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Removal of Phenol from Aqueous Solution by Liquid Emulsion Membrane

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Abstract−In the removal of phenol from aqueous solution by liquid emulsion membrane, we investigated the effect of surfactants and their concentrations, volume ratio of the internal phase to surfactant solution and sodium hydroxide concentration of the internal phase on the removal efficiency and membrane stability by using ultrasonic homogenization and mechanical stirring. Using an ultrasonic homogenizer, the highest removal was achieved at the emulsification time of 30 sec and the amplitude of 48.5 μm. The removal efficiency by the ultrasonic homogenizer was higher than that by mechanical stirring.

Key words: Liquid Membrane, Phenol, Removal, Ultrasonic Homogenization, Stirring

INTRODUCTION

Liquid emulsion membrane processes consist of an internal phase, a membrane phase and an external phase. The external phase contains a solute to be separated, the solute being phenol in this study. Phenol is one of common contaminants dissolved in waste water. The membrane phase, containing a surfactant to maintain emulsion stability, separates the external phase and the internal phase. In the internal phase containing sodium hydroxide, the permeated phenol is converted into sodium phenolate which cannot diffuse back to the external phase because of its insolubility in the membrane.

The solute diffuses from the external phase to the membrane phase, permeates through the membrane phase and reaches the internal phase where it is converted into another compound by reaction. Therefore, the concentration of the solute at the interface between the membrane phase and the internal phase is maintained at zero, allowing a continuous driving force for the solute permeation through the membrane [Terry et al., 1982]. The permeation depends on the concentration gradient of the solute between the external phase and the internal phase. The membrane phase usually contains surfactants, additives and a base material that is a solvent for all the other ingredients. The surfactants and additives are chosen to enhance the stability, selectivity and permeability of the membrane.

In the external phase the emulsion is dispersed by agitation or ultrasonic homogenization, during which numerous small globules of emulsion are formed. Their size depends not only on the nature and concentration of the surfactants used but also on the mode and intensity of mixing. Each emulsion globule (diameter of 0.1-2 mm) contains many tiny encapsulated droplets (diameter of 1-100 μm) [Marr and Kopp, 1982]. A large number of globules of emulsion formed produce a correspondingly large membrane surface area for enhanced mass transfer between the external phase and the internal phase [Lee et al., 1978; Plucinski, 1985]. Typical equipment for emulsification includes a mechanical stirrer, an ultrasonic homogenizer and a colloid mill [Becher, 1983]. Ultrasonic homogenization is known as one of the most effective methods for producing small and stable globules of emulsion [Hanna and Larson, 1985] and its efficacy has been shown in the separation of benzene-n-heptane mixture by liquid membrane [Kim and Chung, 1999] as well as in the preparation of zirconia-pillared montmorillorite [Awate et al., 2001]. The liquid membrane process has various applications such as treatment of waste water [Goswami et al., 1992], separation and concentration of metals [Guha et al., 1994; Jeong and Ju, 2002] and protein separation [Hong and Yang, 1994]. The separation of phenol from aqueous solution has been reported in a supported liquid membrane with a carrier [Park et al., 1996].

In this study the effect of surfactants and their concentration, volume ratio of the internal phase to the surfactant solution and sodium hydroxide concentration on the phenol removal and membrane stability was investigated by using ultrasonic homogenization and mechanical stirring. Comparison of phenol removal was made between ultrasonic homogenization and mechanical stirring.

EXPERIMENTAL

Phenol (Junsei Chem., first class), sodium hydroxide (Yakuri Chem., special class), kerosene (Junsei Chem., first class) were used. Aqueous solution of Direct Red 2 (Sigma Chem.) was used for the membrane breakup experiment. The two surfactants used were SO-10 (sorbitan monooleate, HLB 4.3, Nikkol Chem.) and Arlacel 83 (sorbitan sesquioleate, HLB 3.7, Imperial Chem.).

Two beakers were used, one as the emulsifier and the other as the contactor. A four-blade propeller of 40 mm diameter was used as a mechanical stirrer and an ultrasonic generator (model 450, Branson, Ultrasonics Co., USA) with flat tip 1/2 in. diameter was used for ultrasonic homogenization. The stirrer used in the contactor was a four-blade paddle of 45 mm diameter. Stirring speed in the emulsifier was controlled by stroboscope (Sugawara Lab., Inc., model MSX-XA) connected to control box. Ultrasonic intensity was controlled by the output controller equipped in the ultrasonic homogenizer. Stirring speed in the contactor was controlled by using GT24 stirring system (model 099D HST220, Glas-Col Co., USA). The temperatures of the emulsifier and contactor were maintained at 25±1 °C by means of a water bath.

In the emulsifier a W/O (water/oil) emulsion was made from the

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sodium hydroxide solution and the mixture of surfactant and kerosene in various proportions by means of mechanical stirring at 1,200 rpm for 10 min as well as ultrasonic homogenization with varying intensity and duration. In the contactor a W/O/W (water/oil/water) emulsion was made by adding the aqueous phenol solution to the W/O emulsion at 400 rpm stirring with varying contact time. After every fixed contact time the stirring was stopped and the solution was allowed to settle for 2.5 min. Then the solution separated into two layers of the emulsion and the aqueous phenol. Samples taken from the aqueous phenol were analyzed by UV spectrophotometer (Hitachi Co., model U-3210). An experiment for membrane breakup was carried out in the same way as above except dissolving Direct Red 2 in the internal phase.

RESULTS AND DISCUSSION

In this study we attempted to find removal characteristics of phenol from the aqueous solution by liquid membrane, on the basis of which the optimal conditions for the best removal were pursued. In every experiment stirring speed was 1,200 rpm and stirring time 10 min with a mechanical stirrer, while ultrasonic frequency was 19.850-20.050 kHz with an ultrasonic homogenizer. The conditions above, as the optimal ones, were chosen by preliminary experiment.

The kind and concentration of surfactants are some of the most influential factors affecting the stability of emulsion membrane. Figs. 1 and 2 show the phenol removal efficiency of SO-10 and Arlacel 83 depending on their concentrations with the conditions of the initial phenol concentration of 1,000 ppm, the internal phase of 3.0 wt% sodium hydroxide, the unit volume ratio of the internal phase to the surfactant solution and 1/5 volume ratio of the emulsion/the external phase. The volume ratio of the emulsion/the external phase gave the best removal at the value of 1/5 in the range of 1/3-1/7.5. The most effective removal was achieved at the concentrations of 5.0 wt% SO-10 and 7.0 wt% Arlacel 83. At low surfactant concentrations such as 1.0 wt% and 3.0 wt% the phenol removal efficiency decreased after 8 min contact time because of membrane breakage owing to unstable emulsion formation. At high surfactant concentrations such as 7.0 wt% SO-10 and 11.0 wt% Arlacel 83 the phenol removal efficiency also decreased owing to mass transfer resistance increase caused by increase of the viscosity and thickness of membrane in spite of stable emulsion.

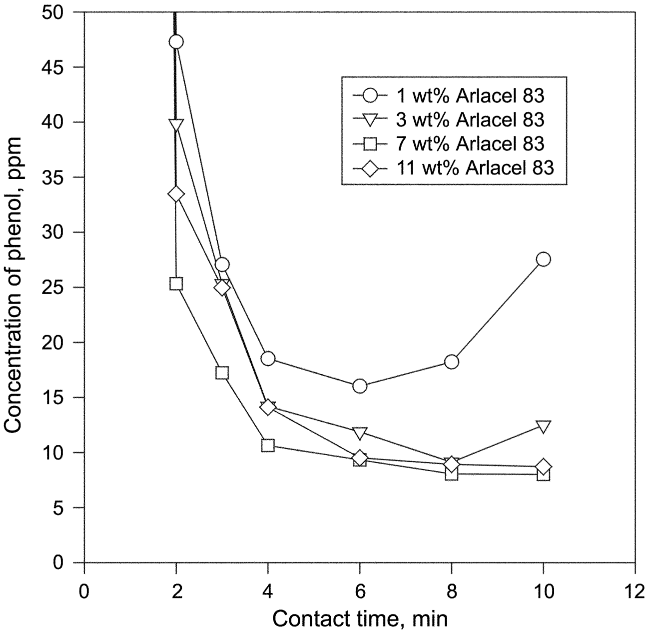

Fig. 2. Effect of Arlacel 83 concentration on phenol removal by mechanical stirring.

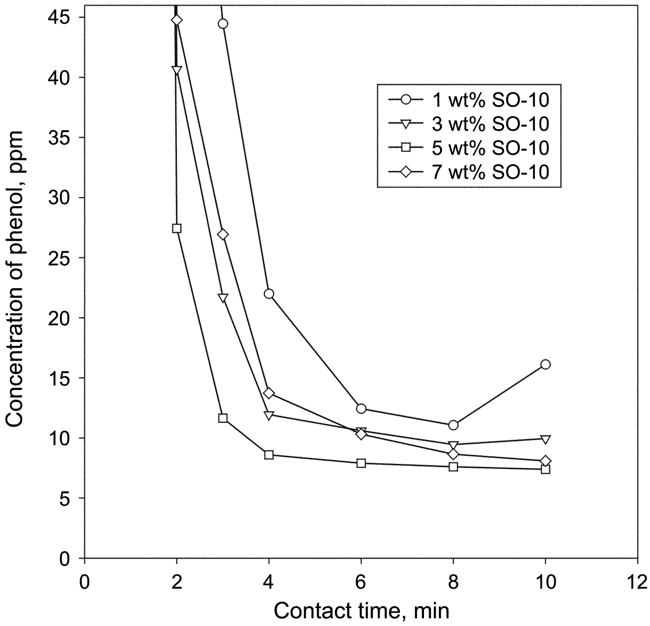

Fig. 1. Effect of SO-10 concentration on phenol removal by mechanical stirring.

Fig. 3 shows the effect of the volume ratio of the sodium hydrox-

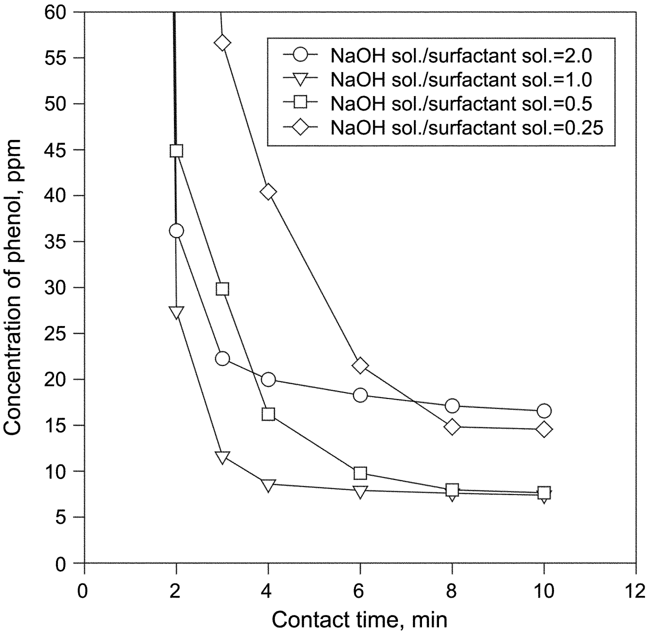

Fig. 3. Effect of NaOH/surfactant ratio in (W/O) emulsion on phenol removal by mechanical stirring.

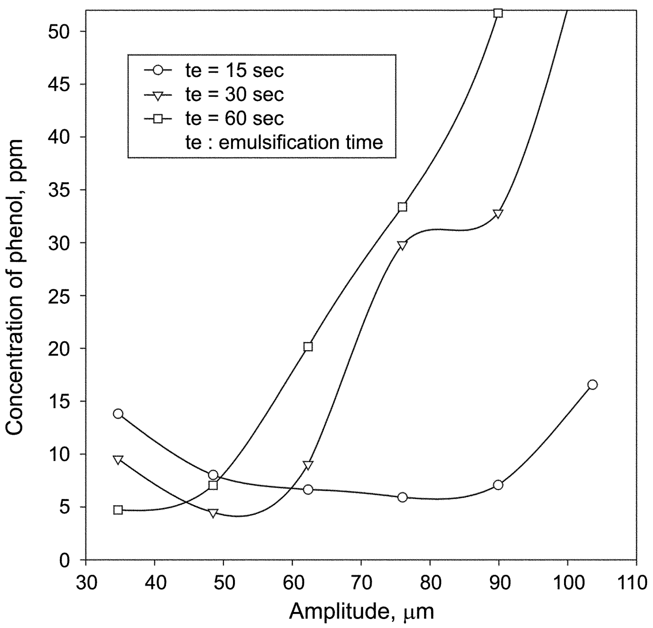

Fig. 4. Effect of emulsification time by ultrasonic homogenization on phenol removal.

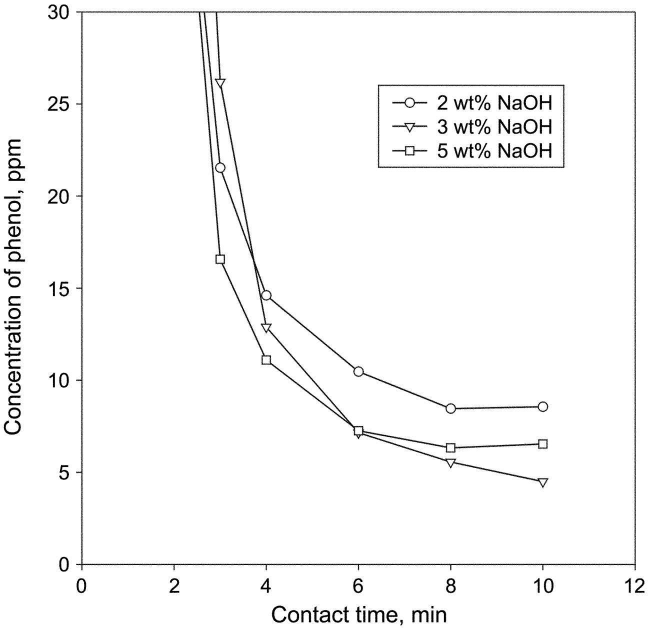

Fig. 5. Effect of NaOH concentration on phenol removal by ultrasonic homogenization.

ide solution to the surfactant solution on the phenol removal with the conditions of the initial phenol concentration of 1,000 ppm, the SO-10 concentration of 5.0 wt%, the sodium hydroxide concentration of 3.0 wt% and 1/5 volume ratio of the emulsion/the external phase. The highest removal of 99.26% was achieved at the volume ratio of 1.0 and the contact time of 10 min where it is considered that the stable emulsion was formed. At the volume ratio of 2.0 the removal decreased owing to membrane breakage caused by decrease in the membrane thickness. At the volume ratios of 0.5 and 0.25 the removal decreased because of insufficient sodium hydroxide required for reaction. In some part the decreased removal was due to increased membrane thickness causing mass transfer resistance increase.

Fig. 4 shows the efficacy of ultrasonic homogenization in emulsification. The highest removal of 99.55% was attained at the emulsification time of 30 sec and the ultrasonic amplitude of 48.5 μm, at which all the experiments with ultrasonic homogenization were carried out thereafter. The experimental conditions were the initial phenol concentration of 1,000 ppm, the SO-10 concentration of 5.0 wt%, the sodium hydroxide concentration of 3.0 wt%, the unit volume ratio of the internal phase to the surfactant solution, 1/5 volume ratio of the emulsion/the external phase and the contact time of 10 min. Although the emulsification time of 15 sec gave quite good phenol removal, it was a little bit short to give the highest removal. At an emulsification time longer than 30 sec and ultrasonic amplitude larger than 48.5 μm, the removal dropped sharply as a stable emulsion could not be formed owing to temperature rise [Kim and Chung, 1999].

Fig. 5 shows the effect of sodium hydroxide concentration on the phenol removal. The highest removal of 99.55% was achieved at the sodium hydroxide concentration of 3 wt%. The experimental conditions were the initial phenol concentration of 1,000 ppm, the SO-10 concentration of 5.0 wt%, the unit volume ratio of the internal phase to the surfactant solution and 1/5 volume ratio of the emulsion/the external phase. At the sodium hydroxide concentration of 2 wt% the phenol removal decreased after the contact time of 4 min because of insufficient sodium hydroxide. On the other hand, at the sodium hydroxide concentration of 5 wt% the phenol removal decreased owing to unstable emulsion formed.

Fig. 6 shows a comparison of phenol removal between ultrasonic homogenization and mechanical stirring in emulsification with the experimental conditions of the initial phenol concentration of 1,000 ppm, sodium hydroxide concentration of 3.0 wt%, unit volume ratio

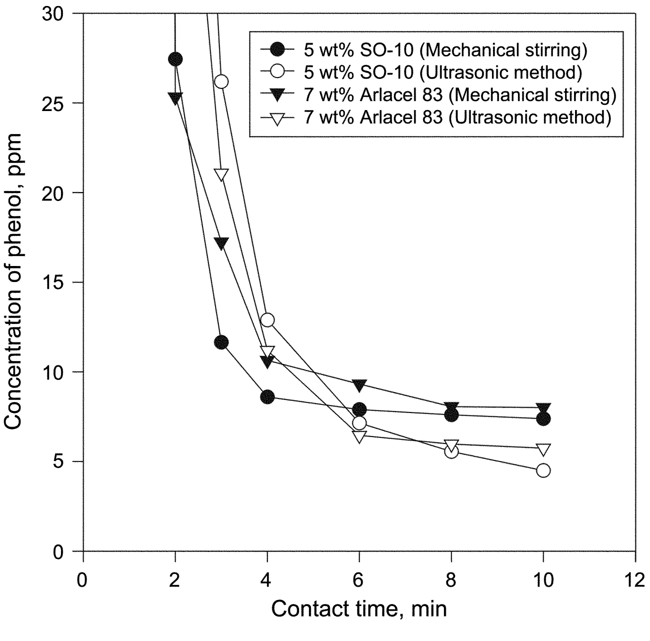

Fig. 6. Comparison of phenol removal between ultrasonic homogenization and mechanical stirring in emulsification.

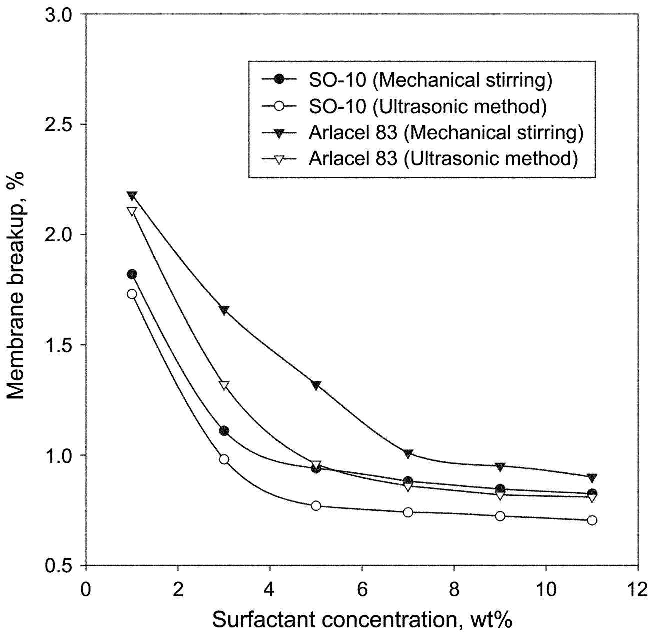

Fig. 7. Membrane breakup vs. surfactant concentration.

of the internal phase to the surfactant solution and 1/5 volume ratio of the emulsion/the external phase. As can be seen in Fig. 6, mechanical stirring was better than ultrasonic homogenization in the beginning; however, after a contact time of 6 min ultrasonic homogenization gave better removal than mechanical stirring with both SO-10 and Arlacel 83. For SO-10 the highest removal of 99.55% by ultrasonic homogenization was larger than that of 99.26% by mechanical stirring at the contact time of 10 min. For Arlacel 83 the highest removal of 99.43% by ultrasonic homogenization also was larger than that of 99.20% by mechanical stirring at the contact time of 10 min. From both results it may be said that ultrasonic homogenization is more efficient than mechanical stirring in the phenol removal. Emulsions made by ultrasonic homogenization must be very small and stable, thus providing larger contact area for better removal.

Fig. 7 shows the result of the membrane breakup experiment. The experimental conditions were an initial phenol concentration of 1,000 ppm, sodium hydroxide solution of 3.0 wt%, unit volume ratio of the internal phase to the surfactant solution, 1/5 volume ratio of the emulsion/the external phase and contact time of 10 min. For SO-10 the membrane breakup decreased greatly with concentration increase in the beginning, but there was almost no decrease beyond the concentration of 5 wt%. For Arlacel 80 there was no distinguishable decrease beyond the concentration of 7 wt%. These observations are in accordance with those explained in Figs. 1 and 2 previously. In Figs. 1 and 2 it was observed that the most effective phenol removal was achieved at the concentrations of 5.0 wt% SO-10 and 7.0 wt% Arlacel 83 where the membrane breakup starts to flatten. At concentrations lower than 5.0 wt% SO-10 and 7.0 wt% Arlacel 83 the phenol removal decreased because of membrane breakup, while at concentrations higher than 5.0 wt% SO-10 and 7.0 wt% Arlacel 83 the phenol removal also decreased owing to mass transfer resistance increase caused by increased membrane thickness and viscosity despite of stable emulsion. It can also be confirmed that ultrasonic homogenization gave the membrane breakup of 0.77% and 0.86% which are lower than those of 0.94% and 1.01% by mechanical stirring for the SO-10 concentration of 5 wt% and the Arlacel 83 concentration of 7 wt%, respectively.

CONCLUSION

Removal characteristics of phenol from the aqueous solution by liquid membrane were analyzed. Comparison was made between ultrasonic homogenization and mechanical stirring in the phenol removal. The highest removal was achieved at the SO-10 concentration of 5.0 wt% and the Arlacel 83 concentration of 7.0 wt%. At concentrations lower than those above, the phenol removal decreased because of unstable emulsion. At concentrations higher than those above, the removal also decreased owing to mass transport resistance increase caused by increase of the viscosity and thickness of membrane. Removal with SO-10 was better than that with Arlacel 83. The highest removal was achieved at the sodium hydroxide concentration of 3.0 wt% and the unit volume ratio of the internal phase to the surfactant solution. The highest removal by ultrasonic homogenization was attained at the ultrasonic duration of 30 sec and the ultrasonic amplitude of 48.5 μm. Ultrasonic homogenization gave higher phenol removal than mechanical stirring.

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