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Effect of polymer addition to membrane phase to improve the stability of emulsion liquid membrane for phenol pertraction

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ABSTRACT

This study is conducted to indicate the importance of emulsion stability in the pertraction operation. Emulsion liquid membrane is stabilized by the addition of a rubbery polymer and dispersed in an external phase containing phenol. Moreover, various parameters such as temperature, intensity of mixing, internal phase concentration, phase ratio, and pH of external phase due to their effect on emulsion stability were studied. Emulsion stability with a specified formulation of primary emulsion without polymer was found in about 5–10 min, but results showed that the addition of the polymer increased the emulsion stability time at least for 35 min. In general, the results showed that by increasing the volume ratio of phases (R_{ew}), internal-phase concentration, and decreasing feed pH, the extraction efficiency increases. It was found that under optimum conditions, more than 85% of phenol presented in a feed solution containing 100 ppm phenol was removed within only 35 min in a single-stage operation.

Keywords: W/O/W double emulsion; ELM; Stabilization; Polymer; Phenol; Pertraction

1. Introduction

Some compounds that are commonly used in many industrial processes such as pesticides, dyes, pharmaceuticals, and plastics are phenol and its derivatives. These compounds are one of the important pollutants that exist in wastewater from many industrial sources, such as coal gasification, petrochemical, wood products, paint, paper, and agroindustries [1–8]. Treatment of this industrial wastewater seems to be necessary because of high toxicity of phenolic compounds. For removal and recovery of phenol from aqueous solutions, various processes and techniques are investigated. Some of these various processes and techniques such as biological digestion, adsorption on active carbon, liquid-phase chemical oxidation, Fenton oxidation, electro- and photo-catalytic oxidation, catalytic wet air oxidation, wet air oxidation (WAO), super critical water oxidation (SCWO), membrane techniques, and liquid–liquid extraction [9–17] can be referred to. For this aim, one of the widely and suitably used methods that seem to be more successful is the emulsion liquid membrane (ELM) technique [18–21] (Fig. 1).

As shown in Fig. 2, an ELM process consists of different steps [22]:

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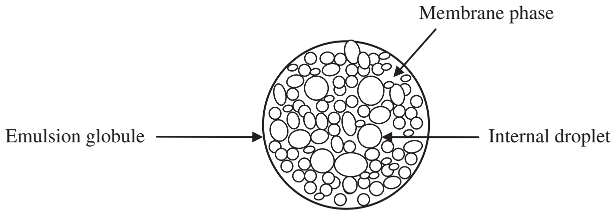

Fig. 1. A schematic representation of an emulsion globule.

- Preparation of primary emulsion:

One of the important parts in this process is its formulation. A successful process depends on choosing a suitable formulation that includes the selection of organic phase, internal phase, emulsifier, carrier, and diluents. As the first step, the primary emulsion should be stable at long durations.

- Dispersing of primary emulsion in the feed phase:

In this part, many emulsion globules can be produced and solutes that are contained in the feed phase pass through the membrane phase and react with the internal reagent. The internal-phase reagent converts the oil-soluble solutes into oil-insoluble solutes, which are trapped in the internal phase. In addition, agitation makes the emulsion globules smaller so that a high number of emulsion globules can be produced and the mass transfer area and consequently mass transfer rate is increased.

- Settling of the emulsion and external phases after extraction:

In this stage, it is allowed to separate the heavy phase (usually external aqueous phase) from the light phase (usually the organic emulsion phase) by gravitational-phase separation. Actually, the primary emulsion takes apart from the raffinate phase.

- De-emulsification:

To recover the internal phase and the depleted solute, the emulsion globules should be broken in this step that is called de-emulsification. After de-emulsification, the resulting phases are separated by gravitational or centrifugal forces, and the membrane phase containing emulsifier is recycled for preparation of primary emulsion. It is necessary to notice that frequent recovery of the emulsifier causes the emulsifier to lose its stabilization property [22–27]. Because of unique advantages of extraction by ELM over the other liquid membranes (bulk, supported, and film liquid membranes) and also liquid extraction methods, many studies have been conducted on the extraction of different species by ELM.

Some of the benefits of pertraction by ELM could be summarized as:

(1) High mass transfer area and high surface area to volume ratio for the removal of the solute from aqueous solutions.
(2) Combining both extraction and stripping steps into one stage. Thus, individual equipment for extraction and stripping is not required.
(3) Increasing the solute transfer rate and selectivity through the membrane by using a carrier that can react with solute in the membrane phase which enhances transport of solute

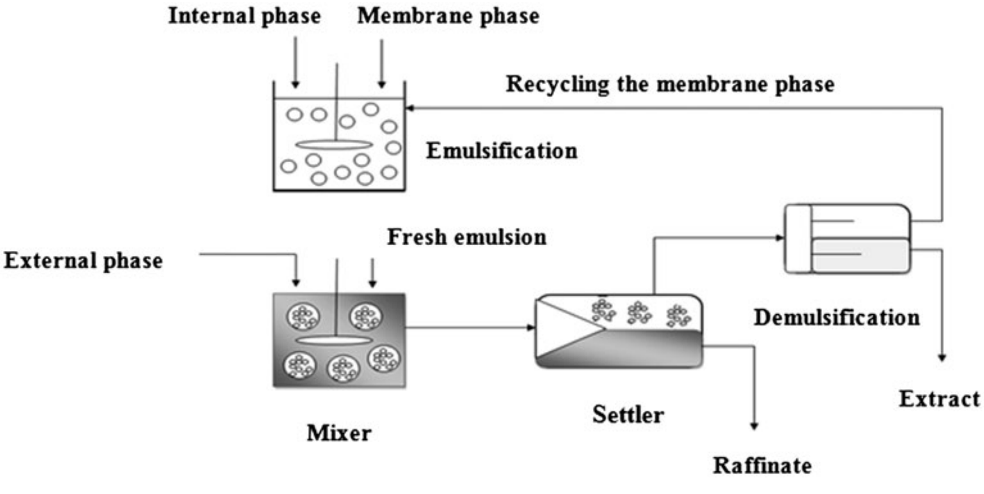

Fig. 2. A scheme of an emulsion liquid membrane process [22].

through the membrane. That is called facilitated transport.

(4) Amount of required solvent in this process, particularly at low solute concentrations, is very small.

(5) The volume of the stripping phase is much smaller than the external phase.

Although emulsion liquid membrane processes have some significant drawbacks:

- De-emulsification: For recovery of internal and membrane phases and also the emulsifier after the extraction step, the emulsion globules should be broken. For this purpose, some methods have been reported such as coalescence of the dispersed droplets into larger droplets, application of electric fields, heat treatment of the emulsion, applying centrifuge and high shear forces, and dilution of the emulsion by proper solvents. The most popular method is the using of high-voltage electric field. However, this requires extensive electrical power.
- Stability of emulsion liquid membrane: The breakage of the emulsion globules happens in the extraction step. The breakage of emulsion globules and subsequent release of the internal-phase reagent into the external feed phase would nullify the extraction process. Some of the important parameters that affected the stability of emulsion globules in this step that can be summarized are:
- Temperature of aqueous solution (feed phase): At high temperatures, because of the decrease in emulsion viscosity, breakage of the emulsion is increased.
- Agitation speed: In this case, due to applying high shear rates, the rupture of the emulsion globules is highly expected.
- Amount of internal phase: Increasing the amount of internal phase thins the membrane-phase thickness and leads to breakage of the emulsion globules [28–36].

In order to modify stability of emulsion globules, several methods have been reported such as increasing the amount of emulsifier, increasing the viscosity of membrane phase by Newtonian additives, using a viscose membrane and non-Newtonian conversion.

Skelland suggested, for the first time, the conversion of the membrane phase from Newtonian to a suitable non-Newtonian liquid by the addition of a proper polymer. In fact, adding a suitable polymer to the membrane phase in a new way would increase the stability of ELM without reduction in permeability of the membrane against the solute by non-Newtonian conversion [37]. One of the predominant benefits of using polymer in the formulation of emulsions is the recovery of polymer without any changes in its property. Some attempts have been made in order to improve the stability of the emulsion globules by the addition of a suitable polymer. Brugger and Richtering studied the effect of poly(*N*-isopropylacrylamide)-*co*-methacrylic acid polymers on the stability of the emulsion [38]. Lee and Yeo studied the role of dilute polymer solution on the stability of the emulsion [39]. Mortaheb et al. used a new polyamine-type surfactant for the extraction of phenol by ELM from aqueous solutions and showed it was more efficient than Span-80 that is the most commonly used emulsifier for ELM systems [40,41]. Park et al. studied the emulsion liquid membranes stabilized by non-Newtonian conversion in a Taylor–Couette flow [31].

In this study, the stability of the primary emulsion during the pertraction of phenol from aqueous solutions is investigated. The effect of polymer concentration, the internal-phase concentration, temperature, feed pH, treat ratio, and speed of agitation on the stability of the emulsion during the pertraction operation is studied.

2. Experimental

2.1. Reagents and apparatus

Phenol, sodium hydroxide, sulfuric acid, potassium ferricyanide, and chloroform were of reagent grade and purchased from Merck Co., Germany. Kerosene was supplied from Tehran petroleum refinery from the Isomax unit. Table 1 shows the specification of the Iso-kerosene from Tehran petroleum refinery. A non-ionic, surfactant sorbitan monooleate, (Montane-80, HLB = 4.5) was kindly received from Seppic, France, and used as emulsifier.

Table 1
The specification of Iso-kerosene from Tehran Refinery Isomax unit

Property	Value	Unit
Density @ 15°C	0.82	kg/dm^3
Distillation:		
Recovered 185°C (max)	50	Vol. %
200°C (min)	70	Vol. %
210°C (min)	90	Vol. %
235°C (min)	95	Vol. %
F.B.P (max)	275	ºC

Ethylene–propylene–diene terpolymer (EPDM, $M_n = 41.204$ and $M_w = 45.308$ kg/mol), Keltan 2340A (DSM Elastomers B.V., the Netherlands) containing 53 wt.% ethylene, 41 wt.% propylene and 6 wt.% ethylidene norbornene was used as the polymer for stabilization of the emulsions.

The concentration of phenol in the aqueous solutions was determined by a sensitive spectrophotometric method at 460˚nm using 4-aminoantipyrine as reagent [42]. A visible-range spectrophotometer (Cecil model CE-1010) was used in this regard. A thermostatic water bath equipped with a water circulation system was used to keep the solutions at the desired temperatures. The stirring driver was a laboratory mixer model RZR 2020 (Heidolph, Germany) with a variable speed of 40–2,000 rpm. The stirring device was a 3-blades Teflon® pitch blade impeller (model PR-39) with 75 mm diameter. The pH of the aqueous solutions was measured with a digital pH meter (Metrohm-780 Herisau, Switzerland) equipped with a Pt-1000 RTD for temperature correction. An ULTRA-TURRAX®T-25 digital homogenizer (IKA, Germany) with a speed range of 3,400–24,000 rpm, equipped with a high-speed dispersing element (S25N-18G) was used for the preparation of the primary emulsions.

The pertraction vessel was a cylindrical glass container with 160 mm diameter and 185 mm height, equipped with four round baffles made of glass with 10 mm diameter and 10 mm clearance from the bottom.

2.2. Procedure

The primary W/O emulsions were prepared by emulsification of kerosene as the organic phase, surfactant (Montane-80) as the emulsifier, and NaOH solution as the internal phase using the homogenizer for 30 min with a rotation speed of 9,000 rpm. A 10 wt.% solution of EPDM in kerosene was prepared and used for modifying the emulsions. A certain amount of the polymer solution was added to the primary emulsion during the homogenization step.

The primary emulsion was then added to the aqueous phase containing phenol at controlled temperature and under agitation. Samples were taken at predetermined time intervals using sanitary syringes and the aqueous phase was quickly separated (within less than 10 s). Then the aqueous phase was placed in a centrifuge to accelerate the separation of the aqueous phase from the remaining droplets of primary emulsion, and then the external aqueous samples were analyzed for phenol concentration (Fig. 3).

3. Result and discussion

3.1. Effect of polymer concentration

The effect of polymer dissolved in the emulsion liquid membrane stability has been studied and the results are shown in Figs. 4–7. The experiments were performed at three different amounts of EPDM (0.8, 1.5 and 3%) and various internal phase concentrations (1,250, 2,500, 5,000 and 7,500 mg/l). As can be seen, the stability of the virgin emulsion was lost after about 10 min of the extraction. At this time, the emulsion started to break and the concentration of phenol in the external phase was increased rapidly. Addition of 0.8% polymer based on the organic phase to the emulsion stabilized the emulsion over 35 min from the extraction process. The rate of phenol extraction was greatly enhanced by the addition of EPDM. The increased extraction rate was caused by increased stability of emulsion and subsequent reduction in the rate of emulsion globules breakage and leakage. In general, with the addition of polymer, the following results can be obtained:

(1) Increased membrane stability against shear stress.
(2) Increased membrane permeability and transport through the membrane phase.
(3) Increase in apparent viscosity of the membrane at near zero-shear rates, which causes an increase in membrane resistance and its stability [34].

3.2. Effect of internal-phase concentration

NaOH as the internal-phase reagent converts phenol to sodium phenolate and traps it in the internal phase. Therefore, high concentration of NaOH may be more favorable for the extraction process. However, it should be mentioned that the difference in electrolyte concentrations between the internal and external

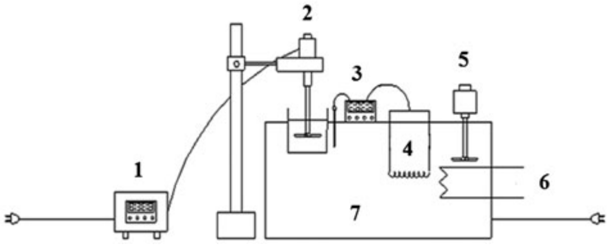

Fig. 3. A scheme of the experimental setup.
Notes: (1): Speed adjuster, (2): Mixer drive, (3): Temperature controller, (4): Heating element, (5): Agitator, (6): Cooling water coil, and (7): Water bath.

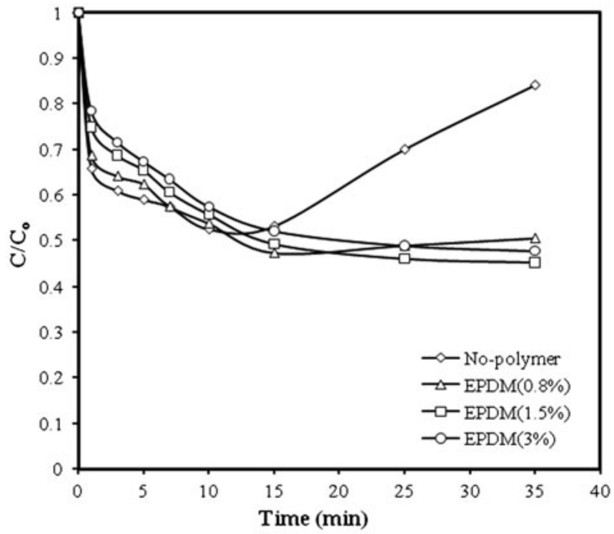

Fig. 4. Effect of polymer concentration (wt.%) on extraction of phenol with 1,250 (mg/l) internal-phase concentration.
Notes: $R_{\mathrm{oi}} = 1$; $\mathrm{pH}_{\mathrm{F}} = 1$; $R_{\mathrm{ew}} = 1{:}10$; $C_{\mathrm{s}} = 4\%$; $C_{\mathrm{o}} = 100$ (mg/l); $T = 30°\mathrm{C}$; 10 rpm.

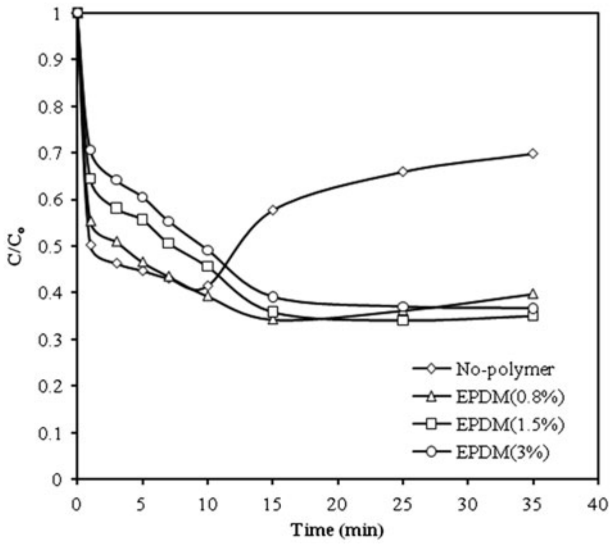

Fig. 5. Effect of polymer concentration (wt.) on phenol extraction with 2,500 (mg/l) internal-phase concentration.
Notes: $R_{\mathrm{oi}} = 1$; $\mathrm{pH}_{F} = 1$; $R_{\mathrm{ew}} = 1{:}10$; $C_{\mathrm{s}} = 4\%$; $C_{\mathrm{o}} = 100$ (mg/l); $T = 30°\mathrm{C}$; 210 rpm.

phases increases by increasing the NaOH concentration, which increases the osmotic pressure between these two phases. The higher the osmotic pressure, more water is transferred from the external phase into the internal phase. This results in swelling and emulsion breakage and subsequently decreasing the removal efficiency. In addition, excessive NaOH concentrations may hydrolyze the emulsifier and decrease the emulsion stability [22]. Thus, an optimum concentration of NaOH should be found. Fig. 8 shows the effect of NaOH concentration on the removal efficiency of phenol by ELM. As it can be seen in this figure, by increasing NaOH concentration from 1,250 to 7,500 mg/l, the removal efficiency is increased from 50 to more than 80% within 35 min.

3.3. Effect of temperature

Both extraction rate and emulsion stability are affected by temperature, which is an important parameter. According to the previous studies, emulsions' stability due to the temperature dependence of liquid's viscosity is very sensitive to extraction temperature. The results of increasing the extraction temperature can be expressed as follows:

(a) Mass transfer rate is enhanced because of a decrease in the viscosity of external, membrane, and internal phases.
(b) Increase in the rate of reaction between the solute and the internal reagent.
(c) Improvement in the overall mass transfer coefficient.
(d) Decrease in the resistance and interface tension against permeation of the solute through the membrane.
(e) Reduction in the emulsion stability because of an increase in emulsifier hydrolysis rate and decrease in the emulsion phase viscosity.

However, viscosity of the emulsion phase has a key role in the stability of the emulsion during the extraction period [5]. Then, the temperature of the extraction should be at an optimum value.

The effect of temperature on the extraction efficiency is shown in Fig. 9. Four levels of 20, 30, 40, and 50°C were considered as the extraction temperature. According to the obtained results, temperature had a great influence on the emulsion stability. The stable emulsion was obtained at 20–30°C. However, at 40–50°C, after nearly 10 min the emulsion started to break. As shown in this figure at the initial times, the extraction efficiency for 50°C was more than that for other temperatures and the effect of temperature on the extraction rate for the 40–50°C interval was greater than that for the 20–30°C interval. In addition, the emulsion breakage for 50°C was higher than that for 40°C. Thus, it is reasonable to choose 30°C as the optimum temperature (with a safe margin) for the extraction operation.

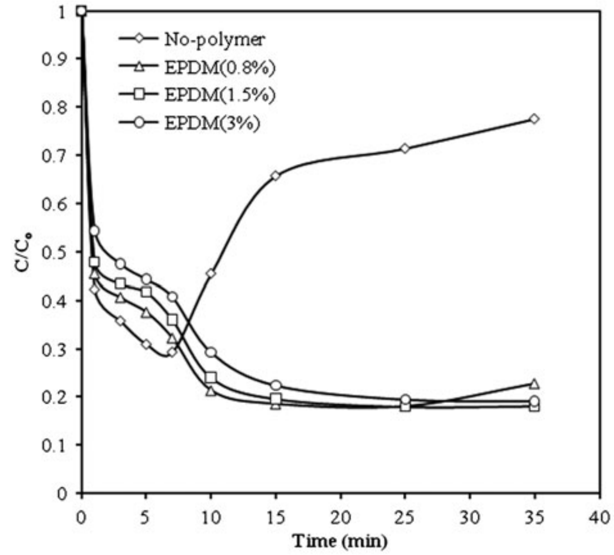

Fig. 6. Effect of polymer concentration (wt.%) on phenol extraction with 5,000 (mg/l) internal-phase concentration.
Notes: $R_{oi} = 1$; $pH_F = 1$; $R_{ew} = 1{:}10$; $C_s = 4\%$; $C_o = 100$ (mg/l); $T = 30°C$; 210 rpm.

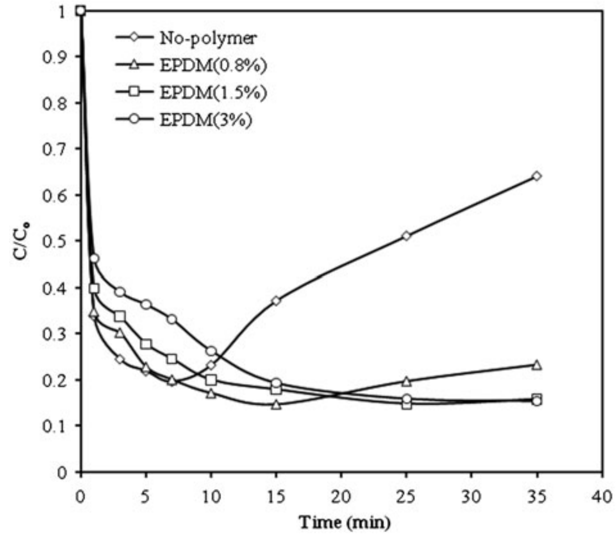

Fig. 7. Effect of polymer concentration (wt.%) on phenol extraction with 7,500 (mg/l) internal-phase concentration.
Notes: $R_{oi} = 1$; $pH_F = 1$; $R_{ew} = 1{:}10$; $C_s = 4\%$; $C_o = 100$ (mg/l); $T = 30°C$; 210 rpm.

3.4. Effect of feed phase pH

Phenol is a weak base and is dissociated in aqueous solutions to form ionic components as follows:

$$\text{Ph-OH} \underset{k_2}{\overset{k_1}{\longleftrightarrow}} \text{Ph-O}^- + \text{H}^+ \tag{1}$$

The equilibrium constant at 25℃ has been reported as [43]:

$$K_a = \frac{k_2}{k_1} = \frac{[\text{Ph}-\text{O}^-][\text{H}^+]}{[\text{Ph-OH}]} = 1.047 \times 10^{-10} \tag{2}$$

The molecular form of phenol as pH-OH is oil soluble where the ionic form is oil insoluble. A decrease in pH value (increase in H^+ concentration) reverses the dissociation reaction and phenol remains in an oil-soluble state, which is desirable for ELM extraction. Fig. 10 shows the effect of pH on the extraction rate of phenol from aqueous solutions. The result shows that the extraction rate of phenol increases with a decrease in pH. At low pH feeds, the emulsions remained stable for more than 35 min which is desirable for a good pertraction operation. But, the amount of needed acid for a feed solution having pH 0.5 is nearly three times more than that for pH 1. However, as shown in Fig. 10, the extraction efficiency in low pH feeds (i.e. pH 0.5–1) becomes almost equal after nearly 35 min, and it does not seem to be considerably increasing in extraction efficiency for the pH < 1. Thus, pH 1 was selected as the most suitable pH for the pertraction process.

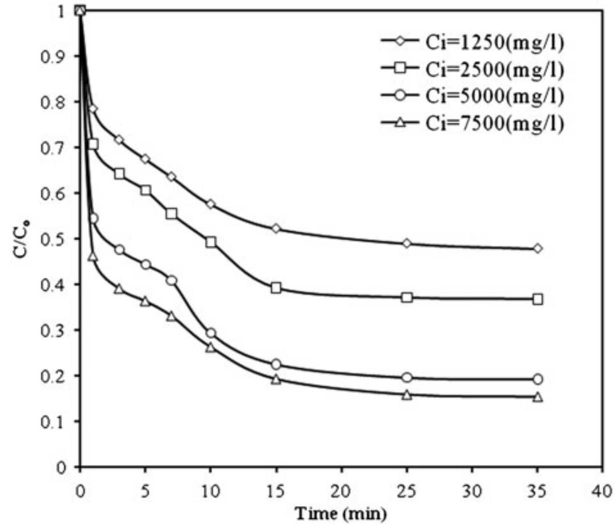

Fig. 8. Effect of internal-phase concentration (wt.%) on phenol extraction with $C_p = 3\%$.
Notes: $R_{oi} = 1$; $pH_F = 1$; $R_{ew} = 1{:}10$; $C_s = 4\%$; $C_o = 100$ (mg/l); $T = 30°C$; 210 rpm.

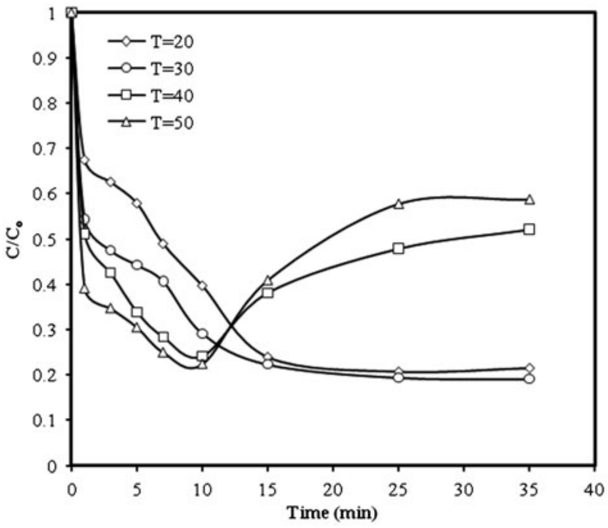

Fig. 9. Effect of operating temperature on phenol extraction with $C_p = 3$ wt.%.
Notes: $R_{oi} = 1$; $pH_F = 1$; $R_{ew} = 1{:}10$; $C_s = 4\%$; $C_o = 100$(mg/l); $C_i = 5000$ (mg/l); 210 rpm.

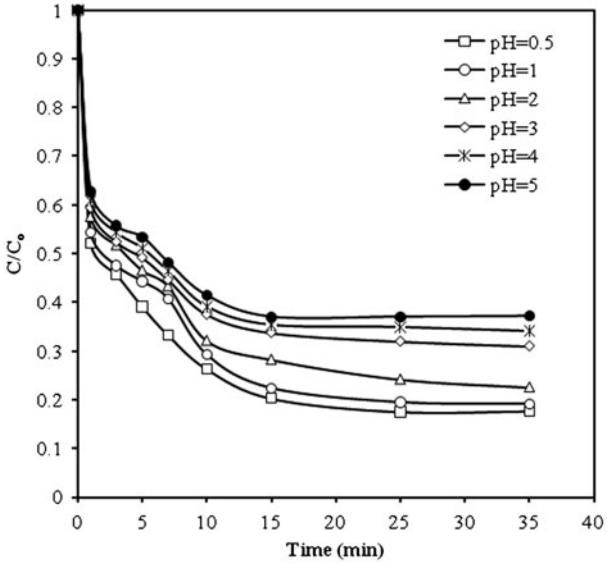

Fig. 10. Effect of feed-phase pH on phenol extraction with $C_p = 3$ wt.%.
Notes: $R_{oi} = 1$; $R_{ew} = 1{:}10$; $C_s = 4\%$; $C_o = 100$ (mg/l); $T = 30$°C; $C_i = 5000$ (mg/l); 210 rpm.

3.5. Effect of treat ratio

Another parameter that plays an important role in the efficiency of extraction by emulsion liquid membranes is the volume ratio of emulsion to external phase which is known as the treat ratio or R_{ew}. As shown in Fig. 11, the extraction rate of phenol increases with an increase in the R_{ew}, which was caused by some reasons, as follows:

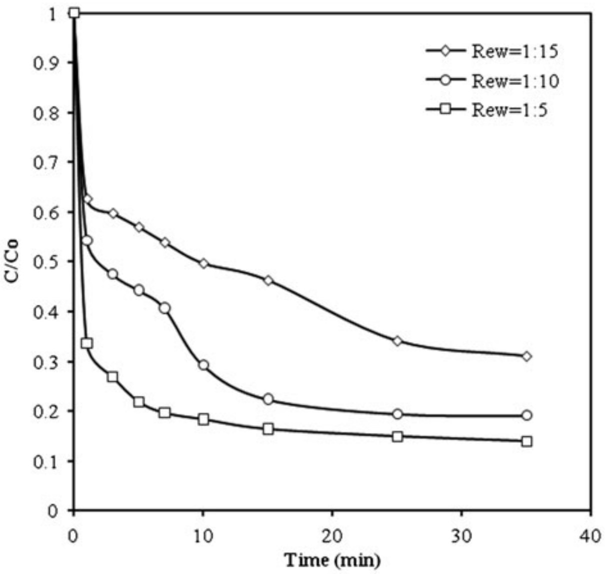

Fig. 11. Effect of volume-phase ratio on phenol extraction with $C_p = 3$ wt%.
Notes: $R_{oi} = 1$; $pH_F = 1$; $C_s = 4\%$; $C_o = 100$ (mg/l); $T = 30$°C; $C_i = 5000$ (mg/l); 210 rpm.

(a) Increasing in the hold-up of the dispersed phase of the emulsion globules.
(b) Increasing in the amount of internal-phase reagent in a unit volume of the ELM system because of an increase in the volume ratio of emulsion to external phase.
(c) Increasing the interfacial area for mass transfer.
(d) Increasing the capacity of the internal stripping phase for the trapping solutes [6].

An increase in the rate of phenol extraction from almost 65 to more than 80% can be observed because of increasing R_{ew} from 1:15 to 1:5. It is clear that an increase in the volume ratio of emulsion to external phase does not have any considerable effect on emulsion breakage. In addition, Fig. 12 shows that after 35 min, the extraction percentage with $R_{ew} = (1{:}10)$ is almost the same and equals $R_{ew} = (1{:}5)$. In general, increasing R_{ew} beyond the optimum value has some disadvantages:

(a) A greater amount of material is needed for preparing the primary emulsion.
(b) For suitable dispersion, more energy and high-speed agitation is needed. High-speed agitation leads to emulsion breakage.

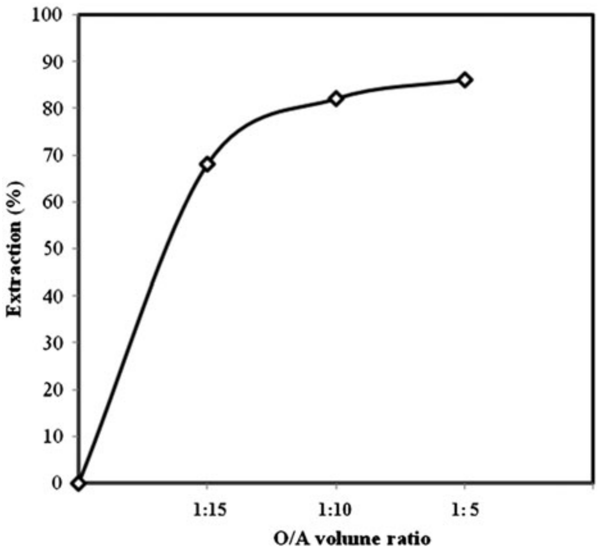

Fig. 12. Effect of volume-phase ratio on phenol extraction with $C_p = 3$ wt.% after 35 min.
Notes: $R_{oi} = 1$; $pH_F = 1$; $C_s = 4\%$; $C_o = 100$ (mg/l); $T = 30°C$; $C_i = 5000$ (mg/l); 210 rpm.

(c) Dispersion of phases and recovery of the internal phase from emulsion become more difficult, and also the internal phase does not saturate completely.

(d) It causes cohesion between the emulsion globules and a decrease in the mass transfer area. The above-mentioned points reveal that R_{ew} should be kept at an optimum value for both economical and operational concerns.

3.6. Effect of stirring speed

Two main reasons for increasing extraction efficiency by increasing the agitation speed are:

(1) The shear forces which act on the emulsion globules increase due to an increase in agitation speed.

(2) Increasing mass transfer area because of smaller globules.

Fig. 13 shows the effect of the extraction efficiency. It is stated that the extraction process with ELMs are controlled by the external surface area of globules rather than the internal-phase droplet surface area, so higher extraction efficiencies could be attained by increasing the area for mass transfer by increasing the agitation speed. It was observed that increasing the agitation speed over a certain limit has the following drawbacks:

(1) Decrease in extraction efficiency due to unstable emulsion.

(2) Increasing the leakage of the internal reagent (including the extracted phenol) because of the rupture of emulsion globules.

(3) The osmotic swelling of the membrane will be increased.

(4) Decrease in globules viscosity because of high shear rates [4,44–47].

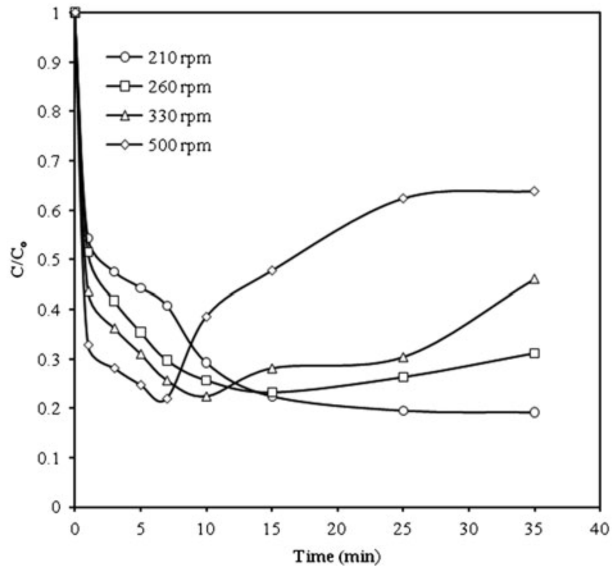

Fig. 13. Effect of agitation speed on phenol extraction $C_p = 3$ wt.%.
Notes: $R_{oi} = 1$; $pH_F = 1$; $R_{ew} = 1{:}10$; $C_s = 4\%$; $C_o = 100$ (mg/l); $T = 30°C$; $C_i = 5000$ (mg/l).

As can be seen, the experiments were done in feed phase containing 100 mg/L of phenol at speeds of 210, 260, 330, and 500 rpm. The results show that the highest extraction efficiency was obtained after 5 min by a speed of 500 rpm. As a result of high shear forces acting on the emulsion globules for longer times, the emulsion globules become smaller and the emulsion breakage and leakage were increased, and consequently, the extraction efficiency was decreased considerably. However, at low agitation speeds, i.e. 210 rpm, the emulsion globules seem more stable than higher agitation speeds. At lower agitation speeds, a layer of the emulsion was formed on the surface of the aqueous external phase which is unfavorable. Then, 210 rpm was selected as the optimum value for agitation speed.

4. Conclusion

It was found through this research that emulsion stability is the most important criterion for achieving a successful ELM process. As suggested in previous studies, non-Newtonian conversion is a good method for stabilization of the emulsions applied for ELM pertractions. In this regard, it was showed that EPDM which is an inexpensive and readily available rubbery polymer is a good candidate for stabilization of the emulsions for ELM application. The effect of addition of EPDM to the membrane phase as a non-Newtonian modifier was investigated. Effect of different parameters on the extraction efficiency was considered during the extraction of phenol from aqueous solutions such as pH of the feed phase, speed of agitation, polymer concentration, internal-phase concentration, temperature, and treat ratio. It was found that the concentration of EPDM in the membrane phase affects the stability of the W/O/W emulsion, considerably and in lesser amount to the speed of agitation, internal-phase concentration, and temperature.

In the range of the studied feed pH and the treat ratio, it was found these parameters have little effect on the emulsion stability. The best stabilized emulsion was obtained by the addition of 3 wt.% of the EPDM to the membrane phase. The best phenol removal by this stabilized emulsion from a 100 (mg/l) feed concentration was obtained at 3℃ with a mixer speed of 210 rpm, 5,000 (mg/l) internal-phase concentration at pH_F 1, $R_{\text{ew}} = 1{:}10$, $R_{\text{oi}} = 1$ and an emulsifier concentration of 4 vol. %. Under this condition, the phenol extraction efficiency obtained was more than 85% within 35 min.

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Nomenclatures

C_i	—	internal-phase concentration (mg/l)
C_o	—	initial phenol concentration (mg/l)
C_p	—	polymer concentration in the membrane phase (wt.%)
C_s	—	emulsifier concentration (vol.%)
C_t	—	phenol concentration at time t (mg/l)
EPDM	—	poly ethylene-propylene diene monomer
PhOH	—	phenol
R_{oi}	—	volume ratio of emulsion phase to internal phase
R_{ew}	—	volume ratio of emulsion phase to external phase
T	—	temperature (℃)

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