Use Of Liquid Emulsion Membrane Technique For Extraction And Enrichment Of Phenol From Synthetic Waste Solution

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Abstract

This work studies phenol extraction and enrichment by liquid emulsion membrane from synthetic waste solution. The influence of several variables such as surfactant concentration, feed concentration, strip phase concentration, diluent variation has been analyzed. In this method, with surfactant 9 wt%, strip phase 3 wt %, kerosene as diluent has given 99.87% of extraction, 8.1enrichment of phenol. Important variables affecting liquid emulsion membrane permeation process included stability of membrane, strip phase concentration, treat ratio (strip phase: organic phase), stirring speed, diluents were systematically studied for percentage of extraction and enrichment of phenol.

1. Introduction

Phenol in wastewater generally consists of variety of hydroxyl benzenes and substituted hydroxyl benzenes. They are harmful and present in effluents of several major industries, petrochemicals synthetic resin, steel, paints, pharmaceutical, plywood and textile processing industries as well as many organic–chemical industries [1]. Discharge of phenolic wastes may cause serious repercussions when water from receiving bodies is employed in industrial or domestic applications. The limit of phenol acceptable in drinking water is 0.002 mg/l [2]; Cresols, Phenol and xylene are strong skin irritants and consumption of water containing these leads to serious pain, vomiting and capillary damage. Toxic effects are felt in the brain, lungs, kidneys, livers, pancreas and spleen. Removal of phenol and phenolic compounds from waste is, therefore of utmost importance to prevent pollution of water. In Liquid membrane, the liquid acts as a membrane. Liquid 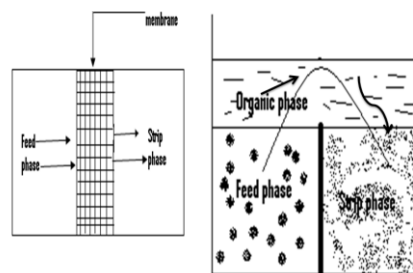membrane offers advantages of higher selectivity and surface area over conventional extraction and solid extraction membrane process. Liquid membrane can be divided into three types: Supported Liquid membrane, Bulk Liquid membrane, Liquid emulsion membrane (Liquid Surfactant membrane) [3]. In supported liquid membrane, strip phase and feed phase are separated by the hollow fiber or polymeric membrane, which contains organic phase as shown in Figure 1. The instability of liquid supported membrane has blamed a major obstacle for industrialization for the process. The solute from the feed solution diffuses through another film to the receiving solution. In the bulk liquid membrane, strip phase and feed phase are separated by partition like glass plate that does not pass anything through it and organic phase act as a membrane as shown in Figure 1.

Figure 1: Sketches for supported and Bulk liquid membrane system[4]

In its simple form, this technique can be carried out in U-tube congregation or laboratory congregation. In liquid emulsion membrane, liquid emulsion acts as a membrane hence it is called as Liquid emulsion membrane. All three types of Liquid membrane are often regarded as a combined extraction and stripping process, where extraction takes place at one side of the membrane and stripping at the other side, it looks like a separate unit, but takes place simultaneously in one

apparatus. The liquid emulsion membrane concept constitutes an elegant way of interposing an extremely thin membrane between two liquid phases without any mechanical support. Some of the problems of supported liquid membrane are insufficient area for mass transfer and instability of membrane in pores of the membrane. The liquid emulsion membrane concept overcomes this problem by generating necessary surface area without mechanical support. In case of metal separation, organic membrane phase also contains a carrier, which is often equivalent to extractant in solvent extraction. Liquid emulsion membranes are of two type i. e., water-oil-water (W-O-W) system and oil-water-oil (O-W-O) system. For W-O-W system oil phase separating two aqueous phase act as a membrane, while O-W-O system, water phase separates two oil phases [4]. In general, liquid emulsion membranes are made by forming an emulsion of two immiscible phases and dispersing emulsion into a third phase (continuous phase) as shown in Figure 2.
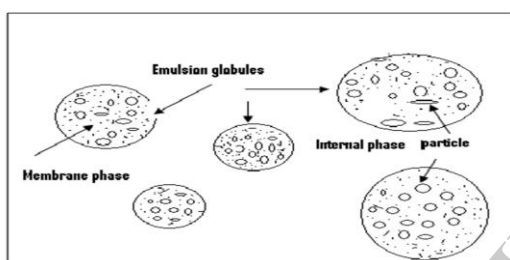

Figure 2: Typical Liquid Emulsion Membrane System [3]

Usually, encapsulated phase and continuous phase are miscible. The membrane phase must not be miscible with either phase if it is to remain stable. Therefore emulsion is of O/W type if continuous phase is oil; W/O type if continuous phase is water. To maintain integrity of emulsion during separation process, membrane phase usually contains surfactant, additives as stabilizing agent, and a base material, which is a solvent for other entire ingredient particle.

2. Materials and Methods

The apparatus used for separation of phenol in LEM system consists of glass vessel (like beaker) which was jacketed by water bath. Water-in-oil (W/O) emulsion was prepared by stirring membrane phase and internal phase at 1200 rpm for 10 minutes at 25°C water bath. Internal phase was aqueous solution of NaOH (3 wt %). Surfactant which is used for formation of emulsion SO10

(Sorbitan Monumal 80) (a branched polyolefin based surfactant) was obtained from Mohini Organics (P) Ltd., Mumbai, India. A standard Crystal Phenol having 99% purity was obtained from Thomas Baker, Mumbai. Toluene, kerosene, hexane were used as organic diluents and extractant for membrane preparation. All diluents were obtained from Thomas Baker, Mumbai. NaOH (99%), KOH (85%) were used for strip phase and were obtained from Thomas Baker, Mumbai. The membrane was prepared by sodium hydroxide solution and mixture of surfactant and kerosene in various proportions by means of mechanical stirring at 1,200-1300 rpm for 10 minutes. The W/O emulsion was poured gently into external phase containing phenol and was stirred at constant speed 400 rpm stirring with varying contact time as shown in Figure 3. After every fixed contact time, stirring was stopped and solution was allowed to settle for 2.5 min, then solution separated into two layers as: emulsion and aqueous phenol. Samples taken from aqueous phenol were analyzed by UV spectrophotometer [5].
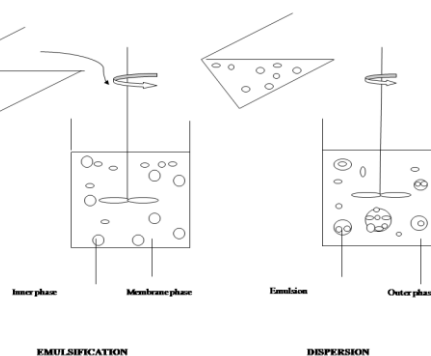

Figure 3: Schematic diagram for steps in preparation of LEM

2.1 Emulsion Preparation

Membrane phase was prepared by blending all necessary components i.e. surfactant and kerosene in advance in predetermined ratio. In experiment, NaOH, KOH etc. acts as on internal phase. Resultant organic solution is treated with known amount of internal phase. Figure 3 shows formation of emulsion, strip phase was added into organic phase continuously in a drop wise manner under intense shear by using glass impeller which is rotating at very high speed i.e.1200-1300 rpm for 8-10 minutes, this results in milky, W/O emulsion.

2.2 Mass Transfer and Separation

Freshly prepared W/O emulsion was poured and dispersed in a baffled containing vessel, measured volume of feed solution in (emulsion: feed=1:5). Stirring Speed during extraction process kept at 400 rpm. The entire LEM process is describe in Figure 4 (Pranshant S. Kulkarni et al., 2002).It is assumed that mass transfer takes place only when stirring of two immiscible liquid is in progress. Samples were withdrawn with frequent intervals of time. Separated aqueous phase and internal phase was then collected for analysis. Analysis was done by using UV spectroscopy (λmax = 269 nm).
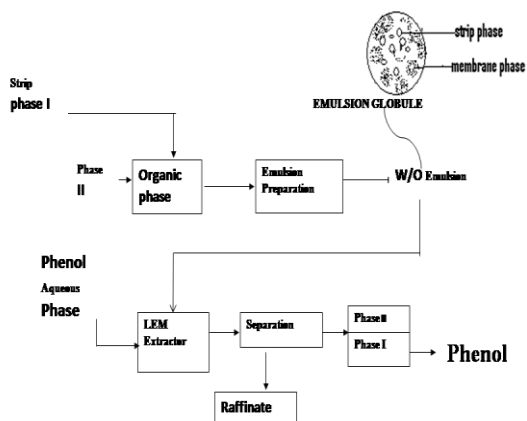

Figure 4: Schematic diagram showing experiment sequence [6]

2.3 De-emulsification

At the end of experiment, emulsion phase was separated from feed phase by using separating funnel. Emulsion is allowed to separate organic membrane phase from external aqueous phase naturally, normally this take around 15-20 minutes; separated (W/O) emulsion was de-emulsified by heating, this converted membrane phase can be recycled for further experiment. After separation, aqueous phase was collected for analysis [6,7].

2.4 Transport Mechanism

Liquid emulsion membrane system consists of three phases: (1) internal phase which is encapsulated by a membrane phase, (2) membrane phase (oil phase) which form W/O (water in oil) emulsion with internal phase, and (3) external phase (continuous phase) in which globules of emulsion are dispersed [8]. Upon dispersion of emulsion into external phase, water-in-oil-water (W/O/W) dispersion system is formed. It should be noted internal phase never directly contact external phase. Carrier is anion exchanger, when it reaches interface between external phase and membrane phase; an ion exchange reaction takes place in which carries forms complex with phenol (Ph). This complex then diffuses through membrane phase. Anion diffuses membrane phase to interface between internal strip phase and membrane phases. At this interface another ion exchange reaction takes place. Due to extremely low pOH in internal phase complex decomposed and released the Ph in internal phase and carrier is immediately protonated[6]. This process is repeated and thus the Phenol is separated and concentrated in internal phase as shown in figure 5. The equations for measurement of extent of extraction (E_x) and enrichment (E_n) had taken from [6].
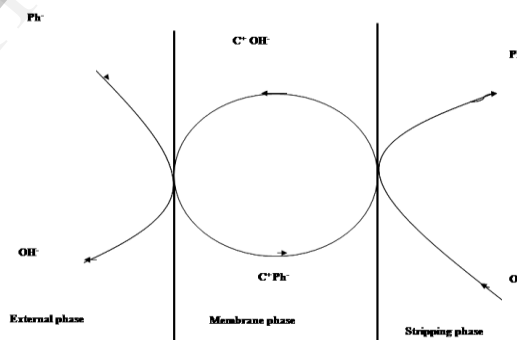

Figure 5: Schematic representation Transport Mechanism of Phenol through LEM

$$Ex = \frac{C_{ex,o} - C_{ex,t}}{C_{ex,o}} \qquad -----1$$

$$En = \frac{C_{i,t}}{C_{ex,o}} \qquad ----2$$

Where,

C_o	Initial phenol ion concentration (mg/l)
$C_{ex,o}$	Concentration of phenol ion in the external phase initially (mg/l)
$C_{ex,t}$	Concentration of phenol ion in the external phase at time t (mg/l)
$C_{i,t}$	Concentration of phenol ion in the internal phase at time t (mg/l)
Ex	Extraction
En	Enrichment

3. Results and Discussion

In this study, we attempted to find % extraction and enrichment characteristics of phenol from synthetic aqueous solution by liquid membrane, on the basis of which the optimal conditions for the best removal were pursued. There are many parameters affecting on LEM including stability of emulsion, contact time, choice of different stripping agent, strip phase concentration, effect of speed of agitation.

3.1 Stability of Emulsion

Purpose of this experiment is to choose an appropriate proportion of organic phase constituents which stabilizes the emulsion during the experiment. Stability tests were conducted by varying concentration of surfactant, Monumal 80 which differ in the amount in organic phase. Table1 shows an experimental values and observations obtained by varying concentration of the organic phase in preparation of emulsion. 10 ml of organic and 5 ml of stripping phase was mixed by stirring at very high speed (1200-1300) for 10 minutes. A white milky emulsion was formed. These tests were conducted at 25^0 C temperature. Figure 6 and 7 gives the % extraction and enrichment at different concentration of the constituents of organic phase. From the Table1 and figure 6 and figure7, it is confirmed that emulsion prepared by run no.05 having stability time 15min, which is proper stable than earlier experiment and good for LEM experiment. In this investigation % extraction 99.87 was achieved, which is relatively higher side as compared to the work done by [5,8,9,10,11,12,13,14] on weight basis such as

Monumal 80 (9%), Kerosene (91%) and stripping agent NaOH is 3wt%.
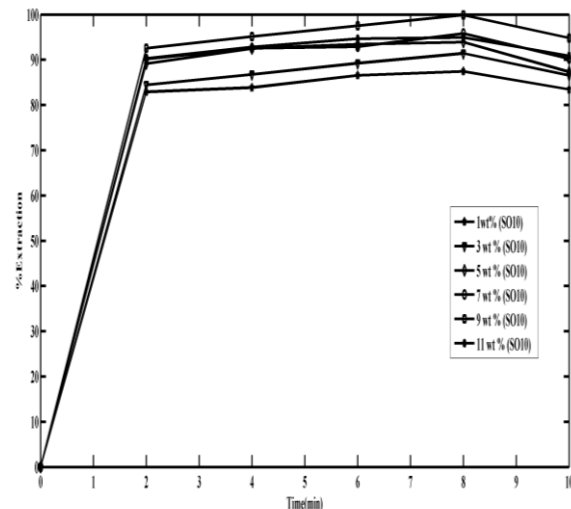

Figure 6: **Effect of surfactant concentration on % extraction** (Experimental condition used : feed phase concentration(1000 mg/l), diluent kerosene, Surfactant Monumal 80 (1wt%,3wt%,5wt%,7wt%,9wt%,11wt%),Strip phase NaOH (3wt%), Treat ratio = 0.5:1 (W/O), 1:5 (W-O/W), Temperature 25^0C, Contact time 8min, speed of agitation = 400 rpm).
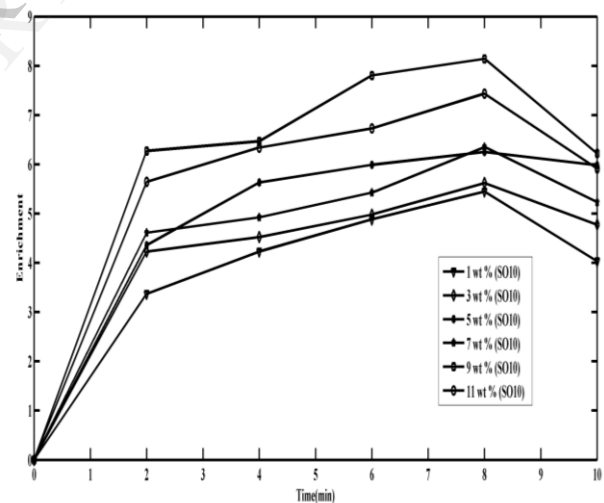

Figure 7: Effect of surfactant concentration on enrichment (Experimental condition used : feed phase concentration(1000 mg/l), diluent kerosene, Surfactant Monumal 80 (1wt%,3wt%,5wt%,7wt%,9wt%,11wt%),Strip phase NaOH (3wt%), Treat ratio = 0.5:1 (W/O), 1:5 (W-O/W), Temperature 25^0C, Contact time 8min, speed of agitation = 400 rpm).

3.2 Effect of Strip Phase Concentration

Experiments were conducted under the same conditions as mentioned previously, using stirring speed of 400 rpm and varying the concentration of the internal phase (1wt% 2wt%, 3wt% 5wt%). The effect of the internal phase concentration on emulsion stability was shown in Figure 8 and figure 9. It is observed that heights enrichment was achieved when NaOH concentration was kept 3wt %, after there was no increase in enrichment and extraction. This may be due to the reaction between internal phase and the surfactant that involves a reduction in the properties of the surfactant that consequently led to a destabilization of the emulsion. As the concentration of weak base increases, concentration difference between feed phase and strip phase increases. Due to this, phenol and water moves towards the internal phase and accumulated in the globule. As the size of globules increases, that results into emulsion breakage [12]. The maximum extraction (99.87%) and enrichment (8.141) was obtained when 3wt% NaOH was used as stripping agent. Therefore, 3wt% is chosen as the optimum concentration of weak base to be used further experiments.
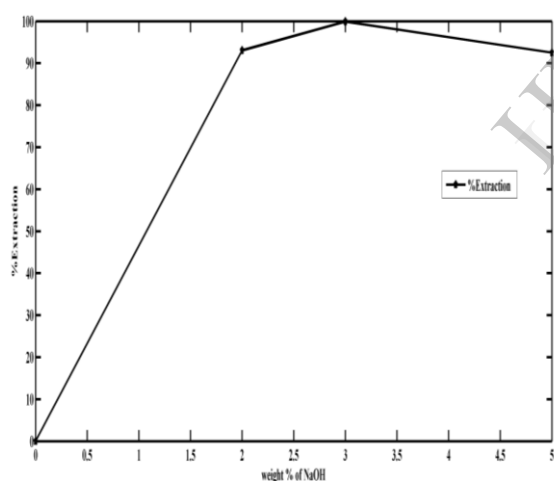

Figure 8: Effect of strip phase concentration on % extraction (Experimental condition used : feed phase concentration(1000 mg/l), diluent kerosene, Surfactant Monumal 80 (9 wt %), Strip phase NaOH (2wt%,3wt%,5wt%), Treat ratio = 0.5:1 (W/O), 1:5 (W-O/W), Temperature 25^0C, Contact time 8 min, speed of agitation = 400 rpm). Where 1,2,3 represent 2wt%,3wt%,5wt% of NaOH respectively
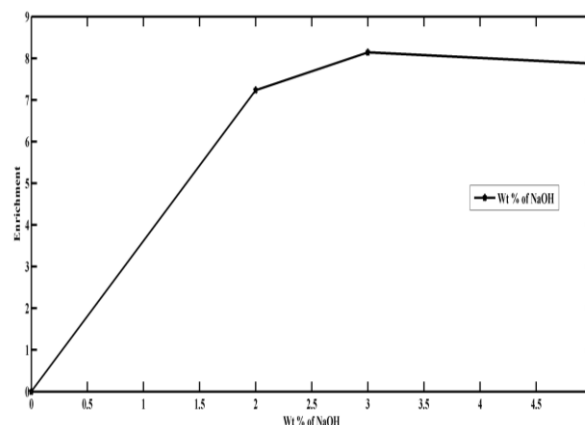

Figure 9: Effect of strip phase concentration on enrichment (Experimental condition used : feed phase concentration(1000 mg/l), diluent kerosene, Surfactant Monumal 80 (9 wt %), Strip phase NaOH (2wt%,3wt%,5wt%), Treat ratio = 0.5:1 (W/O), 1:5 (W-O/W), Temperature 25^0C, Contact time 8 min, speed of agitation = 400 rpm).

3.3 Effect of the Volume Ratio of the Sodium Hydroxide to the Surfactant Solution

The volume ratio of base as stripping agent to the surfactant solution plays an important role in LEM experiment. Hence its optimum concentration for emulsion preparation in LEM can be made on the basis of enrichment of the phenol in the internal phase. The highest extraction 99.87% and enrichment 8.14 was achieved at the volume ratio 0.5 where it is considered that the stable emulsion was formed. Effect of the volume ratio of the sodium hydroxide to the surfactant solution on enrichment and percentage of extraction as shown in figure 10 and figure 11 respectively. At the volume ratio of 1 and 1.5 the extraction decreased owing to membrane breakage caused by decrease in the membrane thickness. At the volume ratios of 0.3, the extraction decreased because of insufficient sodium hydroxide required for reaction [10]. In some part, the decreased extraction was due to increased membrane thickness causing mass transfer resistance increase [4]. Hence, the volume ratio of the sodium hydroxide to the surfactant solution used was 0.5 for further LEM experiments. For the ratio of sodium hydroxide to the surfactant solution of 0.5, highest enrichment ratio of 8.1was achieved. This figure may be relatively higher as when compared with other investigation in the past [10,11], and main improvement in enrichment may be because of lower concentration of strip phase. This has resulted in a more stable emulsion and thus less reversible transport of phenol from

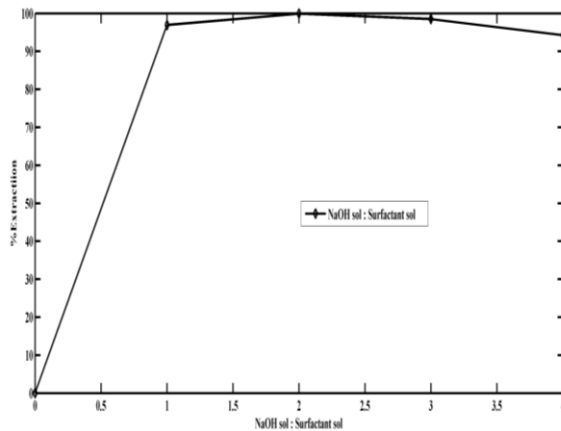emulsion phase to external phase during experimental run.

Figure 10: Effect of the volume ratio of the sodium hydroxide to the surfactant solution on % extraction (Experimental condition used : the volume ratio of the sodium hydroxide to the surfactant solution(0.3:1,0.5:1,1:1,1.5:1),feed phase concentration(1000 mg/l), diluent kerosene, Surfactant Monumal 80 (9 wt %), Strip phase NaOH (3 wt %), Treat ratio = 1:5 (W-O/W), Temperature 25^0C, Contact time 8 min, speed of agitation = 400 rpm). Where 1,2,3,4 represent the volume ratio of the sodium hydroxide to the surfactant solution 0.3:1, 0.5:1, 1:1, and 1.5:1respectively

Figure 11: Effect of the volume ratio of the sodium hydroxide to the surfactant solution on enrichment (Experimental condition used : the volume ratio of the sodium hydroxide to the surfactant solution(0.3:1,0.5:1,1:1,1.5:1), feed phase concentration(1000 mg/l), diluent kerosene,

Surfactant Monumal 80 (9 wt %), Strip phase NaOH (3 wt %), Treat ratio = 1:5 (W-O/W), Temperature 25^0C, Contact time 8 min, speed of agitation = 400 rpm).. Where 1,2,3,4 represent the volume ratio of the sodium hydroxide to the surfactant solution 0.3:1, 0.5:1, 1:1, and 1.5:1respectively.
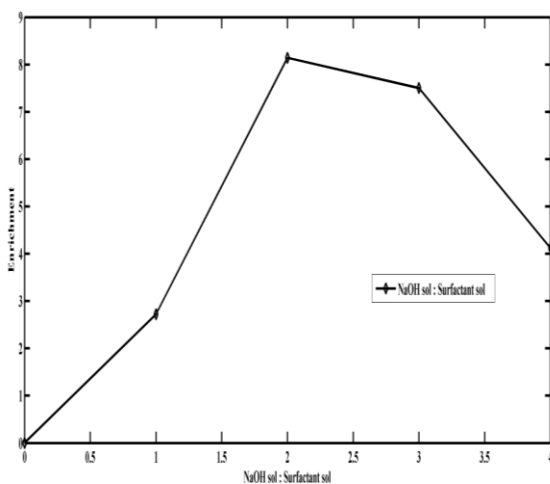
3.4 Effect of Stirring Speed

Effect of stirring speed was studied in the range of 300 to 600 rpm. Stirring speed at 400 rpm gives higher percentage of extraction and enrichment is shown in figure 12 and figure 13. When the speed of agitation is increased, the interfacial area available for mass transfer also increased. On the other hand, the break-up of the emulsion is more pronounced and leakage of the internal phase occurs, because of which percentage of extraction and enrichment is decreases. This is due to increase of the osmotic swelling of the membrane [15]. Increasing the speed of the agitation above 400 rpm not only affects the stability of the emulsion but affect the extraction adversely. By increasing the agitation speed, the sheer force, which acts on emulsion globules, is increased and this makes the globules smaller. The area for mass transfer increases but the performance of the membrane rupture and spilling the internal striping phase into the outer continuous phase increases [6]. Hence, the optimum stirring speed was decided as 400 rpm for the further experiments.
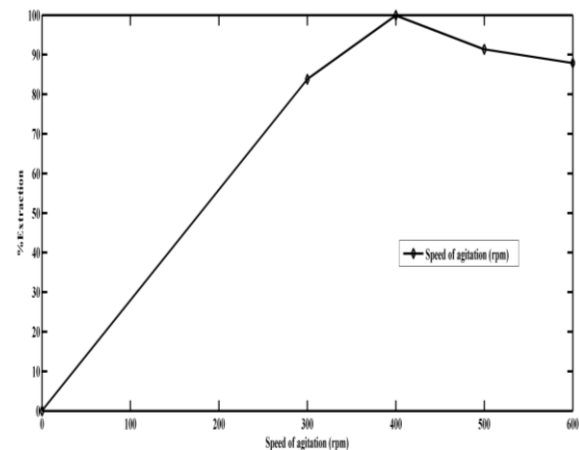

Figure 12: Effect of stirring speed on % extraction (Experimental condition used : speed of agitation (300rpm,400rpm,500rpm,600rpm),feed phase concentration(1000 mg/l), diluent kerosene, Surfactant Monumal 80 (9 wt %), Strip phase NaOH (3 wt %), Treat ratio =0.5:1(W/O), 1:5 (W-O/W), Temperature 25^0C, Contact time 8 min).

Figure 13: Effect of stirring speed on enrichment (Experimental condition used : speed of agitation **(**300rpm,400rpm,500rpm,600rpm**),**feed phase concentration**(**1000 mg/l**),** diluent kerosene, Surfactant Monumal 80 (9 wt %), Strip phase NaOH (3 wt %), Treat ratio =0.5:1(W/O), 1:5 (W-O/W), Temperature 25^{0}C, Contact time 8 min)
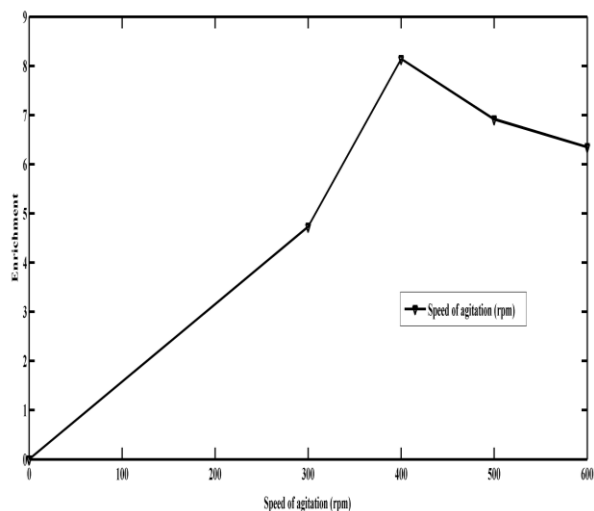
3.5 Choice of Different Diluents or Extractant

In Liquid Emulsion membrane, diluents are used to prepared membrane. They are the main part of the organic phase (emulsion). Major part of the organic phase is occupied by the diluents. The viscosity and density of the diluents are the main parameters which decide the thickness of the membrane and permeability of the membrane for the solute [14,16]. Change in organic diluent in emulsion preparation produces change in emulsion stability, percent extraction and enrichment. In this experiment of LEM diluent itself act as the extractant. Hence diluents play an important role in extraction and enrichment of phenol. Its optimum diluent concentration for emulsion preparation in LEM can be made on the basis of enrichment of the phenol in the internal phase. Different diluents were used as extractant. Figure 14 shows the choice of extractant agent on percentage extraction and Figure 15 shows that with respect to enrichment.

In present investigation, an attention has been focused on enrichment and percentage of extraction (concentration) of phenol from aqueous solution by

LEM. From result it is investigated that Toluene, kerosene, n-heptane and n-hexane were form good complex with surfactant solution, but it is clear that Kerosene gives highest extraction result than the other extractant agent and Toluene gives best enrichment. The main purpose of these experiments of LEM for phenol is best extraction than the best enrichment.   It means that Kerosene form a good complex with the phenol, which is moving very, fast from feed towered the surface of internal phase due to concentration difference and accumulated inside the internal phase [4]. Hence, it was decided that to use Kerosene as extractant agent in these experiments.
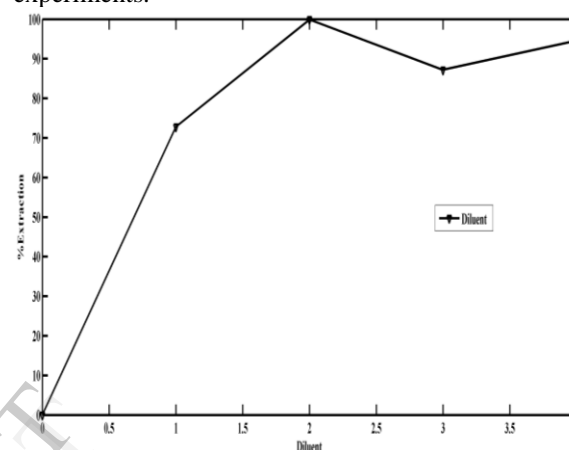

Figure 14: Choice of diluents on % extraction (Experimental condition used : diluents toluene, kerosene, n-heptane and n-hexane, feed phase concentration**(**1000 mg/l**),** Surfactant Monumal 80 (9 wt %), Strip phase NaOH (3 wt %), Treat ratio = 0.5:1 (W/O), 1:5 (W-O/W), Temperature 25^{0}C, Contact time 8 min, speed of agitation = 400 rpm). Where 1,2,3,4 represent diluents toluene, kerosene, n-heptane and n-hexane respectively.
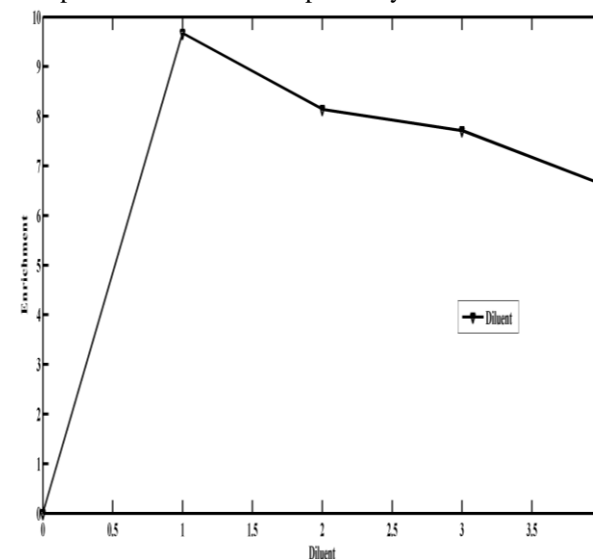

Figure 15: Choice of diluents on enrichment (Experimental condition used : diluents toluene,

kerosene, n-heptane and n-hexane, eed phase concentration(1000 mg/l)**,** Surfactant Monumal 80 (9 wt %), Strip phase NaOH (3 wt %), Treat ratio = 0.5:1 (W/O), 1:5 (W-O/W), Temperature 25^{0}C, Contact time 8 min, speed of agitation = 400 rpm). Where 1,2,3,4 represent the volume ratio of the sodium hydroxide to the surfactant solution 0.3:1, 0.5:1, 1:1, and 1.5:1respectively

Conclusions

The use of liquid emulsion membranes technology for removal of phenol is well known. An experiment for extraction and enrichment of phenol from synthetic solution was investigated in this work. Experiment were carried out for extrcation of phenol of various concentrations in synthetic solution so as to study the effect of various parameters such as surfactant, strip phase, diluents, speed of agitation, volume ratio of surfactant to strip phase. Following are the important conclusion resulted from the experimental work. The highest extraction and enrichment were achieved at the monumal 80 concentration 9.0 wt% and at 8 minutes contact time. The highest extraction and enrichment were achieved at the sodium hydroxide concentration of 3.0 wt% and 0.5 volume ratio of the internal phase to the surfactant solution. The highest extraction and enrichment were achieved at speed 400 rpm. Kerosene was found to be the best diluent amongst diluents used. In nutshell it can be said that the optimum conditions for phenol extraction and enrichment are feed phase concentration (1000 mg/l)**,** diluent kerosene, Surfactant Monumal 80 (9 wt %), Strip phase NaOH (3wt%), Treat ratio = 0.5:1 (W/O), 1:5 (W-O/W), Temperature 25^{0}C, Contact time 8 minutes, speed of agitation = 400 rpm. The extraction efficiency is 99.87% and enrichment is 8.1. For the first time we get highest extraction and enrichment at lower strip phase concentration and lower treat ratio i.e. 0.5 (W/O).

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