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Removal of Phenol from Wastewater by Supported Liquid Membrane Process

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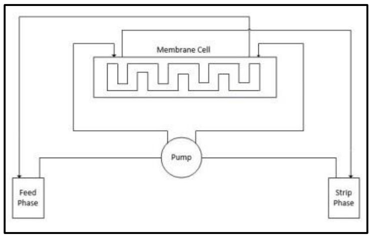
Graphical abstract



Abstract

Phenol is considered a pollutant in the environment due to its toxicity and carcinogenic effect. Supported liquid membrane (SLM) is a good and promising technology for the removal of phenol from wastewater because it provides maximum driving force for the separation of targeted solute and simultaneous extraction and stripping process which lead to excellent separation. In this research, kerosene and palm oil liquid membranes were used as liquid membrane phase, aqueous phenol as the feed phase and aqueous sodium hydroxide as the stripping phase. Several factors such as feed phase pH, feed phase flow rate and concentration of stripping phase were studied. The results show that the best extraction performance can achieve 35% at pH 4 of feed phase, 150 ml/min feed flow rate and 1.0 M of stripping phase concentration. The result was used to determine the probability of using palm oil as a liquid membrane. In the determination of the potential of using palm oil as the membrane phase, the results show that an equal portion of palm oil and kerosene mixture performed the best extraction with 43% efficiency.

Keywords: Phenol; supported liquid membrane; wastewater

■1.0 INTRODUCTION

Phenol and its derivatives are among the most common forms of chemical pollutants in wastewater. They are present in wastewater of various industries, such as refineries (6–500 mg/l), coking operations (28–3900 mg/l), coal processing (9–6800 mg/l), and manufacture of petrochemicals (2.8–1220 mg/l). Other sources of waste stream water containing phenols are pharmaceutical, plastics, wood products, paint, and pulp and paper industries (0.1–1600 mg/l) [1]. Nowadays, the manufacturing and use of chemical compounds around the world have increased significantly which are bringing impact to the environment. Due to its toxicity and carcinogenic effect, phenol is considered a pollutant in the environment. Therefore, treatment of wastewater before it is discharged into environment has become the recent major concern [2]. In contrast, phenolic compounds are considered as valuable chemicals for industrial processes. It can be used in the production of some chemical products such as adhesives, dyes, germicides and the chemical intermediates. Therefore, a variety of innovative methods for separation and recovery of phenolic compounds are developed in order to remove the unwanted phenol from wastewater and to obtain valuable phenolic compound.

Recently, membrane technology exists as the important alternative used by industry for separation and purification purpose [3-5]. The usage of this technology has increased significantly. Liquid membrane (LM) is a new introduced separation system consisting of a liquid film through which selective mass transfers of gases, ions, or molecules occur via permeation and transport processes. Among the liquid membranes, supported liquid membrane (SLM) is a good and promising technology for the recovery of organic compounds or metals [6]. In SLM, the extraction and stripping process are combined in one unit. The two aqueous phases are separated by a polymeric support which contains a complex agent in an organic phase. The solute is transported from the feed phase to the stripping phase through the supported liquid membrane. Combining both extraction and stripping processes in a single unit enable SLM to possess some advantages such as possible usage of expensive carriers, high separation factors, easy scale-up, low energy requirements, low capital and operating costs [7]. The most significant disadvantage is lack of long term stability which is due to the emulsification at the membrane-aqueous interfaces and the osmotic pressure differences across the membrane displaces the organic solution occupied in the micropores of the membrane. Thus it leads to the reduction of solute flux and membrane selectivity. On the other hand, the high volatility of organic solvent in nature leads to its loss and this render to unstable SLM.

The solubility difference of the phenol between the aqueous phase and the organic phase is the driving force of the phenol recovery using the SLM technique. In this technique, the liquid membrane is impregnated in the pore structure of a polymeric support. In a SLM process, the phenol diffuses from the feed phase, permeate through the membrane phase and reach the stripping phase. In the stripping phase, it reacts with sodium hydroxide and then is converted into sodium phenolate. Sodium phenolate cannot diffuse back to the feed phase since it is not soluble in the membrane. The transport of solute through the membrane is driven by the concentration gradient of the solute across the membrane. As long as the concentration gradient exists, the transportation of solute will continue. There is no equilibrium limitation for SLM process [8]. Generally, the solvents used for liquid membrane process are flammable, toxic, volatile and able to cause environmental and safety risks. The room temperature ionic liquids (RTILs) are one of the alternatives for environmental-friendly purpose. Generally, vegetable oil is easily available, naturally occurring, low cost and renewable source. Works by Venkateswaran and Palanivelu [9] have shown that palm oil was found to be the most efficient, stable liquid membrane for the separation of phenol and dyes.

In this study, supported liquid membrane was used to study the parameters that affect the extraction efficiency of phenol such as feed pH, feed flow rate and concentration of stripping agent. The possibility of using palm oil as liquid membrane for the removal of phenol from wastewater using supported liquid membrane is also determined.

■2.0 EXPERIMENTAL

2.1 Materials

In this study, the solvent used for the experiment was kerosene and palm oil. Kerosene was purchased from Sigma-Aldrich while palm oil was purchased from the supermarket. Sodium hydroxide pellets branded J.T.Baker® (assay: 98 %) was purchased from Avantor Performance Materials Sdn Bhd. Phenol was obtained from Sigma-Aldrich. Polypropylene (PP) membrane support (pore size 0.1 µm) obtained from Accurel Membrana.

2.2 Experimental Procedures

2.2.1 Preparation of Supported Liquid Membrane

The thin sheet of membrane support was immersed in the liquid membrane phase of kerosene or kerosene-palm oil mixture for 24 hours before being used for phenol extraction process [10]. The immersed membrane support was taken out of the liquid in the container and the excess liquid that attached to the surface of the membrane support was removed gently by using a filter paper.

2.2.2 Experimental Set Up

Membrane cell was made up of two Teflon blocks with a length 10 cm and width 15 cm. There is a flow route in each block for feed and strip solution. The feed solution flows in a direction which is the opposite to the flow direction of strip solution to enhance the diffusion of solute from feed phase to membrane phase. The microporous polypropylene membrane was placed between two Teflon blocks. Teflon Tape was applied at the edges of membrane to prevent any leakage of feed or strip solution to the outside of membrane cell. Then the membrane cell was clamped with the four stainless bolts fastened on the two Teflon blocks. The feed and strip solutions were pumped into membrane cell with recycled operation. Figure 1 shows the schematic diagram of experimental set up.

In the study, aqueous phenol and NaOH solutions were used as the feed and strip solutions respectively. The membrane phase consists of kerosene or mixture of kerosene-palm oil. The experiments were carried out at room temperature for 5 hours. The feed phase and strip phase were 400 mL of 500 ppm phenol and 400 mL of 1.0 M NaOH solutions respectively. Both feed and strip flow rates were adjusted to 150mL/min. The pH of the feed phase was monitored by adding sulphuric acid drop wise. An overview of the experimental series is given in Table 1.

Table 1 Experimental parameter

Parameter	Range of study
pH of feed phase	pH 4, 5, 9
Flow rate of feed phase (ml/min)	50, 100, 150
Concentration of stripping agent, NaOH (M)	0.2, 0.5, 0.8,1.0
Kerosene : Palm oil ratio	0:100,25:75:50:50, 75:25, 100:0

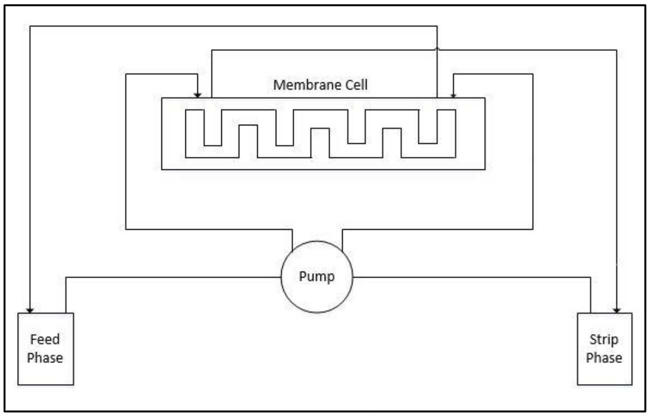


Figure 1 Schematic diagram of experimental set up

2.2.3 Analytical Procedure and Determination of Extraction Efficiency

A UV-vis spectrophotometer (Jenway 7305) was used to measure the concentration of phenol in the samples. The concentrations of phenol in 10mL samples were determined by measuring the absorption at 270nm wavelengths [8] and substitute the absorption values into the equation obtained from the calibration curve.

The equation used to calculate the extraction efficiency of phenol was given below:

$$\text{Extraction efficiency, } E\,(\%) = 100\,(C_0 - C_t)/\,C_0 \qquad (1)$$

Where, C_0 is the initial concentration of phenol in feed phase and C_t is the instantaneous concentration of phenol in feed phase.

■3.0 RESULTS AND DISCUSSIONS

3.1 Phenol Extraction Mechanism in Supported Liquid Membrane

The diffusion of phenol through the membrane is a simple permeation. The membrane was impregnated with kerosene as solvent. In this mechanism, the transported phenol molecule diffuse in the liquid membrane phase and stripped out to the strip phase due to the different concentration gradient between two phases and its solubility in kerosene. In the recovery stage, the extracted phenol recovers from the organic solvent by aqueous NaOH solution according to the following reaction which is an irreversible and instantaneous reaction [11].

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O \qquad (2)$$

If palm oil is used as liquid membrane, the reaction of phenol takes place with triglycerides present in the membrane leading to the formation of phenol-triglyceride complex by hydrogen bonding or intermolecular interactions between them. The phenol-triglyceride complex reacts with the aqueous sodium hydroxide solution leading to the formation of sodium phenolate and triglyceride molecules return back to the liquid membrane to form complex with incoming phenol.

3.2 Phenol Extraction

3.2.1 Effect of Feed pH

The effect of feed pH on the extraction of phenol was studied at three different pH values that are 4, 5 and 9. The results are shown in Figure 2.

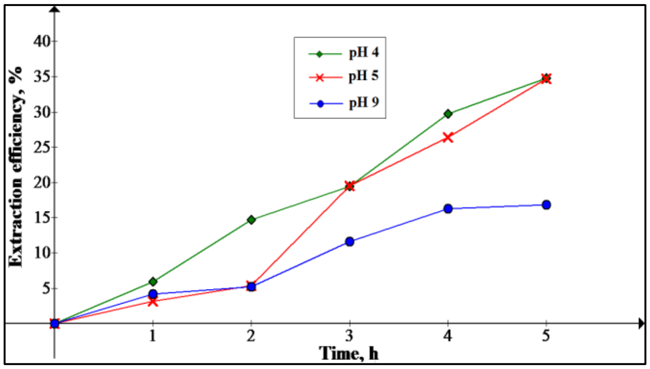


Figure 2 Effect of feed phase pH on phenol extraction (Experimental conditions: feed flow rate = 150 ml/min; strip phase concentration = 1.0 M NaOH).

The feed phase pH substantially influences the extraction and the efficiency of phenol removal. It was shown that at pH 4, the maximum extraction of phenol from feed phase had achieved with the percentage of 35%. The initial pH of phenol was adjusted to 4 in order to exist in molecular state in the aqueous solution which is essential for its transportation through the membrane phase [12]. At pH higher than 4, the extraction of phenol decreases as the extent of dissociation of phenol into phenoxide increases with the increases of pH value. Hence, the phenol extraction at feed pH 9 is lower as compared to pH 4 throughout the experiment as phenol dissociate into phenoxide ion which is not favourable for the extraction process. Therefore, pH value of 4 was selected as the optimum feed phase pH for the extraction of phenol throughout the study.

3.2.2 Effect of Feed Flow Rate

The effect of feed flow rate on phenol extraction efficiency was investigated in the range from 50 to 150 mL/min. The results are shown in Figure 3. It was indicated that the feed flow rate influences the phenol extraction significantly. From the results obtained, the extraction efficiency for the feed flow rate at 50 mL/min is the lowest among the three feed flow rates used. At 50 mL/min, the extraction efficiency reached 18% after 5 hours. For the flow rate at 100 mL/min, the extraction efficiency achieved is 30% after 5 hours. The highest extraction efficiency achieved after 5 hours of phenol extraction is recorded when the flow rate was increased to 150 mL/min with the value 35%. This indicates that as the feed flow rate increases, the extraction efficiency increases. This can be explained where low feed flow rate is inadequate to reduce the thickness of boundary layer near feed-membrane interface but at the same time increase their thickness [13]. The phenol molecules experience high resistance to diffuse across the boundary layer near feed-membrane interface and thus reducing the extraction efficiency. On the other hand, enough mechanical energy supplied can help in reducing the thickness of boundary layer and thus reducing the phenol transport [14]. Therefore, the favourable feed flow rate for phenol extraction is 150 mL/min and it is fixed for the entire study.

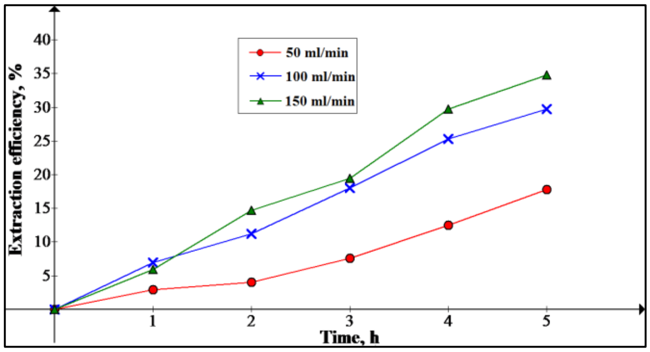


Figure 3 Effect of feed flow rate on phenol extraction (Experimental conditions : feed pH = 4; strip phase concentration = 1.0 M NaOH)

3.2.3 Effect of Stripping Agent Concentration

At the membrane strip interface, phenol gets into the strip phase by reaction with sodium hydroxide to form sodium phenolate. The sodium phenolate formed cannot permeate back to membrane phase because it is not soluble in the membrane phase. The stripping agent concentrations were set at 0.2 M, 0.5 M, 0.8 M and 1.0 M. The results are shown in Figure 4.

In the first hour, 1.0 M of NaOH records the highest extraction efficiency with the value 6%, followed by 0.8 M (5 %), 0.2 M (4%) and 0.5 M (2%). The reason that leads to this result is the amount of Na+ ions is insufficient for 0.2 M and 0.5 M of NaOH solution to strip out the phenol from the membrane phase. Therefore, the phenol molecule accumulates in the membrane support and leads to low extraction efficiency [15]. In the second hour, the extraction efficiencies for 0.2 M, 0.5 M and 0.8M NaOH solutions are almost the same with the value around 7%. However, 1.0 M NaOH solution achieves much higher extraction efficiency than the others with the value 15%. Then, when the extraction comes to the third, fourth and fifth hour, 1.0 M NaOH solution significantly achieves higher phenol extraction efficiency than other NaOH solution. The extraction efficiency achieved after 5 hours for 1.0 M NaOH solution is 35%. The results obtained in this study can be explained as higher concentration of NaOH in strip phase provides more adequate amount of Na^+ ions to strip phenol from the membrane strip interface and thus increases the extraction efficiency [16].

Therefore, the optimum NaOH concentration in the strip phase for the phenol extraction is 1.0 M and will be maintained throughout the study.

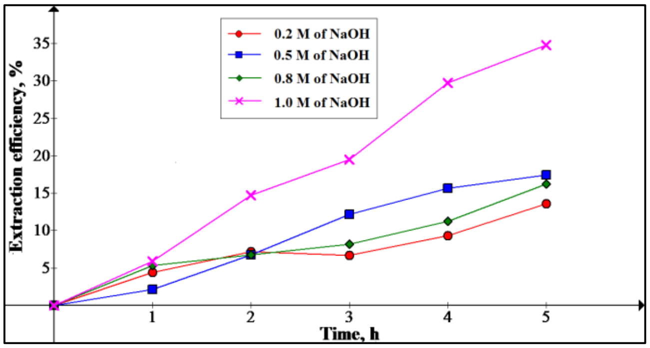


Figure 4 Effect of NaOH concentration on phenol extraction (Experimental conditions : feed pH = 4; feed flow rate = 150 mL/min)

3.2.4 Effect of Palm Oil in Liquid Membrane Organic Phase

The effect of fractions of palm oil in palm oil-kerosene mixture as liquid membrane on phenol extraction was studied by varying the fractions of palm oil at 0, 0.25, 0.5, 0.75 and 1.0. This study aims to identify the potential used of palm oil as liquid membrane. The results are shown in Figure 5. Palm oil-kerosene mixture with 50% palm oil provided the highest phenol efficiency after 5 hours with the value 43%. The diffusion coefficient linearly increases with T/η.[13] The relationship refers to the following equation:

$$D = kT/(6\pi\eta r) \tag{3}$$

where, D is the diffusion coefficient, k is the mass-transfer coefficient based on concentration, T is the temperature, η is the solvent viscosity, and r is the molecular radius.

Hence, the diffusion coefficient increases linearly with the reciprocal viscosity of the membrane solvent. Table 2 shows the respective viscosity of each palm oil-kerosene mixture with different fraction of palm oil.

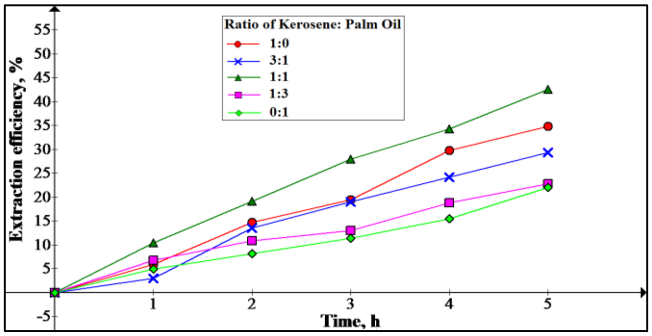


Figure 5 Effect of fraction of palm oil in palm oil-kerosene mixture on phenol extraction (Experimental conditions: feed pH = 4; feed flow rate = 150 mL/min, strip phase concentration = 1.0 M NaOH)

Table 2 Viscosity of palm oil-kerosene mixture with different fraction of palm oil

Palm Oil-Kerosene Ratio	Viscosity, cP
0:100	2.730
25:75	4.988
50:50	4.062
75:25	14.920
100:0	51.710

As the viscosity of the solvent increases, the diffusion coefficient of the membrane decreases, thus the extraction efficiency decreases. However, the mixture with palm oil-kerosene ratio of 50:50 as membrane phase has achieved higher extraction efficiency than kerosene as membrane phase although the viscosity of palm oil-kerosene mixture with palm oil-kerosene ratio 50:50 is higher than the viscosity of kerosene. This is because at the composition of 50:50, the rate of decomplexation of phenol–triglyceride complex at membrane strip phase to phenol compound significantly influences the solvent extraction kinetics. The rate of decomplexation can be rate controlling in the transport through SLMs [17]. Therefore, there are two mechanisms for the transport of phenol through equal ratio of palm oil-kerosene mixture which are chemical reaction of decomplexation and diffusion rate through the membrane. While there is only rate of film diffusion process which influences the extraction efficiency.

3.2.5 Stability Test

SLM stability is one of important factor to ensure the performance of the process. The solvent loss and membrane damage should be avoided. Figure 6 shows the stability of supported liquid membrane in terms of extraction performance to time. The stability of supported liquid membrane is examined at the optimum condition for the extraction of phenol which are feed phase at pH 4, 150 ml/min feed flowrate, 1 M NaOH in stripping phase and 50% palm oil in palm oil-kerosene mixture as membrane phase. The result shows that the phenol extraction efficiency increases steadily in the first 8 hours and reach maximum with the value 45.8%. Further increasing the time, it is expected that the membrane becomes unstable and the extraction efficiency drops. The loss of solvent from the support can be due to several factors, such as the pressure difference over the membrane, solubility of the membrane solvent in the adjacent feed and strip solutions, wetting of support pores by the aqueous phases and blockage of support pores by water or by the emulsion formation of the liquid membrane phase in water induced by lateral shear forces [18]. In short, the supported liquid membrane is stable in the first ten hours in this study.

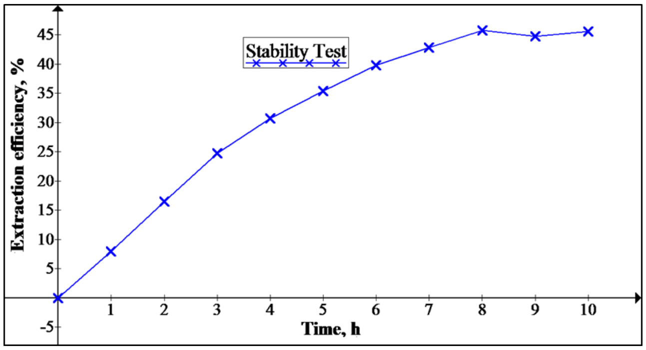


Figure 6 Stability Test (Experimental conditions : feed pH = 4; feed flow rate = 150 mL/min, strip phase concentration = 1.0 M NaOH, membrane phase = 50% palm oil, 50% kerosene)

■4.0 CONCLUSION

The extraction of phenol from phenol solution by using SLM was studied in this research. From the results obtained, it was shown that the SLM technique can achieve phenol extraction efficiency 35% at optimum condition. The optimum conditions are feed pH 4, feed flow rate 150 mL/min and 1.0 M of stripping agent concentration. It was indicated that by having 50% of palm oil and 50% of kerosene in palm oil-kerosene mixture as membrane phase, the phenol extraction performance becomes better which is around 45.8%. The stability of the SLM was also studied. It was shown that the phenol extraction efficiency achieved its maximum after 8 hours of extraction process. Thus, this process has been proven attractive and high potential for industrial used due to an excellent performance in separation and recovery of desired solute.

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