Carrier Comparative Study of Phenol Removal from Aqueous Solution using Aliquate-336 and Isodecanol through Liquid Emulsion Membrane

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***Abstract*:** *This study consists of removal of phenol from aqueous solution using emulsion liquid membrane (ELM). ELM proves to be a promising alternative to the other separation processes, demonstrating a wide range of selectivity, effectively and operation expenses. Surfactant type and its concentration play a major and promising role towards productivity of the process. In this study Span 80 (sorbitan monooleate) was chosen as an emulsifying agent, Aliquat-336 and isodecanol taken as an extractant. In this study kerosene was chosen as a diluent. To determine the optimum operating conditions various parameters such as volume ratio of external to membrane phase, membrane to internal phase volume ratio, surfactant concentration, carrier concentration, change in solute concentration, agitation speed, time of extraction has been investigated. An optimum condition was found out and about 89.52% removal of phenol has been recorded. The percentage removal changes with respect to time and it was seen that percentage removal tends to remain constant after some period of time. The experiment was also carried out in two stages taking into account of higher concentration of phenol of around 1000ppm to a lower concentration of around 100 ppm. It was observed that the final concentration of phenol after two stage process had been reduced to around 7-10 ppm*

Keywords: *Phenol, emulsion liquid membrane, Aliquat-336, Isodecanol, surfactant, Span-80*

1. Introduction

Phenol is a toxic substance which is normally present in the waste water generated from refineries, pharmaceuticals and petrochemical industries, which in small quantities is toxic to living organisms. Various other sources of phenol includes leather and textile industry, paper and pulp industry, resin and plastic industries and agro-operation industries [1]. Various methods such as oxidation, adsorption, membrane process, enzymatic treatment has been adopted for separation of phenol from waste water. Chemical oxidation is one of the destructive way of removal of phenol by using an oxidizing agent. Chlorine dioxide, ferrate [Fe (VI)], permanganate [Mn (VII)] etc. are some of the widely used chemicals used for oxidative treatment. Ferrate and permanganate are the most widely used chemicals because of their high reduction potential. Ferrate reduces to ferrous hydroxide which coagulates leading to easy removal. Permanganate was found to be stable and easy to handle [2]. Jiang et al [3] studied the formation of brominated phenol using Mn (VII) for the treatment of waste water containing bis-phenol. Du et al [4] has observed that a second order rate constant follows with the formation of products by the mechanism described by them. for chlorophenols. Electrochemical oxidation consist of direct and indirect process for removal of aqueous phenol without the need of any reagents. Direct oxidation is the one in which the pollutant is made to adsorbed on the surface of the anode surface. Indirect oxidation consists of removal using by a redox reagent for the transfer of ions between electrode and pollutant [5]. Use of chemical modification of activated carbon, impregnation of nanoparticles, lignocellulose etc. were used in the research study of pollutants removal from waste water by adsorption processes [6].

ELM process started with the possibility of finding out a technique which could provide an economic way of separating organics from linear paraffins. In 1974, Cahn and Li, who has first demonstrated the process [7]. Because of its wide range of advantages, it has widely been used for separation of metal ions, dyes from effluents, separation of hydrocarbons etc [8].

The ELM process first consists of preparation of an emulsion phase between two immiscible phase, the membrane phase and the internal phase. Membrane phase is carried out with the help of a surfactant, a carrier and a diluent. Then the emulsion phase is dispersed in the external phase and a mild agitation is given. As the two phase mixes, it either results into w/o/w or o/w/o emulsion. As the emulsion phase is dispersed in the external phase, tiny globules are formed which remains stable and does not disintegrate when agitation is carried out [9]. The globules coalesce with each other to form the membrane for the effective mass transfer to the internal stripping phase. After the agitation is done, it is sent to a separating column where the pure water free from impure solute separates out. The impure solute permeates through the membrane phase and enters into the internal phase and forms complexes. The complex formed does not diffuses back into the bulk system. The two phases separates out and the solvent free from impure solute is obtained in the bottom. The upper emulsion phase can be demulsified and can be reused further. The diffusion goes on until there is a driving force to carry forward the process and provided solubility of solute in the liquid membrane phase. The process is also possible in a batch and continuous process. Various other parameters such as external to membrane phase ratio, membrane to internal phase ratio, concentration of surfactant, carrier concentration, agitator speed plays an important role in the process.

2. Experimental Procedure

The feed solution of phenol was prepared by dissolving phenol crystals into distilled water to obtain stock solution of 1000 ppm. Membrane phase consists of diluent (Kerosene), emulsifier (surfactant) and carrier (Aliquat-336 or Isodecanol). All the constituents were taken in predetermined amount and mixed in homogenizer for 3 minutes to get membrane phase. NaOH pellets were dissolved into distilled water to obtain 2 M solution for stock. Membrane phase and stripping phase were taken in predetermined volume ratio. They were mixed in IKA ES-ULTRA-HB18 homogenizer at 15000 rpm for 15 minutes to get milky white emulsion liquid. The stability of emulsion varies as rpm and emulsification time is varied. Stability of emulsion depends upon NaOH concentration, surfactant, and carrier concentration as well as membrane to internal phase ratio also. Prepared emulsion was dispersed into external phase (phenol solution) and stirred at 300 rpm to achieve proper dispersion of emulsion globules in phenol solution. Solution from extraction cell is taken in to separating funnel to separate emulsion from external solution. After 1-2 min, samples were collected from bottom of the separating funnel to examine remaining phenol concentration by UV spectrophotometer at wavelength of 270 nm in UV region [10].

3. Results and Discussions

3.1. Effect of External to Membrane phase ratio

The effect of external to membrane phase ratio was examined for the removal of phenol is illustrated in Figure 1. At lower ratios, coalescence of emulsion globules tends to reduce mass transfer surface area [11]. As the ratio was increased, a gradual increase in removal was observed because of good dispersion of emulsion phase into external phase. Globules formed at external to membrane phase ratio of 4:1 were thoroughly dispersed and provided more surface area for mass transfer [12], thus increasing the permeation flux of phenol into membrane. Result of that, it showed highest percentage of removal of phenol. But, at ratios above this despite good dispersion, removal was reduced due to comparatively lower membrane surface area per total external phase volume [13].

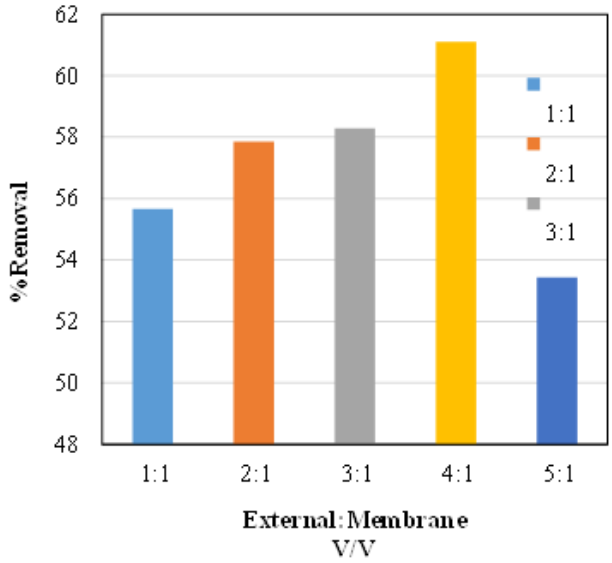


Fig. 1: Effect of External to Membrane Phase Ratio on Percentage Phenol Removal

3.2. Effect of Membrane to Internal phase ratio

To examine the effect of membrane to internal phase different ratios has been varied as shown in the Figure 2. The percentage removal of phenol was continuously increased up to the ratio of 2:1. At ratio emulsion formed was comparatively stable thus resulting in highest removal of phenol was observed around 70%. Above ratio of 2:1 removal drastically reduces as emulsion becomes extremely dilute and less effective, possible reason can be increased membrane thickness that hinders phenol transfer through the membrane [14]. Although, simultaneously at higher membrane to internal phase ratio less amount of stripping phase is available resulting in reduces the stripping efficiency of phenol. No separation was fund at ratio 5:1.

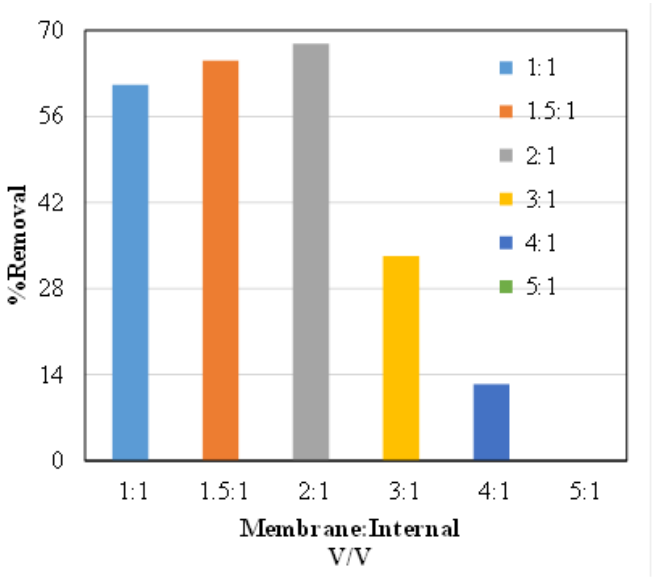


Fig. 2: Effect of Membrane to Internal Phase Ratio on percentage Removal

3.3. Effect of carrier concentration

The effect of two different carriers, aliquat-336 and Isodecanol has been observed on percentage removal of phenol as shown in the Figure 3. At higher carrier concentrations, the formed emulsion was unstable because carrier molecule changes emulsion properties by making reverse emulsion [14]. As increases the carrier concentration (>3% v/v) leads to emulsion swelling which led to emulsion rupture. The effect of carriers

concentration were observed upto 2%. Aliquat-336 significantly reduces level of removal in comparison to Isodecanol. It is evident that complex 3D structure of Aliquat-336 creates hindrance in permeation of phenol instead of supporting phenol molecules as carrier, whereas Isodecanol tends to carry phenol through the membrane. Since, Isodecanol and phenol have same functional groups, it attaches to phenol by hydrogen bonding and thus helping the smaller molecules of phenol to permeate through the membrane without any restriction in mass transfer.

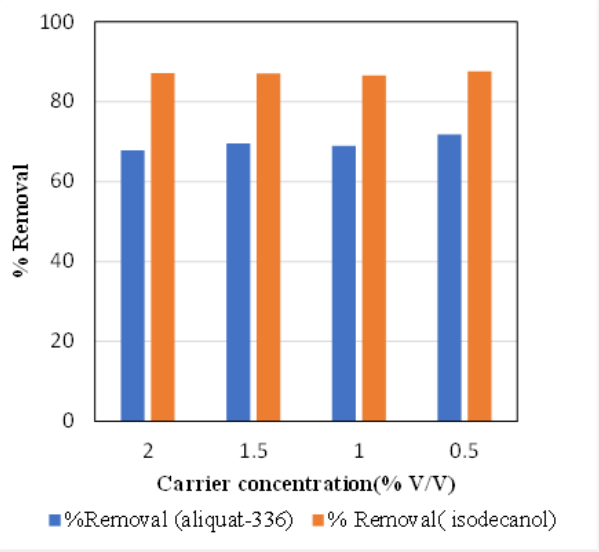


Fig. 3: Effect of carrier concentration on Phenol Removal

3.4. Effect of surfactant concentration

Surfactant is added to act as an emulsifier. It creates a barrier between external and membrane phase to stabilize W/O/W emulsion system. Increase in surfactant concentration stabilizes emulsion and provides less amount of leakage [15]. In this study, a surfactant concentration of 2% showed the highest removal of around 90% as illustrated in the Figure 4. However, at the lower concentration of surfactant, emulsion formed was highly unstable resulting in lowest removal. It was also observed that as surfactant concentration was increased, removal of phenol decreased due to unstable emulsion. The possible reason for this could be the hindrance created by surfactant molecules for mass transfer and increment in emulsion viscosity & thickness [16].

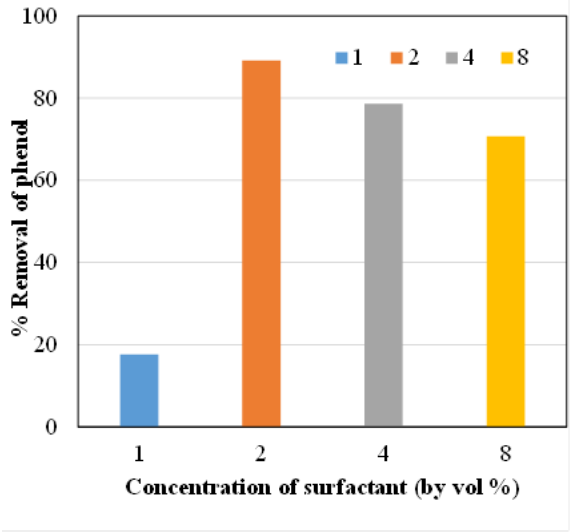


Fig. 4: Effect of surfactant concentration on percentage removal

3.5. Effect of Change in NaOH concentration

Effect of NaOH concentration as internal phase is illustrated in figure 5. Increasing the molarity of NaOH resulted in the reduction of removal of phenol. At higher NaOH concentration (>0.5 M) elevated pH in internal phase would create an osmotic swelling because high pH difference between external and membrane phase tends to form less stable emulsion leading to early emulsion breakage during extraction [17]. In this study, 0.5 M NaOH concentration resulted in stable emulsion, thus yielding highest removal of phenol. 0.5 M NaOH was set as an optimum stripping phase concentration.

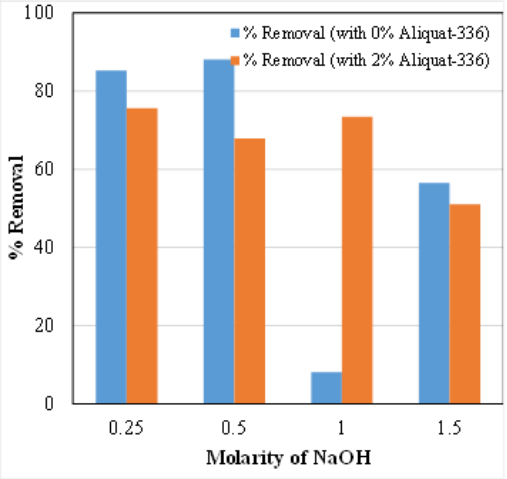


Fig. 5: Effect of NaOH concentration on percentage removal

3.6. Effect of agitator speed in extraction cell

Figure 6 illustrates the percentage removal of phenol for different agitator speeds. It was observed that the percentage removal has been increased at high agitation speed. At lower speed, agitator cannot disperse emulsion properly into external phase. On elevated agitator speeds upto 300 rpm higher removal was obtained. At this speed dispersion was good, stable, and smaller globules were formed that resulted in more surface area. But at very high speed (> 370 rpm) emulsion and globules breaks due to high shear. Thus, 300 rpm was used as optimum agitator speed.

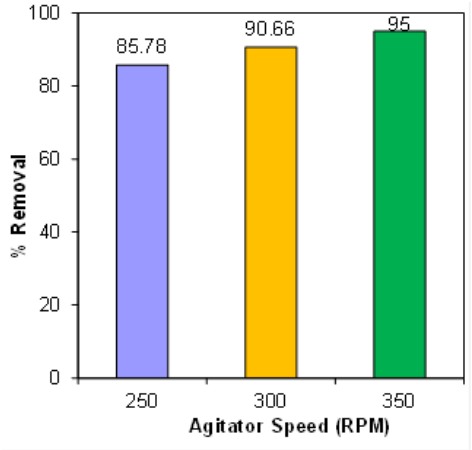


Fig. 6: Effect of agitator speed on % removal

3.7. Double stage removal of phenol at different phenol concentrations in External phase (Feed Phase) solution

In this study, it was observed that a good amount of phenol was extracted from external phase containing higher concentrations of phenol. External phase was treated in two stages to achieve lowest concentration level of phenol in water. Figure 7 illustrates the analysis of different phenol concentration. It was observed that in the

first stage the concentration of phenol was brought down to around 15ppm (on average) while after the second stage process the phenol concentration was brought down to 8ppm (on average).

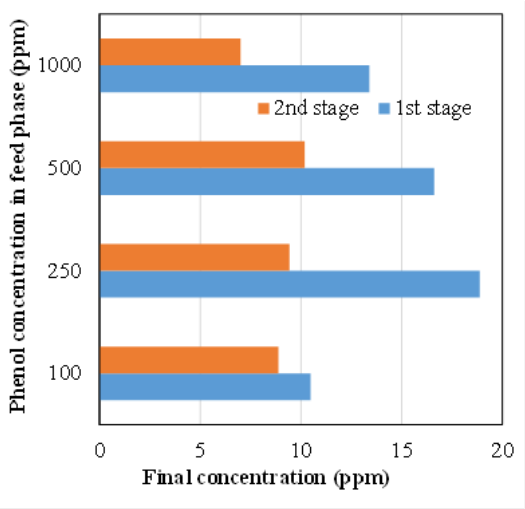
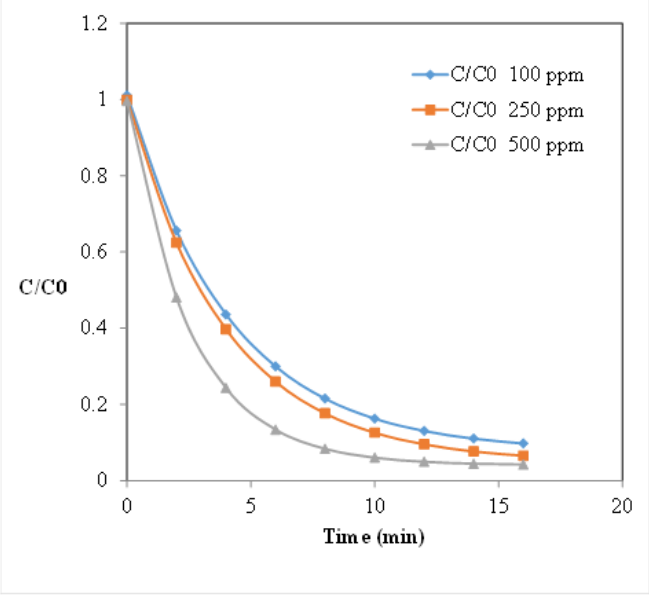


Fig. 7: Removal for higher external phase concentration

3.8. Time study for removal

Figure 8 shows variation of fractional removal of phenol from external solution at different time intervals. Samples were collected from extraction cell at 2 minute interval and examined in spectrophotometer to calculate final Phenol concentrations. The graph shows that most of the removal takes place in initial 10 minutes only and removal becomes constant after it. Initially, high rate of removal is seen because of higher concentration difference of phenol between external and internal phase [18]. But as concentration difference decreases with time, removal tends to decrease and eventually becomes constant. Similarly, at different feed concentration solutions was examined and observed the same trend for removal of phenol from the aqueous solution.



4. Conclusion

Removal of phenol using emulsion liquid membrane was studied at different parameter viz external to membrane phase ratio, membrane to internal phase ratio, carrier concentration, NaOH stripping phase

concentration and agitator speed. The Emulsion Liquid membrane process was thoroughly studied to obtain optimum parameters for highest removal of phenol by this process. The variations for all the parameters were noted and it was found that phenol removal is high at external to membrane phase ratio of 4:1 and membrane to internal phase ratio of 2:1 up to limit of 8ppm. Higher concentration of stripping phase led to instability of the emulsion and early breakage of membrane phase, thus, 0.5 M NaOH provides good removal of phenol. Optimum surfactant concentration was found to be 2% which makes stable emulsion with less mass transfer hindrance. In our study, we have found that in two stage process finally reduced amount of phenol was around 8ppm. Following table concludes different parameters tested.

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