (96 well UV-micro plate) at a fixed wavelength,  $\lambda$  of 270 nm, from which an absorbance calibration curve was created. The emulsifier and contactor were maintained at room temperature,  $22^\circ C \pm 1^\circ C$ , and the pH of the mixture was adjusted to 7 using a pH conductivity meter in order to avoid the precipitation of ELM the pH of the mixture was maintained at 7 [15,41]. The extractions are shown in figures in terms of remaining fraction of the phenols ( $C_t/C_0$ ) vs. contact time  $t$  (minute) which gives better illustration of the extraction results.

### 3. Results and discussion

#### 3.1. Effect of the amount of $Fe_2O_3$ -NPs on the extraction efficiency of phenols

Two surfactant ratios (2% and 3%) and two NaOH concentrations (0.3 and 0.5 M/L) were tested to find the best ratio for phenol extraction, as shown in Figs. 3–6. The emulsion was stabilized using different  $Fe_2O_3$  (20–40 nm) nanoparticles ratios (i.e., 0.05, 0.1, 0.15, and 0.2) (nano/NaOH) (w/w). The external phenol concentration was 40 ppm. The best percentage removal of phenol was obtained using span 80 (surfactant) at 2% (w/v) and 0.5 M/L NaOH with a magnetic  $Fe_2O_3$  nanoparticles concentration of 0.1%w/w. This result is in agreements with the finding obtained by Lin et al. [15] and Mohammed et al. [35], the stability of the emulsion improved with an increasing the ratio of magnetic nanoparticles, by covering more of the emulsion interface. This improves the extraction efficiency, however, with further increases in concentration, the extraction efficiency decreased due to the dispersion of

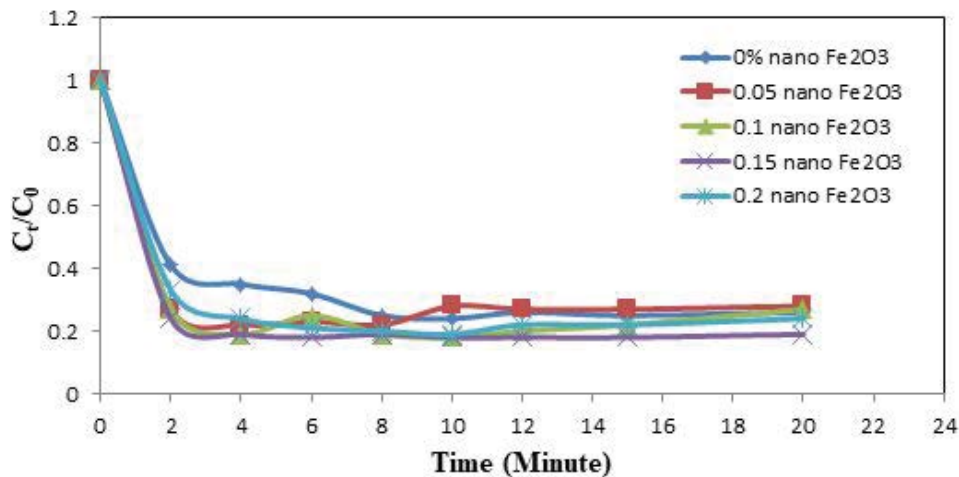


Fig. 3. Effect of magnetic  $Fe_2O_3$  nanoparticles concentration on the phenol extraction, 3% (w/v) span 80, and 0.5 M/L NaOH.

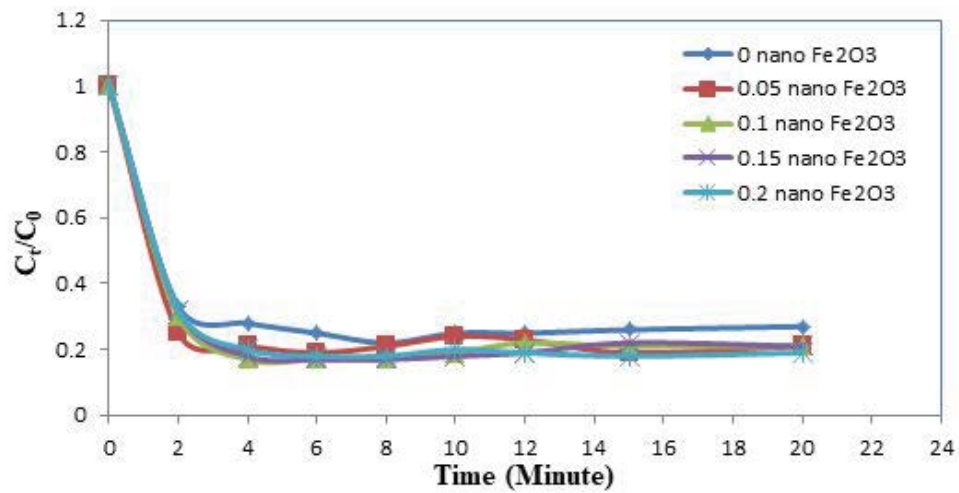


Fig. 4. Effect of magnetic Fe<sub>2</sub>O<sub>3</sub> nanoparticles concentration on the phenol extraction, 3% (w/v) span 80, and 0.3 M/L NaOH.

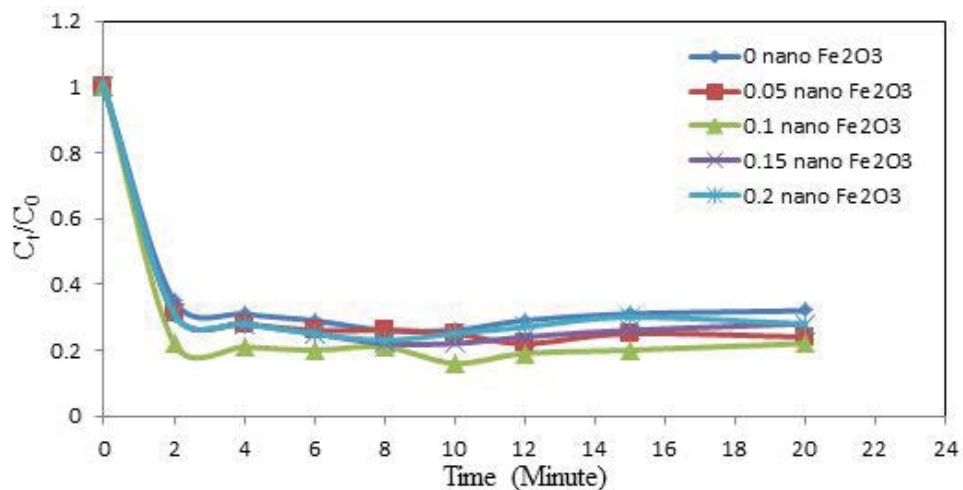


Fig. 5. Effect of magnetic Fe<sub>2</sub>O<sub>3</sub> nanoparticles concentration on the phenol extraction, 2% (w/v) span 80, and 0.5 M/L NaOH.

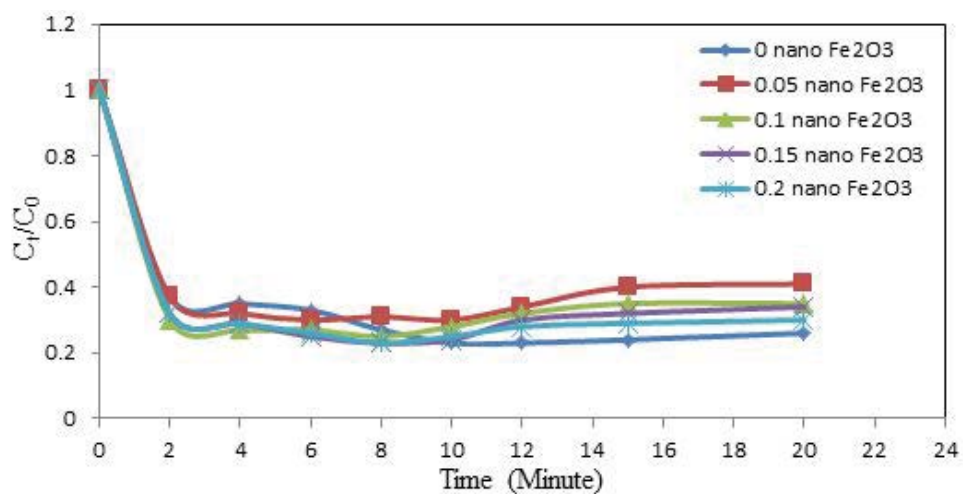


Fig. 6. Effect of magnetic Fe<sub>2</sub>O<sub>3</sub> nanoparticles concentration on the phenol extraction, 2% (w/v) span 80, and 0.3 M/L NaOH.

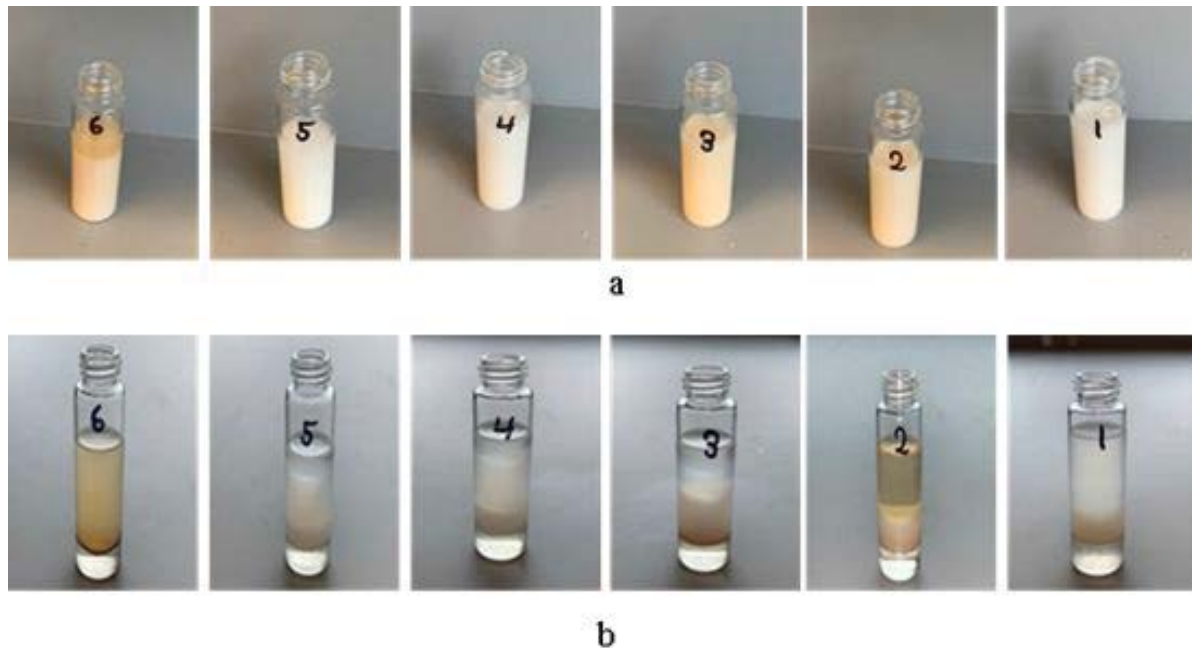


Fig. 7. Prepared Pickering emulsion liquid stability under static condition at (a) time 0 and (b) after separation ((1) no nanoparticles, 6 h, (2) magnetic  $\text{Fe}_2\text{O}_3$  8–10 nm nanoparticles, 44 h, (3) magnetic  $\text{Fe}_2\text{O}_3$  20–40 nm nanoparticles, 18 h, (4)  $\text{Al}_2\text{O}_3$  20 nm nanoparticles, 20 h, (5)  $\text{MgO}$   $\leq 50$  nm nanoparticles, 14 h, (6) magnetic  $\text{Fe}_2\text{O}_3$  3 nm nanoparticles, 52 h).

particles in the continuous phase. These may form aggregates on the W/O interface that affect the stability of the emulsion and obstruct the transfer process.

One of the important factors in an ELM processes is a suitable concentration of the stripping agent in the internal phase. When NaOH concentration is low, stripping process will slow down and there is not enough NaOH to react with solute in internal phase because an excess amount of the stoichiometric NaOH is required in order to neutralize solute and achieve acid removal rate as high as possible. When NaOH concentration is high, the liquid membrane is unstable causing the emulsion leakage, and the removal efficiency decreases [12]. However, an excessive amount of surfactant will increase the viscosity of the membrane phase, which decreases the removal of phenols through the highly viscous membrane [42,43]. Accordingly, span 80 at 2% with 0.5 M/L NaOH, and 0.1  $\text{Fe}_2\text{O}_3$  concentrations was chosen.

### 3.2. Stability of ELM in static conditions

The breakage of the membrane because of instable emulsion results lead to a reduction in the efficiency of the extraction process and loss of phenols. Therefore, the stabilization of PELM by a combination of nanoparticles and surfactant was also assessed by this study. Thus, the stability and phase separation of Pickering emulsions with different nanoparticles were studied. Emulsification experiments were conducted using the above mentioned best operating parameters, and was kept under a static condition, to facilitate the visualization of the separated membrane phase with respect to time. The images of all prepared emulsions (those stabilized by nanoparticles and zero-nano emulsions) are shown in Fig. 7a. Over time, all

emulsions clearly became unstable and combined with the clear water layer, starting phase separation, after 6 h, as depicted in Fig. 7b. At the beginning of the experiments, all emulsions were stable for the first 6 h with no clear phase separation. But the magnetic  $\text{Fe}_2\text{O}_3$  nanoparticle (20–40 nm),  $\text{Al}_2\text{O}_3$  (20 nm), and  $\text{MgO}$  ( $\leq 50$  nm) nanoparticles exhibited an aqueous phase separation after 18, 20, and 14 h, occur for each type of nanoparticles, and the volume fraction of the water increased. Separated water occurred on the bottom, for all emulsions indicating their instability. The magnetic  $\text{Fe}_2\text{O}_3$  nanoparticles (8–10 nm) and (3 nm) started showing phase separation after 44 and 52 h, respectively, thereby showing an increase in the stability time as compared with the other types of nanoparticles shown in Fig. 8. This may be due to the small size of particles, the larger number of the particles, and/or the larger surface area. Increased stability resulted from the stabilizing mechanism explained above, the PELM become more stable when using nanoparticles with kerosene, span 80, and NaOH. Moreover, the combination of surfactant (span 80) with NPs resulted in the formation of a 3-dimensional lattice among the nanoparticles and droplets, which meant the droplets of the emulsion, should be stable.

### 3.3. Effect of NPs on the extraction efficiency at different phenol concentrations

The present study investigated the optimum parameter values for the extraction of phenols by Pickering emulsion liquid membranes stabilized by both a surfactant and five metal-based nanoparticles:  $\text{Fe}_2\text{O}_3$  (8–10, 20–40, and 3 nm),  $\text{Al}_2\text{O}_3$  (20 nm), and  $\text{MgO}$  ( $\leq 50$  nm). Magnetic  $\text{Fe}_2\text{O}_3$  nanoparticles were selected as Pickering emulsions stabilizers due to their low-cost, environmental friendliness, and



low-toxicity [44]. The rates of phenol extraction were examined at different phenol concentrations (i.e., 1,000; 500; 100; and 50 ppm).

At the beginning, extraction by ELM stabilized with span 80 without adding any nanoparticles was examined. The results show that the extraction was very low at the higher external concentration of 1,000 ppm, with a maximum of 50% removal at 10 min, as shown in Fig. 9. After this, the breakage started, which means that the ELM was inefficient for the removal of phenols from high concentrations of aqueous solution. The maximum extraction of phenol was 93% for a 100 ppm solute concentration at 12 min.

The effect of magnetic  $\text{Fe}_2\text{O}_3$  nanoparticles (8–10 nm) on the percentage removal of phenols vs. time is shown in Fig. 10. At a high phenol concentration (i.e., 1,000 and 500 ppm), the percentage removal was 27.5% and 55%, respectively at 4 min, which increased slowly to 63% and 87% after 15 min. For external phenol concentrations of 100 ppm, the extracted efficiency was 59% within 2 min and 87% at 4 min.

This rate continued until it reached a maximum removal rate of 98% after 15 min. This was due to the high surface area of the magnetic  $\text{Fe}_2\text{O}_3$  particles (250  $\text{m}^2/\text{g}$ , according to the supplier company, section 2.1 (Materials)) and the rate slightly decreased thereafter. The maximum removal efficiency of phenols for an aqueous solution of 50 ppm was 96% at 12 min and 92% after 15 min. Lee et al. [45] reported that increasing the extraction time increased the emulsion breakage and caused the membrane to swell due to more water being transferred into the internal phase, such that breakage happened when the solute transferred from the internal to the external phase.

The comparison of removal efficiencies for different solute concentrations using magnetic  $\text{Fe}_2\text{O}_3$  nanoparticles (20–40 nm) is shown in Fig. 11. At a high external phenol concentration (1,000 and 500 ppm), the percentage removal of phenols after 12 min was 65% and 90%, respectively, which increased slowly to 73% and 87% after 15 min. It is clear that the removal efficiency was higher at lower concentrations

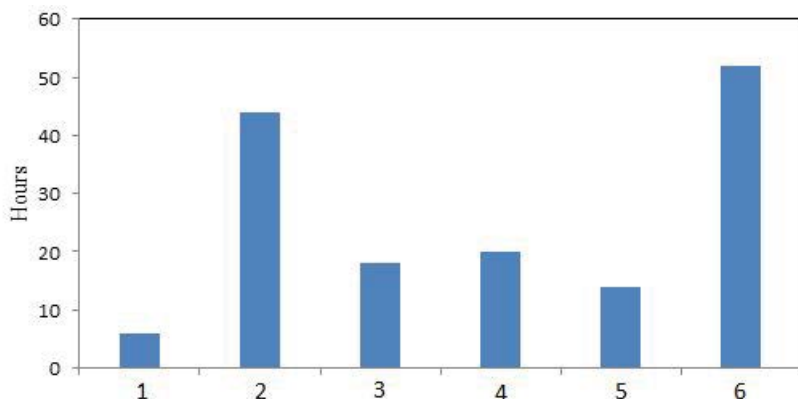


Fig. 8. Stability of emulsions liquid membrane stored at room temperature vs. time (1) no nanoparticles, (2)  $\text{Fe}_2\text{O}_3$  (8–10 nm), (3)  $\text{Fe}_2\text{O}_3$  (20–40 nm), (4)  $\text{Al}_2\text{O}_3$  (20 nm), (5)  $\text{MgO}$  ( $\leq 50$  nm), (6)  $\text{Fe}_2\text{O}_3$  (3 nm).

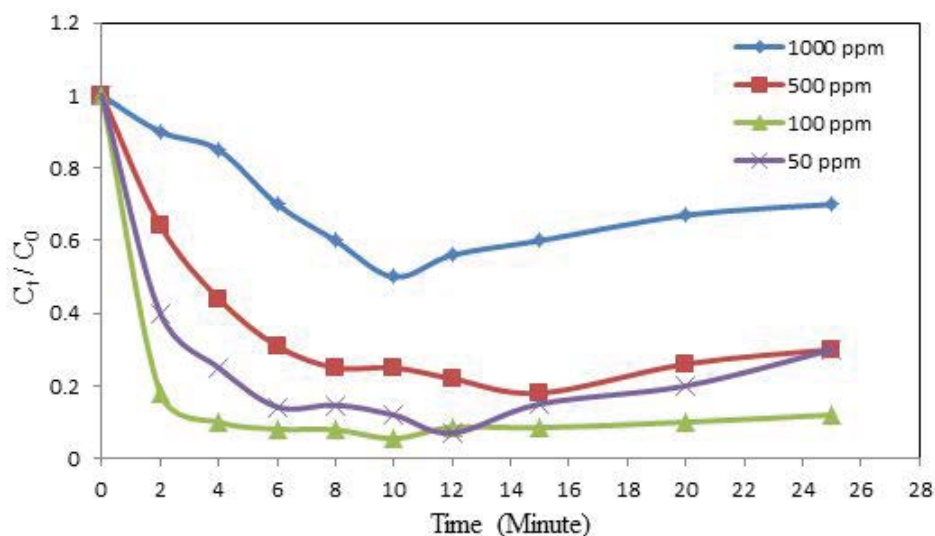


Fig. 9. Rates of phenol extraction by ELM stabilized with 2% (w/v) span 80, and 0.5 M/L NaOH, without nanoparticles for different solute concentrations.

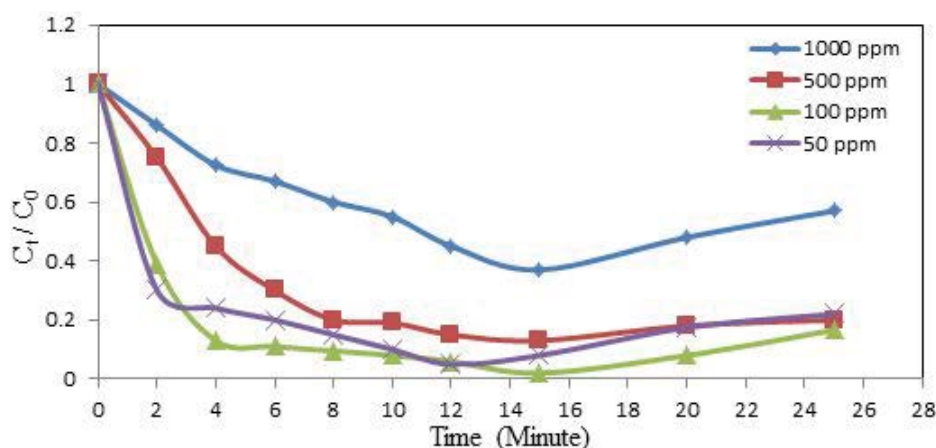


Fig. 10. Rates of phenol extraction by Pickering emulsions stabilized with 2% (w/v) span 80, 0.5 M/L NaOH, and 0.1% (w/w) magnetic  $\text{Fe}_2\text{O}_3$  (8–10 nm) nanoparticles for different solute concentrations.

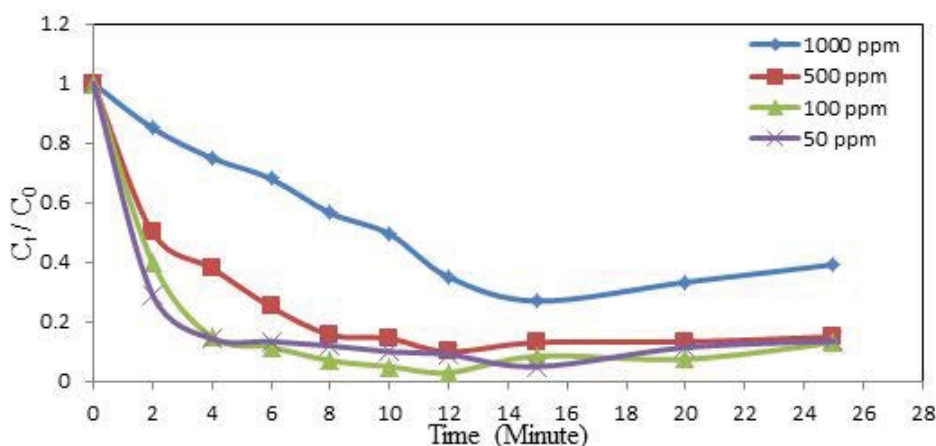


Fig. 11. Rates of phenol extraction by Pickering emulsions stabilized with 2% (w/v) span 80, 0.5 M/L NaOH, and 0.1% (w/w) magnetic  $\text{Fe}_2\text{O}_3$  (20–40 nm) nanoparticles for different solute concentrations.

(100 and 50 ppm) and reached 85% and 86%, respectively, in the first 4 min then continued to increase until it reach 97% and 91% at 12 min and 91% and 95% at 15 min, respectively. At lower solute concentrations, the extraction process was controlled by the external mass transfer transported into the stripping phase continuously [45], and most of the phenols extracted within the emulsion globule reacted with the internal phase droplets situated in the peripheral regions of the emulsion globule [41,46]. However, with continuous operation and as the solute concentration in the external phase decreased, the efficiency decreased in comparison with the process when using a higher solute concentration. By increasing the external feed, the NaOH concentration in the peripheral droplets rapidly decreased, necessitating the solute to permeate deeper within the globule prior to reacting with the NaOH. Any increase in the external phase concentration led to an increase in the diffusional path lengths of the solute within the emulsion globules [22]. The most effective removal was achieved at concentrations of 100 ppm.

The results obtained by applying  $\text{Al}_2\text{O}_3$  and MgO nanoparticles as stabilizers are presented in Figs. 12 and 13, respectively; the results are approximately the same

as those mentioned above. MgO has many advantages, including the high purity of synthesized powders, a better control of stoichiometry, the regular shape of the particles, and continuous working [46]. PELM stabilized by  $\text{Al}_2\text{O}_3$  had the best extraction ability of any nanoparticles when a high concentration load (i.e., 1,000 ppm) was applied, reaching 45% after 4 min and 75% at 15 min. The extraction percentage was 90% at 4 min for both types at 100 ppm, and  $\text{Al}_2\text{O}_3$  reached 91% at 12 min and 93% at 15 min, with a maximum of 96.5% at time 10 min.

The removal efficiency of phenols at an initial concentration of 1,000 ppm using MgO was 25% at 4 min and 57% when using 500 ppm. The removal of phenols reached 92.2% and 86% at 12 min for an initial phenol concentration of 100 and 50 ppm, respectively, while at 15 min the removal efficiency was 96% and 94%, respectively.

The phenol extraction using the magnetic  $\text{Fe}_2\text{O}_3$  nanoparticle (3 nm) as the ELM stabilizer is illustrated in Fig. 14. This system produced a removal percentage of 91% at 4 min for an initial concentration of 100 ppm, demonstrating that phenols were extracted when they came in contact with the ELM. Better extraction was obtained with a lower  $C_i/C_0$



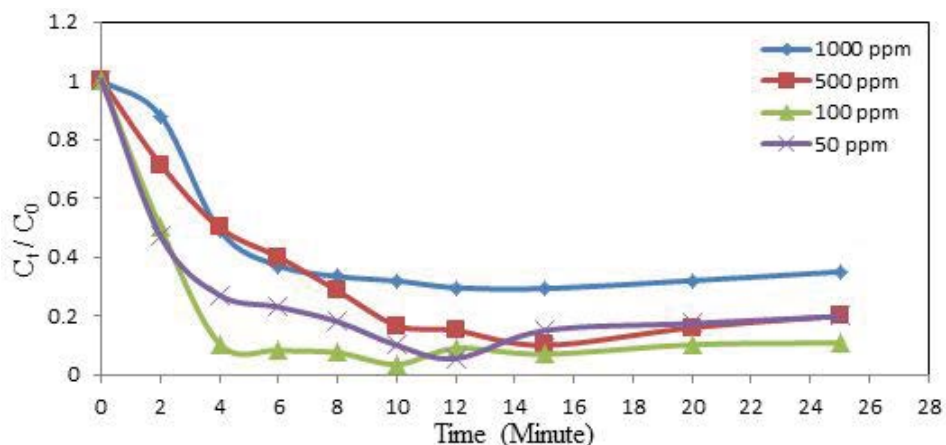


Fig. 12. Rates of phenol extraction by Pickering emulsions stabilized with 2% (w/v) span 80, 0.5 M/L NaOH, and 0.1% (w/w) Al<sub>2</sub>O<sub>3</sub> (20 nm) nanoparticles for different solute concentrations.

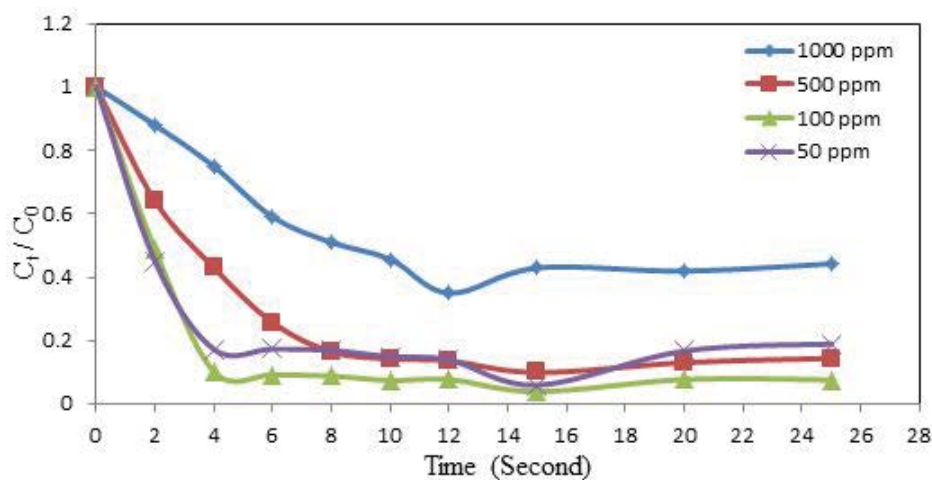


Fig. 13. Rates of phenol extraction by Pickering emulsions stabilized with 2% (w/v) span 80, 0.5 M/L NaOH, and 0.1% (w/w) MgO ( $\leq 50$  nm) nanoparticles for different solute concentrations.

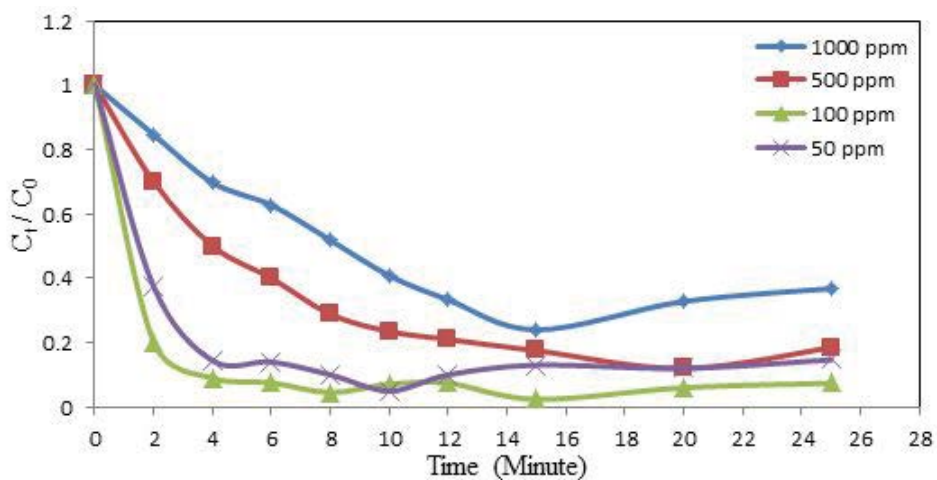


Fig. 14. Rates of phenol extraction by Pickering emulsions stabilized with 2% (w/v) span 80, 0.5 M/L NaOH, and 0.1% (w/w) magnetic Fe<sub>2</sub>O<sub>3</sub> (3 nm) nanoparticles for different solute concentrations.

of 95.5% for an external solute concentration of 100 ppm; this was obtained at 8 min with a maximum extraction of 97.6% at 15 min, and a good extraction ratio was sustained until 25 min. This reduction in the remaining compounds indicates improved extraction efficiency. In addition, the percentage removal for other external concentrations, including a higher external concentration, gave a higher percentage removal of 76% at 15 min for 1,000 ppm and 88% at 20 min for 500 ppm. Magnetic  $\text{Fe}_2\text{O}_3$  nanoparticles can form emulsions which are stable when they exhibit coalescence because of the protective film formed by the particles at the oil–water interface [34], and a large surface area for mass transfer is generated because of the small size of the emulsion globules formed. Iron oxide ( $\text{Fe}_2\text{O}_3$ ), the most common oxide of iron, has important magnetic properties too. From the viewpoint of basic research, iron(III) oxide is a convenient compound for the general study of polymorphism, and the magnetic and structural phase transitions of nanoparticles [47].

Utilizing the emulsion liquid membrane process with enhanced stability by adding nanoparticles as a stabilizer will result in a good extraction of phenols with a low emulsion leakage. The low shear stress obtained by using nanoparticles decreases the emulsion instability, thus providing high extraction efficiency. By using an external magnetic field, a magnetic emulsion can be readily demulsified by attracting the particle emulsifier from the interface of the droplet [15]. Overall, the extraction percentage of phenols can be preserved at 98% by carefully selecting the parameters of the membrane process and enhancing its stabilization.

The maximum phenol extraction for all types of PELM was obtained at approximately 12 min, as shown in Table 1. At a high phenol concentration (1,000 ppm), the  $\text{Al}_2\text{O}_3$  nanoparticles achieved a higher extraction of 71% and phase separation at 20 h, while the magnetic  $\text{Fe}_2\text{O}_3$  nanoparticles (20–40 nm) have better extraction efficiency for phenol concentrations of 500, 100, and 50 ppm as compared with other nanoparticle types, with a phase separation of 18 h. This can also be observed by using microscopy images as shown in Fig. 15 with scale bars of 50  $\mu\text{m}$ . The emulsion was initially stable and consisted of a diluent, surfactant, aqueous solution, and nanoparticles as the stabilizer. The photos were taken after 10 min of homogenization during the emulsion preparation, before applying the emulsion to the external phase. Fig. 15a illustrates that the emulsion drops size with no addition of nanoparticles was larger than the drops size when magnetic  $\text{Fe}_2\text{O}_3$  nanoparticles were added (Figs. 15b–d and f).

After using nanoparticles, the droplets were spherical, and the distribution of nanoparticles within the membrane

was clear. Some agglomeration of the droplets can be observed in the image in Figs. 15b and f, which may have been caused by the very small nanoparticles of magnetic  $\text{Fe}_2\text{O}_3$  (8–10 and 3 nm) acting as a coagulant. Less agglomeration of droplets can be observed in Fig. 15c for magnetic  $\text{Fe}_2\text{O}_3$  nanoparticles (20–40 nm) which explains the higher removal efficiency compared with other types. Figs. 15d and e show the droplets when using  $\text{Al}_2\text{O}_3$  and MgO nanoparticles, respectively, where the droplet size is also small and tends to be non-spherical, particularly when using  $\text{Al}_2\text{O}_3$  nanoparticles. When using nanoparticles, a large surface area for mass transfer is generated because of the small size of the emulsion globules formed, and because the internal encapsulated droplets within the emulsion globules are small in diameter; this leads to a large internal mass transfer area, thus increasing the extraction efficiency.

In general, the sizes of NPs have an effect on the interaction energies during their transfer in aqueous solutions. For example, the behavior of NPs with a size smaller than 20 nm was similar to that of a molecular solute. Therefore, the aggregation of NPs could be significantly affected by intermolecular forces. Thus, a scale of smaller than 20 nm (e.g., 8–10 nm) affects positively the homogeneity of the surfaces, which in turn improves the extraction efficiency. However, due to small NPs size, the transfer of NPs is recognized in high diffusion coefficients, leading to increased contact time, and consequently to fast aggregation.

#### 4. Conclusions

This study was conducted to extract phenols from aqueous solutions and to enhance the emulsion liquid membrane system stability by developing a Pickering emulsion liquid membrane that was stabilized by different types of nanoparticles with span 80. The followings conclusions can be drawn:

- The operational conditions that caused the highest percentage removal efficiency of phenols were the combination of a surfactant concentration of 2% w/v and a stripping agent in the internal phase of 0.5 M NaOH, with a magnetic  $\text{Fe}_2\text{O}_3$  nanoparticles concentration ratio of 0.1% w/w.
- The most effective removal was achieved at a concentration of 100 ppm, in which the maximum extractions using magnetic  $\text{Fe}_2\text{O}_3$  nanoparticle (8–10, 20–40, and 3 nm),  $\text{Al}_2\text{O}_3$ , and MgO were 98% at 15 min, 97% at 12 min, 97.5% at 15 min, 96.5% at 10 min, and 96% at 15 min, respectively.

Table 1  
Extraction efficiency and phase separation of different ELMs at 12 min

Phenol concentration (ppm)	Without nano (%)	$\text{Fe}_2\text{O}_3$ 3 nm (%)	$\text{Fe}_2\text{O}_3$ 8–10 nm (%)	$\text{Fe}_2\text{O}_3$ 20–40 nm (%)	$\text{Al}_2\text{O}_3$ 20 nm (%)	MgO $\leq 50$ nm (%)
1,000	42	66.7	55	65	71	65
500	78	79	85	90	85	86.3
100	91.4	92.6	95	97	91	92.2
50	88	90	96	96	94.5	86

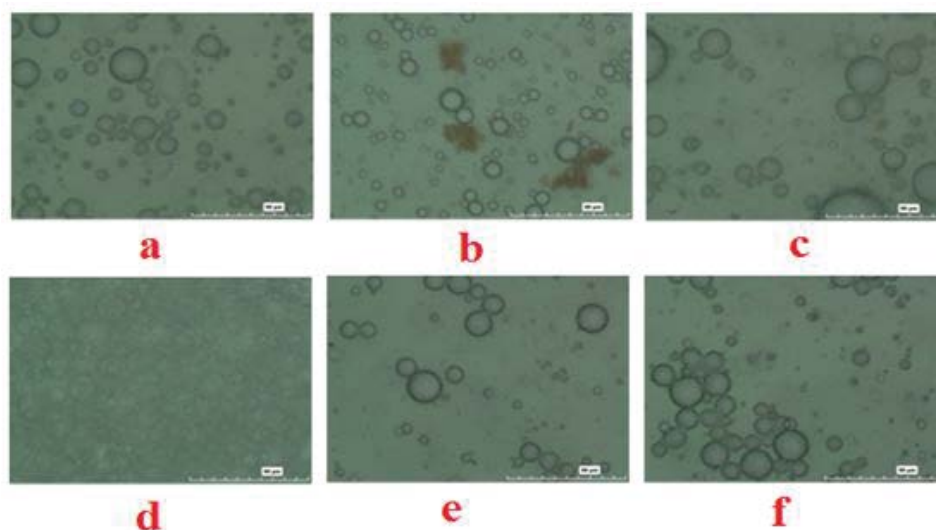


Fig. 15. Optical microscopy images of Pickering emulsions by (a) no addition of nanoparticles, (b) magnetic  $\text{Fe}_2\text{O}_3$  (8–10 nm) nanoparticles, (c) magnetic  $\text{Fe}_2\text{O}_3$  (20–40 nm) nanoparticles, (d)  $\text{Al}_2\text{O}_3$  (20 nm) nanoparticles, (e)  $\text{MgO}$  ( $\leq 50$  nm) nanoparticles, (f) magnetic  $\text{Fe}_2\text{O}_3$  (3 nm) nanoparticles, 0.20% (w/v) span 80, and (0.50 mol/L) NaOH.

- ELM without nanoparticles as a stabilizer was not efficient at removing a high concentration of phenols. The maximum extraction attained was 92% at 10 min for a 100 ppm solute.
- ELM stabilized by magnetic  $\text{Fe}_2\text{O}_3$  nanoparticles (20–40 nm) achieved higher extraction efficiency at 500, 100, and 50 ppm and mixing time of 12 min, as compared with other nanoparticle stabilizers.
- All nanoparticles combined with span 80 can be used to improve the stability of Pickering emulsion liquid membranes, and to increase the percentage of phenol extraction to 98%. Additionally, the emulsions droplets become more stable due to the nanoparticles' ability to form a protective film at the O/W mediator, and as a result of an increased number of binding sites on the phenols surfaces.

### Acknowledgments

First, I would like to express my deepest gratitude and thanks to Prof. Muthanna Al-Dahhan at the Department of Chemical and Biochemical Engineering, at Missouri University of Science and Technology, Rolla, Missouri (USA), for his support and the funds provided by the Multiphase Reactors Engineering and Applications Laboratory, directed by him to carry out this study. I would also like to thank Ass. Prof. Puro Sutaba and Mr. Russel at the Department of Chemical and Biochemical Engineering for providing access to a lab for conduct some tests. Thanks to Prof. Dr. Sawsan Mohammed, and Ass. Prof. Dr. Dhiyaa. Finally, I would like to thank the University of Technology for giving me the opportunity for a 1 y sabbatical.

### References

- [1] Oligae, New Technologies in Phenol Removal from Wastewater, Oligae, 2015. Available at: <http://www.oilgae.com/algae/cult/sew/new/phe/phe.html>
- [2] Z. Rappoport, The Chemistry of Phenols, Part 1: The Chemistry of Functional Groups, John Wiley & Sons, Hoboken, NJ, 2003.
- [3] Health and Safety Guide for Phenol No. 88, 1994. Available at: [http://www.inchem.org/documents/hsg/hsg/hsg88\\_e.htm](http://www.inchem.org/documents/hsg/hsg/hsg88_e.htm) (Retrieved December 02, 2009)
- [4] C. Mahugo-Santana, Z. Sosa Ferrera, E.M. Torres Padrón, J.J. Santana Rodríguez, Methodologies for the extraction of phenolic compounds from environmental samples: new approaches, *Molecules*, 14 (2009) 298–320.
- [5] C.L. De Silva, Removal of Phenol from Oil/Gas Wastewater by Catalytic Supercritical Water Treatment, A Master of Science Thesis Presented to the Faculty of the Russ College of Engineering and Technology of Ohio University, 2016.
- [6] E.E.P. Ramírez, M. de la Luz Asunción, V.S. Rivalcoba, A.L.M. Hernández, C.V. Santos, Removal of Phenolic Compounds from Water by Adsorption and Photocatalysis, *Book Citation Index in Web of Science™ Core Collection (BKCI)*, Ch14, 2017. Available at: <https://www.intechopen.com/books/phenolic-compounds-natural-sources-importance-and-applications/removal-of-phenolic-compounds-from-water-by-a-dsorption-and-photocatalysis>
- [7] V.A. Rangari, A.V. Deshmukh, A.K. Chaudhari, K.S. Deshmukh, Review paper on preparation of liquid emulsion membrane for separation of phenol, *Int. J. Innovative Res. Adv. Stud.*, 3 (2016) 63–65.
- [8] M. Shourian, K.A. Noghabi, H.S. Zahiri, T. Bagheri, G. Karballaei, M. Mollaei, I. Rad, S. Ahadi, J. Raheb, H. Abbasi, Efficient phenol degradation by a newly characterized *Pseudomonas* sp. SA01 isolated from pharmaceutical wastewaters, *Desalination*, 246 (2009) 577–594.
- [9] R. Noyes, *Handbook of Pollution Control Processes*, Noyes Publication, New Jersey, 1991, p. 423.
- [10] B.H. Hameed, A.A. Rahman, Removal of phenol from aqueous solutions by adsorption onto activated carbon prepared from biomass material, *J. Hazard. Mater.*, 160 (2008) 576–581.
- [11] K.P. Singh, A. Malik, S. Sinha, P. Ojha, Liquid-phase adsorption of phenols using activated carbons derived from agricultural waste material, *J. Hazard. Mater.*, 150 (2008) 626–641.
- [12] H.R. Mortaheb, M.H. Amini, F. Sadeghian, B. Mokhtarani, H. Daneshyar, Study on a new surfactant for removal of phenol from wastewater by emulsion liquid membrane, *J. Hazard. Mater.*, 160 (2008) 582–588.
- [13] G. Busca, S. Berardinelli, C. Resini, L. Arrighi, Technologies for the removal of phenol from fluid streams: a short review of recent developments, *J. Hazard. Mater.*, 160 (2008) 265–288.

- [14] Y.S. Ng, N.S. Jayakumar, M.A. Hashim, Performance evaluation of organic emulsion liquid membrane on phenol removal, *J. Hazard. Mater.*, 184 (2010) 255–260.
- [15] Z. Lin, Z. Zhang, Y. Li, Y. Deng, Magnetic nano-Fe<sub>3</sub>O<sub>4</sub> stabilized Pickering emulsion liquid membrane for selective extraction and separation, *Chem. Eng. J.*, 288 (2016) 305–311.
- [16] J.W. Frankenfeld, N.N. Li, Recent Advances in Liquid Membrane Technology, R.W. Rousseau, Ed., Handbook of Separation Process Technology, John Wiley & Sons Inc., New York, NY, 1987, pp. 840–861.
- [17] R.K. Goyal, N.S. Jayakumar, M.A. Hashim, A comparative study of experimental optimization and response surface optimization of Cr removal by emulsion ionic liquid membrane, *J. Hazard. Mater.*, 195 (2011) 383–390.
- [18] S. Björkregren, R.F. Karimi, A. Martinelli, N.S. Jayakumar, M.A. Hashim, A new emulsion liquid membrane based on a palm oil for the extraction of heavy metals, *Membranes*, 5 (2015) 168–179.
- [19] W. Cai, Y. Wang, S. Zhu, Flow and mass transfer characteristics in a falling-film extractor using hollow fiber as packing, *Chem. Eng. J.*, 108 (2005) 161–168.
- [20] Z. Ren, W. Zhang, Y. Liu, Y. Dai, C. Cui, New liquid membrane technology for simultaneous extraction and stripping of copper(II) from wastewater, *Chem. Eng. Sci.*, 62 (2007) 6090–6101.
- [21] A. Benichou, A. Aserin, N. Garti, Double emulsions stabilized with hybrids of natural polymers for entrapment and slow release of active matters, *Adv. Colloid Interface Sci.*, 108–109 (2004) 29–41.
- [22] B. Panchal, J. Pandya, Extraction of phenol from aqueous stream into emulsion liquid membrane, *Int. J. Curr. Trends Eng. Res.*, 2 (2016) 145–153.
- [23] V.S. Kislik, *Liquid Membrane: Principles and Application in Chemical Separation and Wastewater Treatment*, Elsevier, Amsterdam, 2010.
- [24] N. Padwal, S.S. Prakash, S. Thakkar, T. Deshpande, Supported liquid membrane technology: advances and review of its applications, *Indian J. Adv. Chem. Sci.*, 6 (2018) 118–129.
- [25] M.B. Rosly, N. Othman, H.A. Rahman, Liquid membrane component selection for removal of phenol from simulated aqueous waste solution, *Malaysian J. Anal. Sci.*, 22 (2018) 702–714.
- [26] J. Jiao, D.G. Rhodes, D.J. Burgess, Multiple emulsion stability: pressure balance and interfacial film strength, *J. Colloid Interface Sci.*, 250 (2002) 444–450.
- [27] N. Jusoh, N. Othman, N.A. Nasruddin, Emulsion liquid membrane technology in organic acid purification, *Malaysian J. Anal. Sci.*, 20 (2016) 436–443.
- [28] A. Gheorghe, A. Stoica, O. Floarea, Emulsion liquid membranes stability, *UPB Sci. Bull., Ser. B: Chem. Mater. Sci.*, 70 (2008) 23–30.
- [29] Y.G. Park, A.H.P. Skelland, L.J. Forney, J.H. Kim, Removal of phenol and substituted phenols by newly developed emulsion liquid membrane process, *Water Res.*, 40 (2006) 1763–1772.
- [30] M. Djenouhat, O. Hamdaoui, M. Chiha, M.H. Samar, Ultrasonication assisted preparation of water-in-oil emulsions and application to the removal of cationic dyes from water by emulsion liquid membrane. Part 1: membrane stability, *J. Sep. Purif. Technol.*, 62 (2008) 636–641.
- [31] A. Kumar, M.S. Manna, A.K. Ghoshal, P. Saha, Study of the supported liquid membrane for the estimation of the synergistic effects of influential parameters on its stability, *J. Environ. Chem. Eng.*, 4 (2016) 943–949.
- [32] M.A. Hasan, Y.T. Selim, K.M. Mohamed, Removal of chromium from aqueous waste solution using liquid emulsion membrane, *J. Hazard. Mater.*, 168 (2009) 1537–1541.
- [33] Y. Park, Development and Optimization of Novel Emulsion Liquid Membranes Stabilized by Non-Newtonian Conversion in Taylor - Couette Flow for Extraction of Selected Organic and Metallic Contaminants, Ph.D. Thesis, Georgia Institute of Technology, 2006.
- [34] J. Zhou, X. Qiao, B.P. Binks, K. Sun, M. Bai, Y. Li, Y. Liu, Magnetic Pickering emulsions stabilized by Fe<sub>3</sub>O<sub>4</sub> nanoparticles, *Langmuir*, 27 (2011) 3308–3316.
- [35] S.A.M. Mohammed, N. Zouli, M. Al-Dahhan, Removal of benzoic acid from wastewater by Pickering emulsion liquid membrane stabilized by magnetic Fe<sub>2</sub>O<sub>3</sub> nanoparticles, *Desal. Water Treat.*, 68 (2017) 114–121.
- [36] M.A. Hussein, A.A. Mohammed, M.A. Atiya, Application of emulsion and pickering emulsion liquid membrane technique for wastewater treatment: an overview, *Environ. Sci. Pollut. Res.*, 26 (2019) 36184–36204.
- [37] H.M. Salman, A.A. Mohammed, Extraction of lead ions from aqueous solution by co-stabilization mechanisms of magnetic Fe<sub>2</sub>O<sub>3</sub> particles and nonionic surfactants in emulsion liquid membrane, *Colloids Surf., A*, 568 (2019) 301–310.
- [38] 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<sub>2</sub>O<sub>3</sub>, *Colloids Surf., A*, 585 (2020) 124044, doi: 10.1016/j.colsurfa.2019.124044.
- [39] B.P. Binks, Particles as surfactants – similarities and differences, *Curr. Opin. Colloid Interface Sci.*, 7 (2002) 21–41.
- [40] B. Panchal, J. Pandya, Extraction of phenol from aqueous stream into emulsion liquid membrane, *Int. J. Curr. Trends Eng. Res.*, 2 (2016) 145–153.
- [41] S.A.M. Mohammed, N. Zouli, M. Al-Dahhan, Removal of phenolic compounds from synthesized produced water by emulsion liquid membrane stabilized by the combination of surfactant and ionic liquid, *Desal. Water Treat.*, 110 (2018) 168–179.
- [42] L.G. Torres, R. Iturbe, M.J. Snowden, B.Z. Chowdhry, S.A. Leharne, Preparation of O/W emulsions stabilized by solid particles and their characterization by oscillatory rheology, *Colloids Surf., A*, 302 (2007) 439–448.
- [43] J.D. Kubicki, L.M. Schroeter, M.J. Itoh, B.N. Nguyen, S.E. Apitz, Attenuated total reflectance Fourier-transform spectroscopy of carboxylic acids adsorbed onto mineral surfaces, *Geochim. Cosmochim. Acta*, 63 (1999) 2709–2725.
- [44] R.K. Goyal, N.S. Jayakumar, M.A. Hashim, Chromium removal by emulsion liquid membrane using [BMIM][NTf<sub>2</sub>] as stabilizer and TOMAC as extractant, *Desalination*, 278 (2011) 50–56.
- [45] S.C. Lee, J.H. Chang, B.S. Ahn, K. Lee, Mathematical modeling of silver extraction by an emulsion liquid membrane process, *J. Membr. Sci.*, 114 (1996) 171–185.
- [46] M. Dineshkumar, A. Sivalingam, M. Thirumarimurugan, Removal of phenol using ZnO nanoparticle in three phase fluidization, *Int. J. Eng. Res. Technol.*, 4 (2015) 1111–1116, doi: 10.17577/IJERTV4IS031155
- [47] M. Chirita, I. Grozescu, Fe<sub>2</sub>O<sub>3</sub> – nanoparticles, physical properties and their photochemical and photoelectrochemical applications, *Chem. Bull.*, 54 (2009) 1–8.