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Phenol Extraction from WasteWater Using Emulsion Liquid Membrane: Extraction, Stripping and Breakage Studies

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ABSTRACT

Emulsion Liquid Membrane (ELM) has received a lot of interest due to its ease of use and great selectivity for the desired solute. The removal of phenol from aqueous solutions using an emulsion liquid membrane (ELM) has been examined in this work. After adding span80 as a surfactant and xylene as a diluent, the emulsion formulation was completed. According to the preliminary experiment, there is no need to utilize a carrier when preparing the membrane formulation for application. Then, the resulting emulsion was disseminated in the exterior phase to obtain the desired effect. Different factors, such as internal phase concentration, surfactant concentration, homogenizer speed, and stirrer speed, were investigated to see what influence they had. The addition of 4 percent (v/v) span80, 5800 rpm homogenizer speed, and 250 rpm stirring speed resulted in a stable emulsion liquid membrane system, which was then tested for stability. The purpose of this work was to investigate the effectiveness of phenol extraction, stripping in internal phase, and membrane rupture. A concentration of 0.1M NaOH in the internal phase was used in conjunction with a stirring speed of 250 rpm, a feed phase pH of 3.0, and an initial concentration of phenol of 100 mg/L to achieve the highest extraction efficiency. In order to obtain the highest extraction efficiency, stripping efficiency, and membrane breakdown percentages possible, 6 minutes were spent in this environment achieving: 90.82 percent, 92.2 percent, and 1.45 percent, respectively.

Keywords: phenol, extraction, waste water, ELM, xylene, span80.

INTRODUCTION

The phenolic compound is used in a wide range of sectors, including pharmaceuticals. Phenol is released by a variety of sectors, including oil refineries, coal processing, coking operations, polymeric resin manufacturing, and others (Venkateswaran and Palanivelu 2006, Reis, de Freitas et al. 2007, Nosrati, Jayakumar et al. 2011). The tremendous toxicity of this substance, even at low quantities, makes it one among the most serious wastewater pollutants on the planet. Given that phenol is readily absorbed via all modalities of contact, it has the potential to produce systemic toxicity (Knop and Pilato 2013). Therefore, phenol must be eliminated from industrial effluents prior to its disposal in the wastewater system. Several approaches for phenol wastewater treatment

have been developed, including liquid-liquid extraction (LLE), steam distillation, biodegradation, adsorption, membrane separation technologies, chemical and photo-oxidation processes (Rosly, Jusoh et al. 2019). Membrane-based technology is a straightforward and cost-effective alternative to solvent extraction techniques that has gained prominence in a wide range of separation and purification processes in a variety of industries and applications. With liquid membranes, the extraction and stripping processes can be combined into a single unit, and achieve the benefits of non-equilibrium mass transfer as well as higher selectivity, higher fluxes, and less energy consumption. Fluid membranes are often classified into three types of configurations, including bulk liquid membranes (BLM), supported liquid membranes (SLM), and emulsion liquid membranes (ELM). Because of the large surface area available within the emulsion globules and internal droplets, ELM processes have great applicability for the extraction and separation of very low to high concentrations of metal ions. When compared to LLE, ELM processes use a lower volume ratio of organic phase to aqueous feed solution, allowing for extremely high mass transfer rates (Jiao, Peng et al. 2013).

Some of the benefits of emulsion liquid membranes (ELM) include a one-step extraction and stripping process, a relatively high speed of water purification, the processing of a double phase end product, and the ease with which treated water may be separated (Daraei, Zereshki et al. 2019). Surfactants are amphiphiles that have both hydrophilic and hydrophobic moieties in their structures. Surfactants are able to reduce surface and interfacial tension as well as generate emulsions as a result of this characteristic. Its wide range of functional qualities, including emulsification, foaming, wetting, cleaning, surface activity, phase separation, and decrease in crude oil viscosity, making it one of the most versatile process chemicals available on the market. The hydrophiliclipophilic balance (HLB) value is a metric used to identify the kind of emulsion being considered (e.g. oil in water or water in oil). When compared to high HLB emulsifiers, the emulsifiers with low HLB stabilize water-in-oil emulsions, whereas the emulsifiers with low HLB do the reverse (De, Malik et al. 2015). Emulsions are unstable according to the second law of thermodynamics, which states that the system will gravitate to the lowest feasible energy level if the system is allowed to continue. Normally, an emulsion would split into two stable phases: oil and water. However, this did not happen. Surface or interfacial tension is reduced as a result of the presence of certain emulsifiers in the mixture. In order to provide the consumer with a stable food emulsion that has outstanding sensory and physical attributes (van Nieuwenhuyzen and Szuhaj 1998), the food processor must first achieve this goal.

For the separation of hydrocarbons, Li devised the ELM or LSM (Yan, Othman et al. 2014), also known as liquid film separation technique, in 1968, which relies on permeation, or changes in permeability of distinct solutes under constant driving force, resulting in separation (Chakraborty, Bhattacharya et al. 2010).

For the ELM process to be successful, the membrane phase must be properly formulated, which includes the proper selection of organic phase compositions, emulsifier compositions, internal phase compositions, diluent compositions, carrier/extractant compositions, and diluent concentrations (Kumar, Thakur et al. 2019). The viscosity of diluents is regarded as one of the most essential parameters in the formulation process. Because of their low cost and low viscosity (Chiha, Hamdaoui et al. 2010), it has been discovered that both kerosene and hexane are the most extensively utilized diluents, according to the literature review. The selection of these organic phase elements has a significant impact on both the extraction efficiency (in percent) and the stability of the ELM. When droplets are created, they become thermodynamically unstable. This is mostly due to the coalescence of droplets, which may be avoided by the addition of a surfactant agent, which also assists in raising the viscosity of the organic phase (Tesch and Schubert 2002, Moyo and Tandlich 2015). Most ELM-based separation methods have relied on petroleum-based organic solvents (such as kerosene, heptane, hexane, 1-decanol, 1-octanol, chloroform, and others) as their organic phase components up to this point (Kumar, Thakur et al. 2018), with the exception of a few.

The investigation was focused on phenol extraction, stripping phenol efficiency, and membrane breaking % study without the use of any carrier. Xylene was selected as a diluent because, according to past research, there has been no study in which xylene has been employed to extract phenol from aqueous solutions. Given the high viscosity of xylene, it presents a challenge in the process of emulsion liquid membrane separation from other diluents such as kerosene, n-heptane, and other similar diluents that are distinguished by their low viscosity and high effectiveness. The results were then compared to those produced by using the emulsion liquid membranes separation approach, which was previously described (ELM).

MATERIAL AND METHOD

Material and equipment

For the manufacturing of simulated phenol wastewater as a feed phase, phenol crystals (99.5 percent purity) supplied by Alpha Chemika were utilized as the raw material. Xylene (98 percent purity) was employed as a diluent in this experiment. In this study, sodium monooleate (Span 80) was utilized for surfactant, sodium hydroxide (NaOH) solution was employed for stripping agents, and both were obtained from Merck & Co Inc. All of these reagents and solutions were applied in their unpurified state, with no additional purification required. An ultra-violet spectrophotometer (UV) (Thermo Spectronic, USA), SR30 digital homogenizer (model: 670/340 W, 10–2000 ml, 3000–27000 arpm), a digital mixer (Heidolph), a RZR 2021

digital overhead stirring system, and a hot-plate magnetic stirrer were all used in the experiment.

Phenol solution and calibration curve preparation

The phenol solution containing 100 parts per million (ppm) was made by dissolving phenol crystals in distilled water. A calibration curve for absorbance-phenol was created in order to verify the absorbance of phenol solution using different concentration samples that were known to be accurate. The detection of phenol and sodium phenolate may be noticed at an absorbance value of 270 nm (Thomas and Burgess 2017), which corresponds to the wavelength of light used. The absorbance-phenol concentration calibration curves were used to measure the concentration of phenol in the sample. Equations. (1, 2, 3) were used to calculate the % removal of phenol, the breaking of membrane, and the stripping efficiency.

extraction (%) =
$$\frac{\text{Ceo} - \text{Ce}}{\text{Ceo}} \times 100$$
 (1)

breakage (%) =
$$\frac{\text{Vei} - \text{Vef}}{\text{Vei}} \times 100$$
 (2)

stripping (%) =
$$\frac{\text{Ci Vi}}{\text{Ceo Veo} - \text{CeVe}} \times 100$$
 (3)

Emulsion liquid membrane preparation

The membrane phase was prepared by dissolving a suitable quantity of span80 as a surfactant in a specific volume of xylene as a dilute (without the use of a carrier) and swirling it for a few minutes with a magnetic stirrer to ensure that it is homogenized. In the same way that phenol solution was prepared, the NaOH solution was prepared by dissolving NaOH solids in distilled water, taking an appropriate volume of alkaline solution and adding it dropwise to the membrane phase while the system was homogenized using a high-speed homogenizer to achieve acceptable emulsification time and speed.

Phenol extraction by emulsion liquid membrane process

The produced ELM was distributed into phenol aqueous solution (external phase) in a beaker at a ratio of 50:250 by volume of membrane to external phase. For 10 minutes contact time, the mixture was mixed using a digital mixer set at a low rotational speed of 250 rpm on a low setting. A 1 mL sample of phenol aqueous solution was obtained and the phenol content was determined using a UV-Spectrophotometer. A number of variables were investigated, including the effect of the carrier, the effect of the internal phase concentration, the speed of the homogenizer, effect of surfactant concentration and effect of stirring speed. The full list of variables is presented in Table 1, and a schematic diagram of the emulsion liquid membrane process is shown in Figure 1.

RESULTS AND DISCUSSION

The impact of the carrier

When it comes to transporting species through liquid membranes, carriers (extractants) play a critical role (Mohammed and Hussein 2018). Once at the feed-membrane interface, they first form a complex with the species, and when this complex is destroyed at the membrane-receiving interface, the carrier returns to the feed-membrane interface to establish a new complex. The instability of the membrane phase is also significantly affected by this factor. The concentrations of trioctylamine (TOA) were varied from 0 percent (without carrier) and 4 percent (v/v) (with carrier) to investigate the influence of trioctylamine (TOA) on phenol extraction efficiency in the presence of a carrier.

Table 1. Operating variable in EML system

Variable	Range
TOA concentration %(v/v)	0, 4
NaOH concentration (M)	0.05, 0.1, 0.2, 0.3
Homogenizer speed (rpm)	3000, 5800, 12700
Span80 concentration % (v/v)	2, 4, 6, 8
Stirrer speed (rpm)	150, 250, 350



Figure 1. Schematic diagram of ELM process



Figure 2. Effect of carrier on phenol removal efficiency (phenol concentration =100 ppm, external phase pH = 9.5, homogenizer speed:12700 rpm, span80 concentration: 6%(v/v), ET: 7 min., stirrer speed: 250 rpm, 0.05M NaOH)

As a result of forming complexes with phenol, TOA was predicted to increase the extraction rate of phenol by allowing more phenol to pass through the solvent/liquid membrane. The influence of the carrier on the efficacy of phenol removal was indicated in Figure 2. This figure clearly demonstrates that the presence of a carrier in membrane components has no significant effect on the behavior of the two curves for the first ten minutes of contact time. After this period, the behavior of the two curves changes, with the membrane without a carrier showing greater efficiency than the membrane with a carrier. As a result, there is no need to include a carrier in the membrane components, which is considered an environmentally friendly method.

Effect of internal phase concentration

In the internal phase, NaOH converts phenol into sodium phenolate, causing it to become trapped in the internal phase. It is possible that a high concentration of NaOH will be preferred throughout the extraction operation as a result of this. Raising the concentration of NaOH, on the other hand, creates an osmotic pressure between the internal and external phases, which raises the difference in electrolyte concentrations between the two phases. The water from the external phase is carried to the interior phase, causing the emulsion to expand and break apart, lowering the efficacy of the emulsion in terms of removal. Furthermore, an increase in NaOH may cause the surfactant to hydrolyze, resulting in a reduction in emulsion stability. As a result, it is necessary to determine the optimal concentration of NaOH. By employing xylene as a diluent and span 80 as a surfactant, the impact of NaOH concentration on extraction, stripping efficiency of phenol, and breakage percentage of membrane in ELM was demonstrated in Figure 3.

In the experiments where the sodium hydroxide concentration was raised from 0.05 M to 0.1M, the removal and stripping efficiencies raised from 78.4% to 83.24%, and from 67.42 to 85.76 percent, respectively, while the breakage percentage reduced from 7.4% to 2.3 percent. However, when the concentration of NaOH raised from 0.1 to 0.2 M, the removal and stripping efficiencies decreased to 81.21% and 77.23 percent, respectively, and the breakage percentage increased to 3.3%. Because of the reasons explained above, when the concentration of NaOH is increased to 0.3M, the same response happens. For the extraction of bisphenol A and phenol, (Dâas and Hamdaoui 2010) and (Mortaheb, Amini et al. 2008) obtained findings that were nearly identical to one another. According to these findings, the 0.1M NaOH concentration was determined to be the ideal NaOH concentration for additional studies to be conducted.



Figure 3. Effect of NaOH concentration on the extraction, stripping and breakage of membrane (external phase pH=3.5, homogenizer speed: 12700 rpm, span80 concentration: 4%(v/v), ET: 7 min., stirrer speed: 250 rpm)

Effect of homogenizer speed

The speed at which the homogenizer spins is one of the most important parameters influencing emulsion stability and the whole extraction process. Emulsion stability is an essential criterion in the ELM process since a lower stability leads the emulsion to collapse, while a very high stability makes it impossible for the emulsion to break down mechanically. As a result of these considerations, the homogenizing speed of the emulsion component was evaluated in the range of 3000 to 12700 rpm. In the experiments, Span 80 (4 percent by volume) was used with xylene as a membrane, with a of 0.1 M NaOH concentration as internal phase, a volume of internal phase: volume of organic phase ratio of 1:1, an emulsification duration of 7 minutes, a stirrer speed of 250 rpm, and various homogenizer speeds. Figure (4) depicts the influence of homogenizer speed on membrane stability, extraction efficiency, and stripping efficiency. On the basis of this figure, it

can be observed that the breakage rate reduced from (4.67% to 2.43%) with increasing homogenizer speed from 3000–5800 rpm, and then climbed slightly to 2.87 percent when the homogenizer speed was increased to 12700 rpm. Recent experiments have revealed that the results of prior studies, which demonstrated that emulsion stability increased along with homogenizer speed up to a certain point but declined beyond that point (Othman, Yi et al. 2013), are consistent with the current findings. In addition, the influence of homogenizer speed on extraction and stripping efficiency was depicted in Figure 4.

When the homogenizer speed was increased from 3000 to 5800 rpm, the extraction and stripping efficiencies climbed from 79.43 percent to 84.63 percent and from 62.23 percent to 82.65 percent, respectively, while the extraction efficiency increased from 79.43 percent to 84.63 percent. Increased homogenizer speed to 12700 rpm results in a slightly reduced phenol removal



Figure 4. Effect of homogenizer speed on the extraction, stripping and breakage of membrane (phenol concentration =100ppm, external phase pH=3.5, span80 concentration: 4%(v/v), ET: 7 min., stirrer speed: 250 rpm, 0.1M NaOH).

efficiency and stripping efficiency to 83.2 percent and 78.54 percent, respectively, as a result of the increased homogenizer speed. Effective emulsification occurs as the internal phase degrades into the membrane phase, resulting in great dispersion at the membrane interface. When agitation intensity is high, internal phase droplets are smaller, resulting in a greater area for permeation and, as a result, a higher proportion of recovered material.

Effect of surfactant concentration

Incorporated into the liquid membrane as an emulsifier, surfactant functioned as a protective barrier between the outer and interior phases, preventing emulsion breakup and allowing the membrane to function properly. By enhancing the stability of the liquid membrane, raising the concentration of the surfactant will result in an increase in the droplet size of the emulsion. Numerous studies (Chung 2003, Park, Skelland et al. 2006) have found this to be true. According to (Lin, Pan et al. 2002), increasing the concentration of surfactant lowered the surface tension of the membrane, resulting in smaller globules and thereby increasing the contact area (Mortaheb, Amini et al. 2008). Although a high surfactant concentration resulted in a low percentage removal of phenol in this experiment, it is possible that this was due to an increase in membrane viscosity and thickness (Park and Chung 2003, Mortaheb, Amini et al. 2008) as a result of the high surfactant concentrations used in this investigation. When the surfactant concentration was increased above its optimal concentration of 4 percent(v/v), the resistance to phenol penetration into the internal phase increased, which resulted in a reduction in the proportion of phenol removed from the external phase. According to Figure 5, which depicts the relationship between phenol extraction and contact duration, it was found that the optimal span80 concentration was 4 percent (v/v) at a contact period of 6 minutes. The greatest removal efficiency of phenol attained was 90.82 percent, with stripping efficiency of 92.21 percent and the lowest membrane breakage of 1.45 percent at a 4 percent (v/v) span 80 concentration as shown in Figure 6.



Figure 5. Effect of span80 concentration on the phenol extraction with time (external phase pH=3.5, homogenizer speed:5800 rpm, ET: 7 min., stirrer speed: 250 rpm, 0.1M NaOH)



Figure 6. Effect of span 80 concentration on the efficiency of extraction, stripping and breakage of membrane (external phase pH=3.5, homogenizer speed:5800 rpm, ET: 7 min., stirrer speed: 250 rpm, 0.1M NaOH)



Figure 7. Effect of stirring speed on the extraction, stripping and breakage of membrane (phenol concentration=100ppm, external phase pH=3.5, homogenizer speed:5800 rpm, span80 concentration: 4%(v/v), ET: 7 min., 0.1M NaOH)

Effect of stirrer speed

In addition, higher stirring rates result in the development of smaller-sized globules, which increases the amount of interfacial area that exists between the continuous and membrane phases, ultimately boosting the rates of mass transfer between both. Swelling and globule rupture can occur as a result of raising the stirring speed above a specific threshold speed. Figure 7 depicts the influence of stirring speed on the removal of phenol by ELM, stripping efficiency, and membrane breakage. a slower stirring speed (150 rpm), the extraction efficiency was lower because larger emulsion globules were formed, reducing the surface area available for mass transfer and lowering the extraction efficiency. When the stirring speed is increased from 150 to 250 rpm, the shear force that acts on the emulsion globules increases, resulting in the globule becoming smaller. As a result of increasing the agitation speed, the area available for mass transfer increases, while the extraction and stripping efficiencies increase from 84 to 91.2 percent and from 66 to 92.51 percent, respectively. In addition, the proportion of membrane breaking was reduced from 3.82 percent to 1.46 percent, a significant improvement. Moreover, it was discovered that raising the stirring speed from 250 to 350 rpm causes the removal effectiveness of phenol to be reduced, as depicted in the following figure. However, an increase in stirring speed over a critical number not only results in a drop in extraction efficiency, but it also has an adverse effect on the stability of the emulsion and causes it to become unstable.

CONCLUSIONS

The study on the percentage removal of phenol, stripping in internal phase and emulsion leakage

for ELM was conducted experimentally and many facts were concluded. Using carrier (TOA) in membrane formulation has no significant effect on the phenol removal efficiency. Emulsion efficiency is strongly influenced by internal phase concentration, homogenizer speed, surfactant concentration and stirrer speed. Optimum membrane properties can yield a stable ELM with a good percentage removal of phenol of 90.82% and the stripping phenol efficiency in internal phase is 92.21% with membrane leakage can be maintained at 1.45%. The parameters for optimum membrane are 0.1M NaOH, 5800 rpm homogenizer speed, 250 rpm stirring speed and 4%(v/v) span 80 concentration without using carrier. For all parameters, the breakage of the membrane decreased when the extraction and stripping efficiency increased. Although of the high viscosity of xylene, it showed a good diluent in emulsion liquid membrane process.

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