



Study on a new surfactant for removal of phenol from wastewater by emulsion liquid membrane

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ABSTRACT

Removal of phenol from wastewater using emulsion liquid membrane (ELM) is studied in present study. A new polyamine-type surfactant was synthesized and used for stabilizing of the emulsion phase. The results for the emulsion made by the synthesized surfactant showed much better stability and performance in the separation process compared to that by conventionally used Span 80. To determine the optimum operation conditions, the effect of several parameters such as emulsifier concentration, concentration of NaOH in the internal phase, oil to internal phase volume ratio, mixing intensity, temperature, solvent type, and stabilizer concentration have been investigated. It was found that under the optimum conditions, more than 98% of phenol can be removed in a single-stage process. The removal efficiency can be increased to 99.8% in a two-stage process.

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1. Introduction

Phenol and its derivatives are toxic pollutants, frequently found in surface and tap waters, and in aqueous effluents from various manufacturing processes [1]. Therefore, they are listed in the US EPA priority list of dangerous substances discarded into the aquatic environment.

Since 1968 that emulsion liquid membrane (ELM) was first invented by Li [2], removal of phenol from wastewater has been intensively investigated using ELM [3–5]. This is because the removal of phenol by this method has many advantages over other separation methods [6–8]. Liquid membrane process incorporates dispersion of an emulsion included organic membrane and aqueous internal phase in a continuous external phase (W/O/W). The solute penetrates from the external phase toward the internal phase through the membrane phase, where it reacts with a stripping agent and converts to a form of material, which is insoluble in the membrane phase and will be trapped in the internal phase. The emulsion phase is then broken in a demulsifier and the oil phase is recycled for reusing in the emulsification process. Fig. 1 shows a schematic diagram of liquid membrane process.

Mass transfer rate depends on concentration driving force of the solute induced by the reaction and permeability of the membrane phase [9–15].

Span 80 has been used conventionally in this method as the emulsifier for stabilizing of the liquid membrane. However, the emulsion membranes made by Span 80 are not stable enough. As a result, breaking of the emulsion decreases separation efficiency that ultimately results in loss of performance in the separation process and tends the whole process to be unreliable. Some attempts have been made to improve the stability of emulsions made by Span 80 [16]. The first treatment is to increase the concentration of surfactant in the membrane phase. However, this reduces the rate of solute transfer by setting up mechanical and adsorption barriers to solute transfer at the interfaces. The second treatment is to increase the viscosity of the membrane phase [17,18]. This will increase the membrane stability but decrease the transfer rates due to decrease in molecular diffusivity. On the other hand, the stability of the emulsion can be increased by adding polymer to organic phase, and converting emulsion to a non-Newtonian phase [16]. This is because the molecular diffusivity of solutes was found to be independent of concentration. Therefore, the emulsion made by adding an appropriate polymer will increase the membrane viscosity under the low shear rates during the dispersion of emulsion in the external phase. Further stabilization of the membrane will also result from the smaller droplets obtained because of the low apparent viscosity of the non-Newtonian emulsion during the emulsification stage

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Nomenclature

C	concentration of phenol in feed at time t (ppm)
$C_{e,I}$	concentration of tracer I in the external phase at time t (mg/l)
$C_{i,I}^0, C_{i,I}$	concentration of tracer I in the internal phase at time 0 and t , respectively (mg/l)
C_0	primary concentration of phenol in feed (ppm)
R_{ew}^0	initial volume ratio of emulsion to the external phase = V_{em}/V_e
R_{oi}^0	initial volume ratio of oil phase to the internal phase = V_o/V_i
t	mixing time (min)
T	temperature ($^{\circ}\text{C}$)
V_e	volume of external phase (cm^3)
V_{em}	volume of emulsion phase (= $V_i + V_o$) (cm^3)
V_i	volume of internal phase (cm^3)
V_o	volume of membrane phase (cm^3)
<i>Greek letters</i>	
ε	membrane breakage ratio at time t (%)
$\eta_{s,ac}$	actual swelling ratio at time t (%)
$\eta_{s,ap}$	apparent swelling ratio at time t (%)
μ	emulsion viscosity (cp)
ρ	emulsion density (g/cm^3)

[19]. However, this will not completely solve the problem of stability of the membranes made by Span 80 as also observed in our early experiments.

In order to overcome this deficiency, a new polyamine-type surfactant has been designed and synthesized in our lab. Stability and performance of the liquid membrane, which is increased significantly by applying the synthesized surfactant is studied in present research.

2. Experimental

The emulsion of internal phase in the liquid membrane phase is prepared by mixing of surfactant (Span 80 (sorbitan monooleate) purchased from Merck or the synthesized polyamine-type), an organic solvent and NaOH solution in a Buhler homogenizer for 20 min with high rotational speed (15,000 rpm). The emulsion is

then gradually added to the external phase in a glass cell equipped with a variable-speed propeller. For proper mixing, the cell is equipped with four baffles with 10 cm height, 1 cm width, and 3 cm distance from the bottom. Ten millilitres of mixture is taken from the extraction cell in certain intervals by using a micropipette. The sample, which contains the emulsion and external phase, is then separated in a decanter. UV-vis Spectrophotometer (PerkinElmer Lambda 2) is used to measure the concentration of phenol in the separated external phase (wavelength 286.9 nm under alkaline media).

The removal percent of phenol is then calculated by using the following equation:

$$\text{Removal of phenol (\%)} = \left[\frac{C_0 - C}{C_0} \right] \times 100 \quad (1)$$

3. Results and discussion

3.1. Effect of type and concentration of surfactant

Since surfactant plays a key role in construction of W/O/W, special care should be paid in selection of a proper surfactant. As mentioned before, Span 80 has been typically used as the emulsifier for stabilizing of the liquid membrane. However, several reports have mentioned to instability of membranes prepared by Span 80 [20–25]. In the present study, we also experienced several evidences of emulsion breakage for the emulsions prepared by Span 80. Some of these experiments are listed in Table 1.

Based on these conditions and in order to increase the stability of the liquid membrane, a new polyamine-type surfactant was designed and synthesized in our lab. The synthesis of the new surfactant consists of the following steps:

- (1) thermal degradation of butyl rubber;
- (2) adding a hydrocarbon solvent;
- (3) reaction with maleic anhydride;
- (4) reaction with polyethylene polyamine with low molecular weight.

The structure and properties of Span 80 and the synthesized surfactant are given in Table 2.

Experiments were made by different concentrations of Span 80 and the synthesized surfactant, and their results are compared in Fig. 2. As shown in the figure, the emulsion made by the synthesized surfactant greatly increases the phenol removal efficiency (up

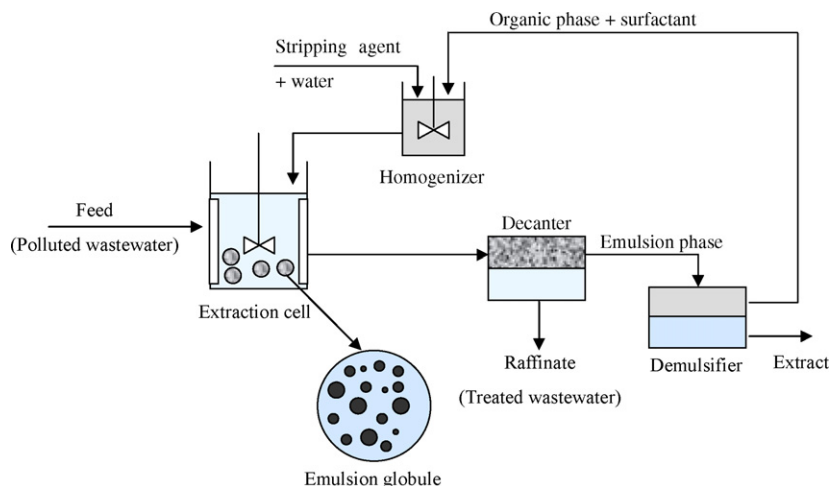


Fig. 1. Schematic diagram of an ELM process.

Table 1
List of experiments with instable emulsion made by using Span 80

Experiment no.	Solvent type	T ($^{\circ}\text{C}$)	R_{oi}°	Span 80 (wt%)	NaOH (wt%)	Extraction intensity (rpm)	Comments
1	Petrol	25	0.18	33.3	0.5	100	Emulsion was dissolved in the external phase
2	Petrol	25	1	10	0.5	100	Emulsion was broken after 35 min mixing with the external phase
3	Petrol	25	0.33	20	0.5	100	Emulsion was dissolved in the external phase
4	Petrol	60	1	10	0.5	50	A three-phase system was formed after mixing in extraction cell
5	Petrol	25	3	6.7	0.5	–	It was separated into two phases immediately after homogenizing.
6	Solvent R	25	3	6.7	0.5	–	It was separated into two phases 2 hrs after homogenizing
7	Paraffin	25	3	6.7	0.5	–	It was separated into two phases immediately after homogenizing
8	iso-Paraffin	25	3	6.7	0.5	15	Emulsion was dissolved in the external phase
9	Petrol	25	3	6.7	0.5	30	It was separated into two phases immediately after homogenizing
10	Petrol	25	3	6.7	0.5	30	Emulsion was made by a high-power ultrasonic probe. Emulsion was dissolved in the external phase

Table 2
Comparison of the structure and physical properties of Span 80 and synthesized surfactant

Property	Span 80	Synthesized surfactant
Molecular Formula	$\text{C}_{24}\text{H}_{44}\text{O}_6$	$\text{R}-\text{C}_6\text{H}_9\text{O}_2\text{N}_2-(\text{C}_2\text{H}_5\text{N})_n$
Molecular weight (g/mol)	428	1250–1450
Density (g/cm^3)	0.99 (at 20°C)	0.8538 (at 60°C)
Viscosity (mPa s)	1200–2000 (at 20°C)	1033 (at 60°C)

to 90%) while this efficiency with Span 80 is up to 52%. Although not shown here, but the concentration of phenol in the external phase is steadily decreased over time by using the synthesized surfactant while the removal efficiency by using Span 80 is declined in some of these experiments (i.e. the experiment with 3 and 20 wt% of surfactant) due to breakage of the emulsion. In addition, when different conditions were applied in our experiments, several evidences were observed, in which the emulsion was broken rapidly after mixing of organic solvent, Span 80, and the internal aqueous phase in the emulsifier. In some cases after homogenizing the emulsion was broken completely in contact with the external phase (see Table 1). These evidences confirm that for separation of phenol in ELM process, Span 80 cannot be considered as a good option for stabilizing of the emulsion. Therefore, the new synthesized surfactant has been used in the rest of experiments.

The concentration of surfactant in oil/water emulsion has a significant role in performance of the emulsion. This is because increasing concentration of surfactant results in lower surface tension of emulsion, smaller globules and therefore higher con-

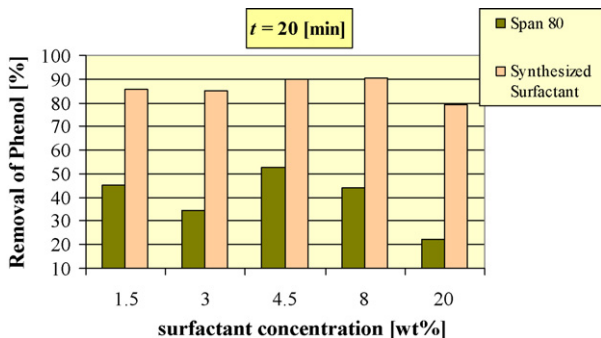


Fig. 2. Effect of surfactant type on phenol removal efficiency at different concentrations, $C_0 = 1000$ ppm, $\text{NaOH} = 0.5$ wt%, $R_{ew}^{\circ} = 0.1$, $R_{oi}^{\circ} = 2$.

tact area between the donor and receiving phases, and therefore increases the removal efficiency. On the other hand, as more surfactant is added, the thickness of emulsion globules increases which causes higher mass transfer resistance, and inversely decreases the removal efficiency. Furthermore, excessive adding of surfactant may increase swelling and therefore instability of emulsion due to secondary emulsification of the entrained solvent by excess surfactant in the primary emulsion [26]. As shown in Fig. 3, by increasing surfactant concentration from 2 to 4%, removal efficiency is increased while by increasing surfactant concentration from 4 to 8%, the removal efficiency is partly decreased. Removal efficiency is decreased steadily by adding more surfactant from 8 to 40% so that at $t = 20$ min, it drops from 91 to 58% when concentration of surfactant increases from 4 to 40%. The figure also shows that the effect of surfactant concentration on removal efficiency has a marginal effect for the concentration range of 2–8 wt% with an offset of less than 8% in removal efficiency.

Although it is not shown here, the results of other tests with different conditions also indicate the same trends, and it was found that the optimum concentration of surfactant is about 3 wt% of membrane phase.

3.2. Effect of NaOH concentration in internal phase

NaOH in internal phase converts phenol to sodium phenolate and traps it in the internal phase. Therefore, high concentration

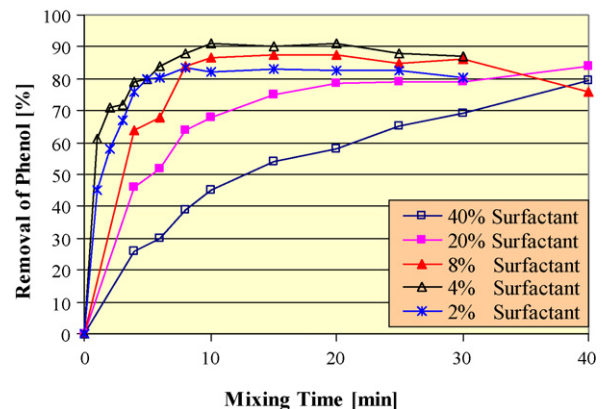


Fig. 3. Effect of surfactant concentration on phenol removal efficiency, $C_0 = 1000$ ppm, $\text{NaOH} = 0.5$ wt%, $R_{ew}^{\circ} = 0.1$, $R_{oi}^{\circ} = 0.33$.

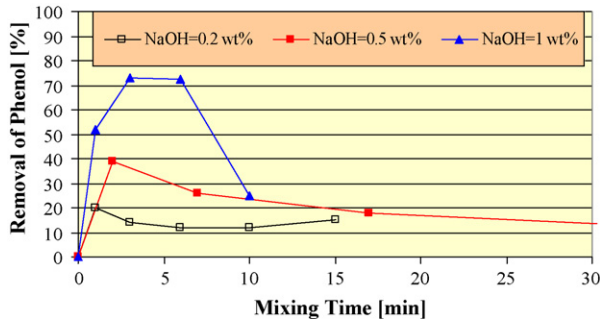


Fig. 4. Effect of NaOH concentration on phenol removal efficiency by using 10% Span 80, $C_0 = 1000$ ppm, $R_{ew}^c = 0.1$, $R_{oi}^c = 1$.

of NaOH may be preferred for the extraction process. However, the difference of electrolyte concentrations between the internal and external phases is increased by increasing NaOH concentration, which causes an osmotic pressure between these two phases. Water in the external phase is then transferred to the internal phase that results in swelling and breakage of the emulsion, and thus decreasing in removal efficiency. In addition, excessive NaOH may hydrolyze the surfactant and decrease the emulsion stability. Therefore, an optimum concentration of NaOH should be found. Fig. 4 shows the effect of NaOH concentration on removal efficiency of phenol in ELMs by using Span 80. As seen in the figure, by increasing NaOH concentration from 0.5 (which is about the stoichiometric value for reaction with phenol) to 1%, the removal efficiency increases from 40 to 62% at $t = 3$ min, while decreases afterward due to the above-mentioned reasons.

On the other hand, as shown in Fig. 5 by using the synthesized surfactant and 1% NaOH, 94% of phenol is removed at $t = 3$ min (this value for 0.5% NaOH is 79%) and the removal efficiency increases continuously up to 98% by further mixing. This result again shows more stability of emulsion made by the synthesized surfactant than that by Span 80. Fig. 5 also shows that increasing NaOH from 1 to 1.5% does not increase the removal efficiency significantly but raises the pH of the external phase. Based on these results, 1% is determined as the optimum value of NaOH concentration.

3.3. Effect of volume ratio of oil phase to internal phase

As the volume ratio of oil phase to internal phase (R_{oi}^c) increases, the strength of emulsion wall and its resistance against breakage increase. Therefore, we expect to have more stable emulsion by increasing this ratio. Fig. 6 confirms this concept. The figure shows

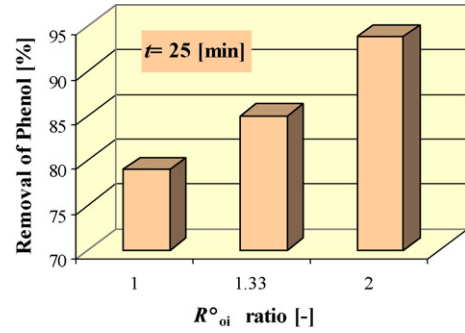


Fig. 6. Effect of R_{oi}^c on phenol removal efficiency using 2% synthesized surfactant, $C_0 = 1000$ ppm, 1% NaOH, $R_{ew}^c = 0.1$ at $t = 25$ min.

that for three different R_{oi}^c ratios of 1, 1.33, and 2 using 2% of the synthesized surfactant, at $t = 25$ min the removal efficiency of the system with $R_{oi}^c = 2$ is 14% higher than that for the system with $R_{oi}^c = 1$. Therefore, the larger value of 2 is selected as R_{oi}^c ratio since it minimizes the waste aqueous effluent, which is produced by breaking of emulsion in the demulsifier.

3.4. Effect of mixing intensity

By increasing the mixing intensity of emulsion and external phases, the contact area for mass transfer is increased due to reduction in the size of globules. However, the emulsion might be broken under higher mixing intensities. Fig. 7 shows such a tendency. By increasing the rotational speed of propeller in the extraction cell from 50 to 100 and 150 rpm, the removal efficiency increases first but it decreases along the time. The figure shows that the decrease in removal efficiency is sharper for higher speed of 150 rpm.

3.5. Effect of temperature

The transfer of phenol into the emulsion is facilitated due to decrease in viscosity by increasing temperature. However, the stability of emulsion is reduced at higher temperatures. Fig. 8 compares the removal efficiency at three different temperatures of 20, 30, and 40 °C. As seen in the figure, the corresponded maximum removal efficiencies are obtained faster at higher temperatures. However, the maximum removal efficiency at higher temperature is lower than that at 20 °C that indicates the ambient temperature is optimum for this process.

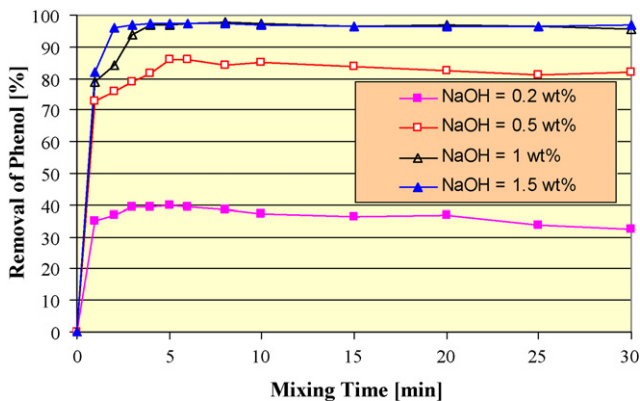


Fig. 5. Effect of NaOH concentration on phenol removal efficiency by using 3% synthesized surfactant, $C_0 = 1000$ ppm, $R_{ew}^c = 0.1$, $R_{oi}^c = 2$.

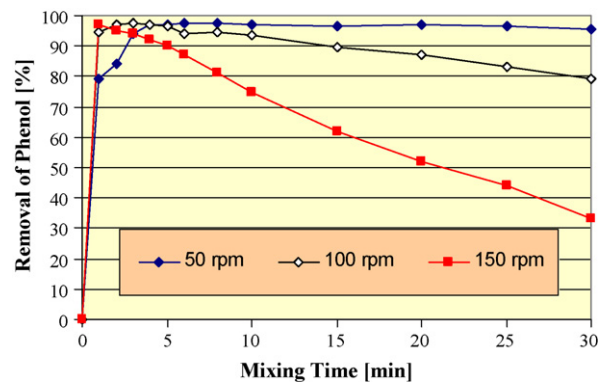


Fig. 7. Effect of mixing intensity on phenol removal efficiency using 3% synthesized surfactant, $C_0 = 1000$ ppm, 1% NaOH, $R_{ew}^c = 0.1$, $R_{oi}^c = 2$.

Table 3
Distribution coefficients of phenol between water and different solvents

Specification	Solvent				
	Solvent R	iso-Paraffin	Petroleum solvent	Solvent A	Toluene
Density (g/cm ³)	0.81	0.75	0.78	0.89	0.84
Viscosity (cp)	8.41	4.24	4.22	4.16	4.19
Aromatic content (wt%)	<8	0.1	17	99	100
Distribution coeff. (phenol ratio in solvent/feed)	0.19	0.23	0.35	0.92	1.63

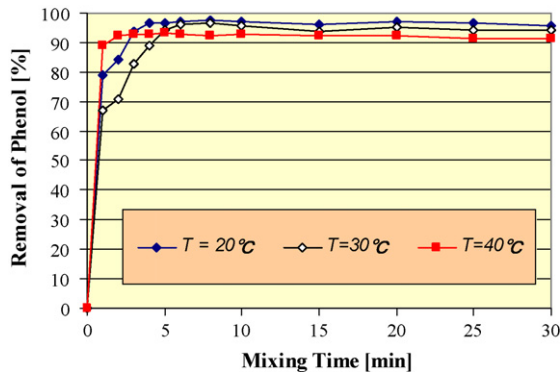


Fig. 8. Effect of temperature on phenol removal efficiency using 3% synthesized surfactant, $C_0 = 1000$ ppm, 1% NaOH, $R_{ew}^c = 0.1$, $R_{oi}^c = 2$.

3.6. Effect of the type of solvent

The mechanism of solute transfer through liquid membrane incorporates several mass transfer resistances, in which transfer of solute through the membrane phase might be considered as an important parameter. Therefore, the type of solvent may have a controlling effect on the efficiency of the process due to different solubilities of solute (i.e. phenol) in different solvents. In order to determine the effect of solvent type on removal efficiency, different solvents including the petroleum solvent, *iso*-paraffin, solvent A, solvent R, and toluene with the properties listed in Table 3 have been used to determine the distribution coefficient of phenol in the external and membrane phases. For this purpose, equal volumes of solvent and feed phases were mixed for a sufficient period of time to establish equilibrium between the two phases. The concentration of phenol in the aqueous phase is then measured. Table 3 shows the distribution coefficients for these solvents. The table shows that solubility of phenol in the solvent increases with increase in aromatic content of the solvent, that is, phenol has the maximum solubility in toluene. It is then expected that a solvent with higher aromatic content can remove phenol more efficiently since it reduces resistance against mass transfer of phenol in the membrane phase. In order to confirm this, experiments were made by different solvents. Fig. 9 shows the results of these experiments. In contrary to our expectation, petroleum solvent has the highest phenol removal. In addition, the removal efficiencies with solvent R and toluene, which have the highest and lowest distribution coefficients, respectively, decrease over the time of mixing while the removal efficiencies with petroleum solvent and *iso*-paraffin do not show significant reduction with the time. These observations do not follow an expected logical trend and it might be due to this fact that mass transfer behavior in emulsion differs from that in the specified solvent.

3.7. Effect of stabilizer

Numerous researches have noted to instability of liquid membrane due to breakage of the emulsion, which results in reduction

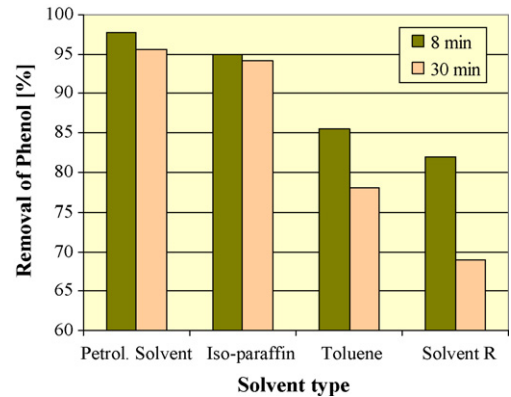


Fig. 9. Effect of solvent type on phenol removal efficiency using 3% synthesized surfactant, $C_0 = 1000$ ppm, 1% NaOH, $R_{ew}^c = 0.1$, $R_{oi}^c = 2$.

in separation efficiency [16,25]. It is often tried to solve the instability problem by increasing of the surfactant concentration, and increasing of the membrane viscosity. On the other hand, the former remedy decreases solute transfer by inhibiting the internal motion within the emulsion globules, and the latter one decreases the transfer rate due to decrease in molecular diffusivity [17,18]. Alternatively, it is recommended to increase the stability of the emulsion by converting it to a non-Newtonian form using an appropriate polymer [25,27]. It was discovered that the molecular diffusivity of solutes is independent of polymer concentration. This may solve the problem of instability in the following ways:

- (1) The membrane viscosity will be increased under the low shear rates used during the dispersion of emulsion in the external phase. Further stabilization of the membrane will also result from the smaller droplets of internal phase obtained because of the low apparent viscosity of the non-Newtonian emulsion during the emulsification stage [19]. The smaller droplets enhance the stability and increase the total internal interfaces and hence the mass transfer rate during extraction.

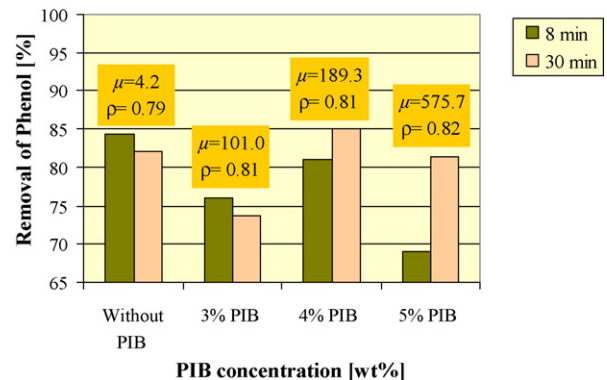


Fig. 10. Effect of polymer addition on phenol removal efficiency using 3% synthesized surfactant, $C_0 = 1000$ ppm, 0.5% NaOH, $R_{ew}^c = 0.1$, $R_{oi}^c = 2$.

- (2) The amount of surfactant needed is also decreased that reduces the retardant effect of surfactant on mass transfer rate.

In order to examine the effect of polymer addition on stability and therefore separation efficiency, experiments were made by adding different percent of PIB as a polymeric additive and the results were compared with those without adding polymer. As shown in Fig. 10, phenol is removed up to 85% after 8 min when no additive is used, and the efficiency decreases slightly after 30 min of mixing possibly due to small rupture of emulsion without adding polymer. The figure also shows that in spite of general belief, adding 3% PIB decreases the removal efficiency. This might show that within the concentration range of added polymer, the emulsion may not be converted to a non-Newtonian emulsion, and that it has a reverse effect on transfer rate. By increasing the polymer concentration from 3 to 4%, the removal efficiency in longer mixing time of 30 min becomes higher than that in short time of 8 min. This may show that adding polymer may provide more stable emulsion and that the rupture of emulsion has been decreased in longer mixing time comparing to when no polymer is added. However, the numeric value of removal efficiency does not show a significant improve compared to when the emulsion is made without increasing polymer. The removal efficiency will decrease more when polymer concentration is increased from 4 to 5%. This might be attributed to the inhibiting of internal motion within the emulsion globules and thus smaller mass transfer rate. In general, it may be concluded that adding PIB cannot increase the efficiency of the process in removal of phenol when the synthesized surfactant is used. A possible reason might be the inherent similarity between the structures of the synthesized surfactant and PIB.

3.8. Effect of solute concentration in external phase

Since the mass transfer in ELM process is directly related to the concentration driving force between internal and external phases, it is expected that changing the concentration of solute in the external phase may affect the removal efficiency. Fig. 11 compares the removal efficiencies in the systems with two different solute concentrations of 25 and 1000 ppm. As seen in the figure, at the beginning the removal efficiency in the system with lower solute concentration is slightly higher than that in the system with higher solute concentration due to enough concentration driving force. However, it declines below the efficiency of the system with higher solute concentration as the experiment proceeds and solute concentration in the external phase decreases. Since the solute concentration in the system with lower concentration (25 ppm) is in

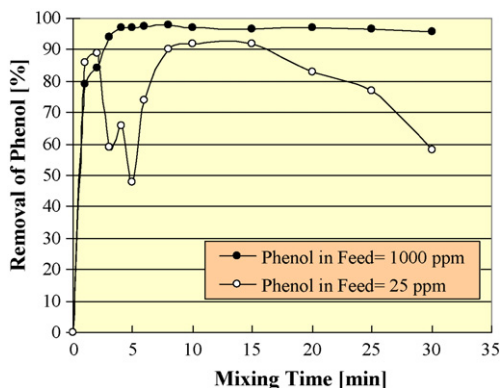


Fig. 11. Effect of solute concentration on phenol removal efficiency using 3% synthesized surfactant, 1% NaOH, $R_{ew}^c = 0.1$, $R_{oi}^c = 2$.

Table 4

Breakage and swelling of emulsions made by using synthesized surfactant and Span 80

Mixing time	ε (%)	$\eta_{s,ap}$ (%)	$\eta_{s,ac}$ (%)	pH
$t = 2$ (min)	0.2	9.7	9.9	8.36
$t = 10$ (min)	0.7	13.2	13.9	9.11
Operating conditions	3% synthesized surfactant, 0.5% NaOH, $R_{ew}^c = 0.1$, $R_{oi}^c = 2$			
$t = 2$ (min)	0.4	40.0	40.4	7.95
$t = 10$ (min)	1.1	43.8	44.8	9.67
Operating conditions	3% synthesized surfactant, 1.0% NaOH, $R_{ew}^c = 0.1$, $R_{oi}^c = 2$			
$t = 2$ (min)	89.1	-50.0	39.1	10.16
$t = 10$ (min)	91.9	-40.0	51.9	12.29
Operating conditions	3% Span 80, 1.0% NaOH, $R_{ew}^c = 0.1$, $R_{oi}^c = 2$			

the range of effluent concentration of the higher concentration system (1000 ppm), by considering the maximum removal efficiency in each case, the overall removal efficiency in a two-stage extraction process is about 99.8%.

3.9. Breakage and swelling of emulsion

Breakage of emulsion nullifies the separation efficiency by transferring back of the separated solute to the feed phase, and it is generally reported as a weakness of ELM processes [16,26]. The breakage of membrane can be caused either by external forces or by swelling of the internal phase [26]. On the other hand, actual swelling of emulsion might be caused by either coalescence of the external phase with the emulsion, namely entrainment swelling, or by transferring of solvent from the external phase to the internal phase (positive osmotic swelling) or vice versa (negative osmotic swelling) due to difference in ion strength and thus difference in osmotic pressure between the two phases [26]. The combined effect of both breakage and swelling is called “apparent swelling”. In order to determine breakage and swelling of emulsion simultaneously, a bi-tracer method is applied. The detail of this method has been described elsewhere [26], and the applied correlations are brought briefly in Appendix A. The bi-tracer method was used in the present research to compare the performance of emulsions by using the synthesized surfactant and that by using Span 80. KCl and $K_2Cr_2O_7$ were used as tracers I and II in the internal and external phases, respectively. The concentrations of K^+ and $Cr(VI)$ in both phases were measured by atomic absorption method. The results are brought in Table 4 for the samples taken at 2 and 10 min. As shown in the table, the breakage of emulsion made by using the synthesized surfactant is within the range of 1% or less while the emulsion made by using Span 80 shows up to 92% breakage that means complete breakage of emulsion. It clearly exhibits the stability of emulsions made by the synthesized surfactant compared to those made by Span 80. The increased pH of the external phase in the experiment with emulsion stabilized by Span 80 also shows high extent of breakage compared to that for the experiment by using the synthesized surfactant.

4. Conclusion

Removal of phenol from aqueous phase by ELM was studied. Span 80 and a newly synthesized polyamine type surfactant were used for stabilizing of emulsion.

- (1) It was found that in spite of emulsions made by using Span 80, which are highly instable and show low removal efficiencies, the emulsions made by using the synthesized surfactant could efficiently remove the phenol from the feed phase.

- (2) Removal efficiency increases by increasing of surfactant up to a certain concentration of surfactant, and then decreases due to inhibiting effect of surfactant on mass transfer rate.
- (3) Although the higher concentration of NaOH in internal phase increases the concentration driving force and hence removal efficiency, it has a reverse effect at high concentrations, which causes swelling and/or hydrolyzing of surfactant and leads to render the removal efficiency.
- (4) It is preferred to use systems with larger values of R_{oi}° ratio since it causes more stable emulsion.
- (5) Increasing of mixing intensity results in breakage of emulsion, and therefore is not recommended.
- (6) It was found that ambient temperature is optimum for the ELM process.
- (7) The experiments with different types of solvents showed that there is no logical relationship between the solute distribution coefficient in solvent/feed and the removal efficiency.
- (8) Addition of polymer to the emulsion stabilized by the synthesized surfactant did not show significant improve in removal efficiency.
- (9) Decreasing in concentration of solute in the external phase decreases removal efficiency of the system.
- (10) By applying a bi-tracer method, it was verified that the breakage in the emulsion stabilized by the synthesized surfactant is much lower than that in the emulsion made by Span 80.

Appendix A. Determination of breakage and swelling ratios by a bi-tracer method

The actual swelling of an emulsion is determined by the following equation:

$$\eta_{s,ac} (\%) = \left\{ \left(1 - \frac{C_{e,l}}{C_{i,l}^{\circ}} \right) \times \left[\frac{C_{i,l}^{\circ} - C_{i,l}}{C_{i,l} - C_{e,l}} - \frac{C_{e,l}(1 + R_{oi}^{\circ})}{R_{ew}^{\circ}(C_{i,l} - C_{e,l})} \right] + \frac{C_{e,l}(1 + R_{oi}^{\circ})}{R_{ew}^{\circ}(C_{i,l} - C_{e,l})} \right\} \times 100 \quad (A.1)$$

The breakage is obtained from the following equation:

$$\varepsilon (\%) = \frac{C_{e,l}}{C_{i,l}^{\circ}(C_{i,l} - C_{e,l})} \left(\frac{1 + R_{oi}^{\circ}}{R_{ew}^{\circ}} (C_{e,l} + C_{i,l}^{\circ}) - (C_{i,l}^{\circ} - C_{i,l}) \right) \times 100 \quad (A.2)$$

Finally the apparent swelling can be determined by deducting of breakage from the actual swelling:

$$\eta_{s,ap} = \eta_{s,ac} - \varepsilon \quad (A.3)$$

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