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Phenol recovery and removal from aqueous solutions by emulsion liquid membranes

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ABSTRACT

Emulsion type liquid membrane process is a new and effective method for separation of mixtures with applications in the nuclear industry, hydrometallurgy and wastewater treatment. The emulsified liquid membrane is made by forming an emulsion of two immiscible phases and then dispersing the emulsion in a third phase (i.e. continuous or feed phase). Phenol is mainly found in the wastewaters of such industries as petroleum refineries and petrochemicals. In addition phenol is also contained in the wastewaters of industries of resins, explosives, paper, plastics, glass and rubbers. Numerous solvent extraction techniques using various ligands are also used as commercial in such processes as hydrometallurgy and wastewater treatment. However one of the disadvantage of solvent extraction is the necessity of solvents and ligands of large quantities. Water-oil-water (W/O/W) type of liquid membrane system provides excellent separation techniques and thus this causes a substantial reduction in the amount of ligands and solvents, Liquid membrane phase consist of a surfactant (Span 80) and solvent (kerosene). In this study the most important parameters that provide the extraction of phenol from aqueous solutions and their effect on extraction efficiency were examined by liquid membrane process. These parameters are determined to be as membrane viscosity, treatment ratio (feed volume/emulsion volume), surfactant concentration, feed concentration and pH, mixing speed and phase ratio (stripping solution volume / membrane volume). The phenol was extracted from the aqueous feed solutions in which phenol concentration ranged from 100 to 550 mg/L. Optimum parameters were found to be as: pH = 4; phase ratio, $\phi = 1$; mixing speed (300 rpm); 3 % Span 80 and 2 % NaOH. Under the suitable conditions, about 96 % of the phenol in the feed solutions could be removed from the solution It has been possible that the phenol concentration were reduced from 550 mg/L to 5-10 mg/L within two minutes.

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1. Introduction

Phenol and its derivatives are used as raw materials for manufacturing a wide variety of useful chemicals including coal gasification, petrochemical, wood products, paints, dyes, polymers, pharmaceuticals and pesticides. The discharges from oil refineries and coal conversion processes are also rich in these contaminants. They are released in industrial wastewater and domestic water, and may directly or indirectly cause serious health and odour problems. As a result, phenols and phenolic compounds are prevalent industrial effluents and major source of water pollution. Therefore, both US Environmental Protection Agency (EPA) and the European Union (EU) directive number 80/778/EC consider phenol as a priority pollutant [1-4]. Most of the overall world production of phenol, which was $7.78x10^6$ tons in 2001, is related to the production of bisphenol A (39%), phenolic resins (27%), and the others [5].

The various techniques available for the treatment of phenolic effluents can be subdivided into two main categories: destruction and recovery methods. Among the destruction methods, there are biological treatments [7-8], incineration, ozonisation in the presence of UV radiation, and oxidation with wet air [6]. Treatment times with chemical or biological methods may be quite high and total mineralization of the effluent stream may not be possible. Existing wastewater treatment methods such as adsorption on activated carbon and chemical oxidation suffer from limitations, such as limited applicability and low efficiency, hence imparting the need research into alternative treatment techniques such as membrane processes[13]. On the other hand, recovery methods include liquid-liquid extraction [3,9], ionic exchange with resins [10]. Solvent extraction is the most often used technique to recover phenol (pK_a =10.0) in its neutral form [11]. This method requires expensive and hazardous organic solvents, which are undesirable for health and environment [12].

Development of new low-cost processes capable to substitute existing separation and purification technologies is a challenging task. Membrane technologies is used in many industrial sectors as important alternative to the classical separation and purification processes. The emulsion liquid membrane (ELM) technique has been regarded as an advance in relation to solvent extraction for separating and concentrating metal ions from aqueous dilute solutions. In this respect, liquid membranes have shown a great potential, especially in cases where solute concentrations are relatively low and other techniques cannot be applied efficiently since they combine the process of extraction and stripping in a single unit operation. The extraction chemistry is basically the same as that in solvent extraction, but the transport is governed by kinetics rather than equilibrium parameters, that is, it is governed by a non-equilibrium mass transfer. Moreover, the large specific interfacial areas associated with ELMs result in higher permeation rates, which together with the reaction rather than equilibrium restrain, enable the achievement of higher solute concentrations in fewer separation stages, maintaining the high selectivity of solvent extraction [14]. Several studies have reported the extraction of phenols by emulsion liquid membranes [13,15-18] and by supported liquid membranes [2-3,12].

In this study the most important parameters that provide the extraction of phenol from aqueous solutions and their effect on extraction efficiency were examined by liquid membrane process. These parameters are determined to be as membrane viscosity, treatment ratio (feed volume / emulsion volume), surfactant concentration, feed concentration and pH, mixing speed and phase ratio (stripping solution volume/membrane volume)..

2. Experimental

2.1 Chemicals

Surface active reagent sorbitan monooleate (Span 80, Fluka), petroleum fractions (kerosene, Tupras, Turkiye), stripping solution (NaOH, Merck), 4-aminoantipyrine, $K_3Fe(CN)_6$, K_2HPO_4 and NH_3 (all being Merck) for phenol analysis were used. All salts and reagents were of analytical grade and used for without further purification.

2.2 Experimental Procedure

The liquid membrane phase is composed of a surfactant (Span 80) and a solvent. The surfactant is a sorbitanmonooleate which is commercially known as Span 80. The solvent is a commercial kerosene, obtained from Tupras Corp., Turkiye (density 830 kg/m^3 and viscosity 1.6 mPa.s at 20 ^{o}C). Batch extraction experiments of phenol were conducted in a 600 mL-glass beaker, stirred vessel with four Teflon-coated baffle plates. A Teflon turbine impeller was used. Phenol stock solutions were prepared by dissolving analytical grade phenol, purchased from Merck, in double-disttilled water. Various feed solutions were prepared by diluting the stock solutions as desired.

The extraction of phenol using emulsion type of liquid membrane (ELM) involves three steps, namely preparation of ELM, extraction of the solute (phenol) from the feed solution by contacting the emulsion, and separation of liquid emulsion from external phase by settling, as shown in Fig. 1.

Sodium hydroxide solutions were used for strip phase. Feed mixture was prepared from the stock solution of phenol. The buffer soution was essential for phenol extraction to maintain the desired feed pH, which was very critical. Unless otherwise stated, pH of feed solution, mixing speed and volume ratio of strip phase/membrane phase/feed phase ($V_s/V_m/V_F$) were kept constant. The 25-mL of strip was added dropwise to the 25 to 30 mL-membrane phase, stirred at 1900 for the period of 20 minutes and passed through a burette in about 8 minutes. The prepared W/O emulsion was immediately dispersed into a 500-mL feed solution. The uptake of phenol was monitored by removing 1-2 mL of samples of the feed phase periodically for analysis with a UV-VIS spectrophotometer (Shimadzu, Japan). All the extraction experiments were carried out batchwise and at the ambient temperature of 20±1 ^{o}C. The aqueous phase pH measurements were determined with a pH meter (Thermo Scientific Inc., Eutech 150 & 450 Series, Singapore).

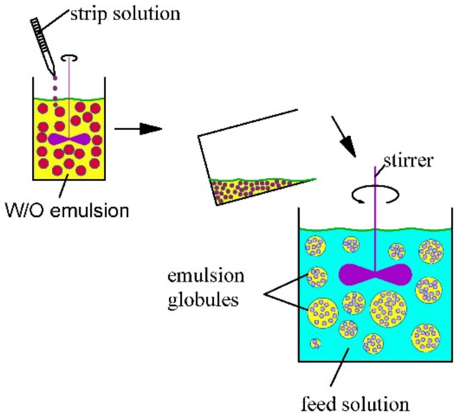
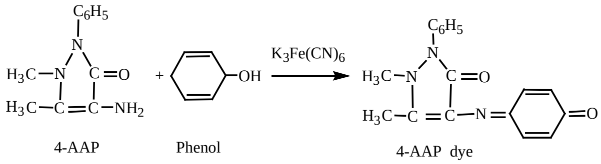


Figure 1. *The preparation of a W-O-W type of emulsion liquid membrane*

2.3. Determination of phenol concentration

The determination of phenol was determined according to the method of Annadurai et al. (19), based on rapid condensation with 4-aminoantipyrine (4-AAP) followed by oxidation with alkaline potassium ferricyanide giving red color detected UV-Vis spectrophotometer at 510 nm wavelength. The reaction is as follows:



(1)

In order not to be a color change in the solution, the phenol samples have to be read within 30 minutes. The 2-mL samples taken are diluted to 100 mL in volumetric flasks, before the 2.5 mL of 0.50 M NH_4OH solution is added to each of the flasks, and pH of the solution is adjusted to 7.9 ∓ 0.1 using a phosphate buffer. 1 mL of 4-aminoantipyrine solution is added to all samples and is well mixed. 15 minutes later, absorbances of all the samples are measured by a UV-Vis spectrophotometer at 510 nm wavelength against the blank. Before the measurements are taken, the spectrophotometer is calibrated using standard phenol solutions and the obtained relation is given by Eqn. (2) as

$$y = 7.962x + 0.1388 \tag{2}$$

where y: phenol concentration, mg/L, and x: absorbance of sample.

3. Results and discussion

3.1. Effect of surfactant concentration

The effect of surfactant concentration on the behavior of the rate extraction and phenol removal was studied in the range of 1 through 3 wt % Span 80, as shown in Fig. 2. From 2, the percentage removal of phenol in 5 min increased from 89.4 to 96.2 % with an increase in the Span 80 from 1 to 3 wt %. After 5 min, as the time increased the membrane stability tended to slightly decreased, as a result the emulsion stability increases as the surfactant concentration increases.

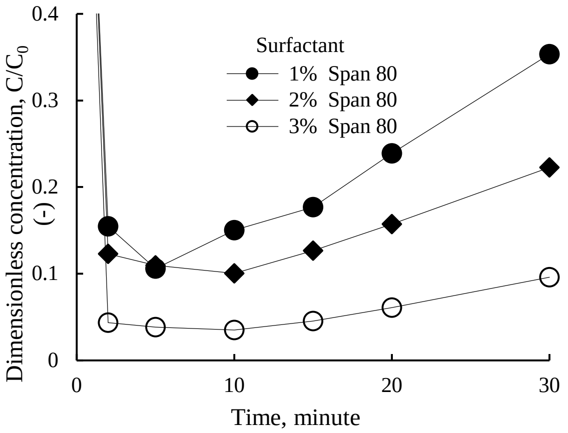


Figure 2. *Effect of surfactant (Span 80) on the rate of extraction (Feed conc.: 565.4 mg/L; strip solution: 25 mL 2 wt % NaOH; treatment ratio (V_F/V_E): 5/1; phase ratio: 1/1; pH: 4; mixing speed: 400 min^{-1})*

3.2. Effect of mixing speed

To investigate the mixing speed on removal of phenol the mixing speed increased from 300 to 400 min^{-1}, as shown in Fig. 3. It is observed from Fig. 3 that mixing speed at 300 min^{-1} provides maximum removal of phenol with higher emulsion stability. From Fig. 3, initially, that is, in the first 5 min the percentage of phenol removal slightly increases, but later there is a notable increase in the extraction efficiency. The reason for that might be, with an increase in the mixing speed relatively smaller emulsion globules may have formed, and thus the phenol removal rate or mass transfer increases. However, after 15 min, the emulsion globules tend to break up, and as a result the extraction efficiency decreases.

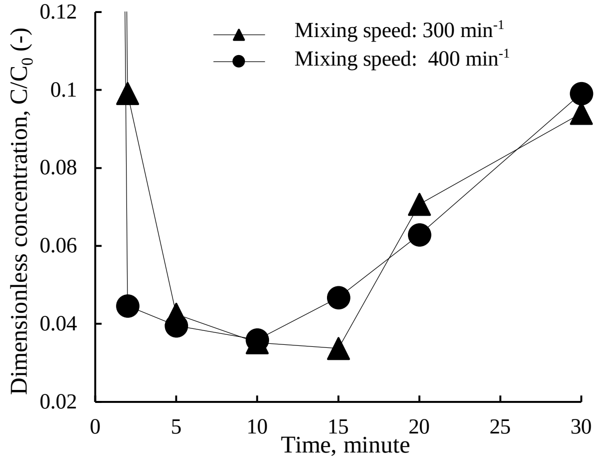


Figure 3. *Effect of mixing speed on the rate of extraction (Feed conc.: 548.8 mg/L; surfactant conc.: 3 wt % Span 80; strip solution: 25 mL 2 wt % NaOH; treatment ratio (V_F/V_E): 5/1; phase ratio: 1/1; pH: 4)*

3.3. Effect of external solution pH

The effect of external phase pH on removal rate of phenol was studied in the range of 2 through 6, as shown in Fig. 4. From Fig. 4, it is clearly evident that the most favorable case was obtained at pH 4, adjusted by concentrated hydrochloric acid. Similar behavior was also experienced and reported elsewhere (18). However, at pH 4 when the pH adjustment was made by H_2SO_4 instead of HCl, the percentage of phenol removal significantly deteriorated. At pH 4, the removal efficiency of phenol remained to be constant between 10 and 20 min, being about 95 %.

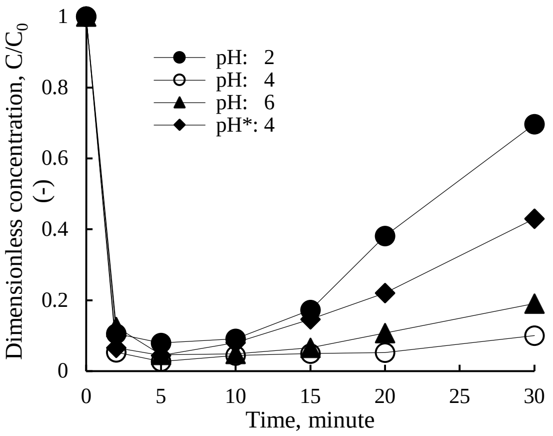


Figure 4. *Effect of external phase pH (Feed conc.: 542 mg/L; surfactant conc.: 3 wt % Span 80; strip solution: 25 mL 2 wt % NaOH; mixing speed: 300 min^{-1}; treatment ratio (V_F/V_E): 5/1; phase ratio: 1/1; Note: pH 4* was adjusted using concentrated H_2SO_4)*

3.4. Effect of treatment ratio

The effect of external phase to emulsion volume ratio (treatment ratio) in the range from 4 to 7 was studied on the removal of phenol and emulsion stability, and the results are indicated in Fig. 5. With an increase in the treatment ratio from 4 to 7 (v/v), decrease in removal of phenol from 96.0 to 89 in the first 5 min. From Fig. 5, if the phenol removals for three treatment ratios in 5 min are compared, the phenol extraction efficiency decreased from 96.0 to 89.6 %. However, the membrane stability tends to break up and deteriorates as time as the time goes on.

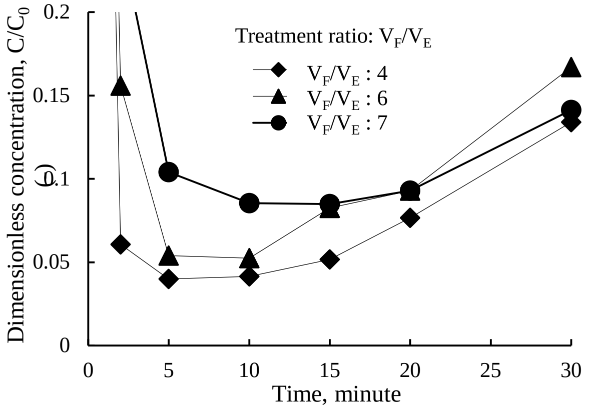


Figure 5. *Effect of treatment ratio on the rate of extraction (Feed conc.: 500 mg/L; surfactant conc.: 3 wt % Span 80; strip solution: 25 mL 2 wt % NaOH; mixing speed: 300 min^{-1}; phase ratio: 1/1; pH: 4)*

3.5. Effect of phase ratio (V_s/V_m)

The effect of internal to membrane phase volume ratio, on removal of phenol and emulsion stability was studied experimentally in the range of 0.8 to 1.4, as shown in Fig. 6. As seen from Fig. 6, the best phase ratio was obtained at ϕ=1.0. The percentage removal of phenol increased from 95.3 to 92.6 %, as the ratio increased from 0.8 to 1.4 in the first 5 min. At the phase ratio of 1.0, the percentage of phenol removal from 5 to 20 min gradually decreases.

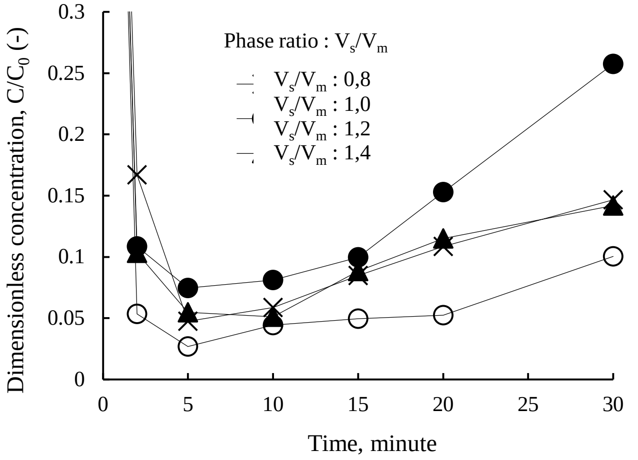


Figure 6. *Effect of phase ratio on the rate of extraction (Feed conc.: 542.4 mg/L; surfactant conc.: 3 wt % Span 80; strip solution: 25 mL 2 wt % NaOH; mixing speed: 300 min^{-1}; treatment ratio (V_F/V_E): 5/1; phase ratio : 1/1; pH: 4)*

3.6. Effect of strip solution concentration

The rol of stripping agent in strip phase in phenol removal was investigated in the concentration range from 0.5 through 2 wt % NaOH, and the results obtained are given in Fig. 7. As observed from Fig. 7, the percentage removal of phenol increased from 91.2 to 96.6 % in 15 min. NaOH in the strip solution gives the following reaction:

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O \qquad (3)$$

The reaction prevents the phenol from returning to the feed solution through the membrane phase. 2 % strip solution of NaOH was found to be more appropriate for the phenol extraction.

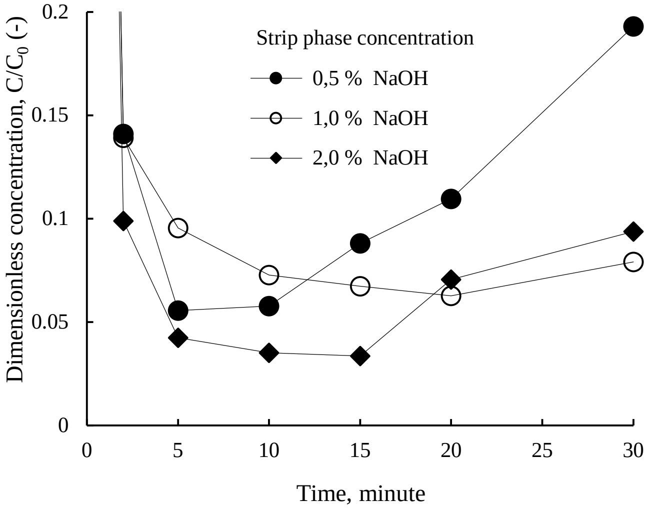


Figure 7. *Effect of strip solution (NaOH) on the rate of extraction (Feed conc.: 550 mg/L; surfactant conc.: 3 wt % Span 80; mixing speed: 300 min^{-1}; treatment ratio (V_F/V_E): 5/1; phase ratio: 1/1; pH: 4)*

3.7. Effect of external solution concentration

Effect of initial phenol concentration in the feed solution on the extent of extraction is shown in Fig. 8, using the optimum parameters. The phenol concentration in the external or feed phase ranging from 100 to 550 mg/L is presented in Fig. 8. In 5 min, the percentage of phenol removal from 100 through 550 mg/L of the external phase concentrations is about 96.0 %. As the time passes from 5 to 20 min, the phenol removal decreases down to about 90 %.

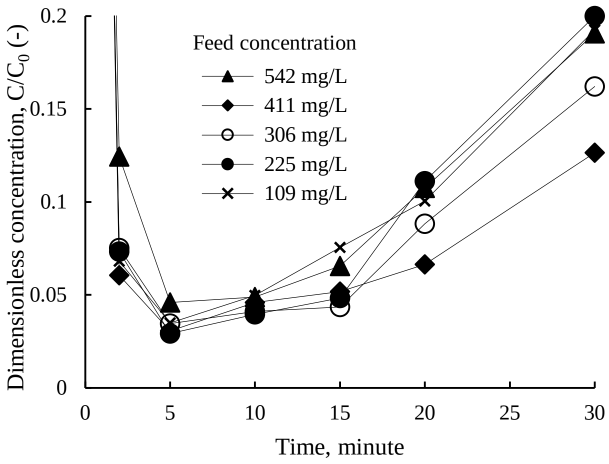


Figure 7. *Effect of initial phenol concentration in the external phase (Feed concs.: 100-550 mg/L; surfactant conc.: 3 wt % Span 80; mixing speed: 300 min^{-1}; strip solution: 25 mL 2 wt % NaOH; treatment ratio (V_F/V_E): 5/1; phase ratio: 1/1; pH: 4)*

4. Conclusion

Removal of phenol from aqueous solutions, containing 550 mg/L phenol, using an emulsion liquid membrane (ELM) was investigated. EML consisted of surfactant Span 80, and diluent kerosene of a petroleum fraction, NaOH solutions was used as strip phase. Such parameters as surfactant (Span 80) concentration, feed solution pH and concentration, mixing speed, treatment ratio, internal phase ratio, and strip phase concentration were studied and from this study following conclusions could be drawn:

1. As the surfactant concentration increased from 1 to 3 wt %, the membrane stability increased, as a result extraction efficiency also raised.

2. As the mixing speed increased from 300 to 400 rpm, the extraction efficiency in the first 5 minutes increased, but later due to the breakages of the emulsion globules, the membrane stability was reduced, as a result the efficiency decreased.

3. As the feed solution pH increased from 2 to 6, the extraction efficiency also increased, pH 4 gave the highest efficiency, that is, feed solution pH is of great significance.

4. As the treatment ratio (V_F/V_E), that is the ratio of feed volume to emulsion volume, increased from 4/1 to 7/1, the extraction efficiency decreased from 96 % to 89.6 %.

5. As the phase ratio ϕ (V_s/V_m), that is, the ratio of strip phase volume to membrane volume, increased from 0.8 to 1.4, the highest efficiency was obtained at $\phi = 1$, being 90 %.

6. As the strip solution (NaOH) concentration increased from 0.5 to 2 %, the highest extraction efficiency was obtained at 2 wt % of NaOH concentration.

7. The optimum conditions, from examining the experimental parameters, were as follows :

- Diluent: Petroleum fraction kerosene
- Surfactant: 3 wt % Span 80
- Feed solution pH: 4.0.
- Strip phase concentration: 2 wt % NaOH
- Treatment ratio : 4
- Phase ratio ϕ (V_s/V_m): 1.0
- Mixing speed : 300 min^{-1}

8. At the optimum conditions, as the phenol concentration in feed phase increased from 108 mg/L to 550 mg/L, the extraction efficiency in this direction decreased. However, for 542.4 mg/L of phenol concentration, 95.5 % of phenol was extracted in 5 minutes, for 108.5 mg/L of phenol feed concentration, 96.5 % of phenol was removed or extracted from the feed solution in 5 minutes.

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