

Phenol Removal from Industrial Effluent Using Emulsion Liquid Membranes

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Abstract

Removal of Phenol from industrial effluents was studied using the emulsion liquid membranes. The effect of various parameters such as stirring speed, oil phase to aqueous phase ratio in emulsion, surfactant concentration, internal reactive phase concentration in the emulsion, treat ratio (ratio of emulsion to waste water phase), initial phenol concentration, effect of change in membrane phase, temperature on the rate of removal of phenol were studied. Studies pertaining to swelling of emulsions due to penetration of water into the emulsion were also conducted and it is found that this phenomenon is primarily responsible for breakage of the dispersed emulsion drops during the operation. With the help of data obtained from this work an optimal recipe for the membrane can be identified which could be conveniently used to design liquid emulsion membrane based separation systems for phenol removal from the waste water streams.

Keywords: Emulsion liquid membranes, Effluents Extraction rate and Phenol.

INTRODUCTION

Phenol is key effluent from various industries like pharmaceuticals, pesticides & paper and pulp industries, dyes manufacturing, synthetic chemicals. Phenol is a colorless-to-white/ light pink solid when pure; however the commercial product, which contains some water, is a liquid. Phenol has a distinct odor that is sickeningly sweet and tarry. Most people begin to smell phenol in air about 40 parts of phenol per billion parts of air (ppb), and begin to smell phenol in water at about 1-8 parts of phenol per million parts of water (ppm; 1 ppm is 1000 times more than 1 ppb). These levels are lower than the levels at which adverse health effects have been observed in animals that breathed air containing phenol, or that drank water containing phenol. Phenol evaporates more slowly than water, and a moderate amount can form a solution with water. Phenol can catch on fire.

Phenol has been measured in effluents (upto 53 ppm), ambient water (from 1.5 to > 100ppb), drinking water, ground water (from 1.9 to >10ppb), rain (0.075 to 1.2ppb), sediment (>10ppb) and ambient air (0.03 to 40 ppb). Occupational exposure occur through inhalation and dermal exposure; air concentrations monitored in various work places range from 0.1 to 12.5 mg/m³ (0.03 to 32 ppm). Occupational as well as consumer exposure may also occur through dermal contact with phenol or with phenol coating products [1]. Different techniques are being used to remove phenol from waste water are Emulsion liquid membranes, Adsorption, Solvent extraction, Electrochemical reduction and Biological degradation.

Severe effects of phenol exposure

As a corrosive substance, phenol denatures proteins and generally acts as a protoplasmic poison. Phenol may also cause peripheral nerve damage. Systematic poisoning can occur after inhalation, skin contact, eye contact, or indigestion. Damage to the nervous system is the primary cause of death from phenol poisoning.

Emulsion Liquid Membranes (ELM'S)

Emulsion Liquid Membranes technique is a novel separation technique and an attractive alternative keeping in view the simplicity of the operation. Emulsion Liquid Membrane was born in the laboratory of Exxon Inc. Of U.S.A. in 1968 in an attempt to search for an economic route for separation of aromatics from linear paraffin by N.N Li, who first demonstrated this process [5]. Since that time this technique has helped the fascination of many investigators in view of its simplicity, rapidity, and selectivity in the separation of various solutes in organic as well as aqueous media. It can be employed for various novel separation applications like the removal and recovery of various compounds (even from very dilute streams) like weak acids as phenol or weak bases [6-8] heavy metals [9-10] and for separation of hydrocarbons [11] etc. Emulsion liquid membranes are a boon to process industry. Using ELM technique heavy metal ions and hydrocarbons can easily be removed from waste water.

ELM is usually prepared by first forming an emulsion between two immiscible phases, one membrane phase and the other internal phase as shown in figure. Emulsifiers and additives are normally included in the membrane phase formulations to control stability and permeability and selectivity of the membrane. Then after the emulsion is dispersed in the external feed phase by gentle agitation as shown in fig I b. Hence ELM is nothing but a double emulsion either w/o/w or o/w/o. When the emulsion is dispersed by mild agitation in a continuous external feed phase, many small globules of emulsion are formed. These globules are stable and do not disintegrate, when the system is agitated. The size of globules depends on the nature and concentration of surfactants, emulsion viscosity, and mode and intensity of mixing. Usually the size of globules ranges in order of 1-2 mm in diameter. Each emulsion contains many tiny encapsulated droplets around 1µm in diameter. Figure shows typical ELM system.

The impurity solute from the external feed phase diffuses inward through the membrane phase and gets entrapped into the encapsulated drops of internal phase. At the end of the extraction, the emulsion and aqueous phase are separated and internal phase can be recovered by breaking the emulsion [12]. Large number of globules can easily be formed to produce correspondingly large membrane surface area for rapid mass transfer into the internal phase. When the emulsion is dispersed by appropriate agitation in the external feed phase having dissolved solutes, the transfer of solute occurs selectively through very thin membrane phase from the external feed phase into the internal phase, which is usually the recipient of the solute [12].

Diffusion occurs as long as there is a driving force for this diffusion, and provided that there is some solubility of the solute in the liquid membrane phase. The operation can be carried out batch wise or in a continuous manner. Laboratory tests are usually done in a batch system on account of simplicity of the method and the relatively straightforward translatability of batch to continuous data. After the desired degree of separation has been achieved, mixing is stopped and globules of emulsion quickly coalesce and form a layer of emulsion, which can be easily separated from continuous phase. With proper emulsion formulation regarding surfactants, thickening additives and complexing agents, emulsion can be prepared which are stable in the extraction process, but allow efficient demulsification of the spent emulsion, i.e. the final separation of membrane oil phase and internal aqueous phase required for the recovery of the solute. Demulsification is usually done in the electronic coalescer. Heat treatment and chemical treatment are being the other methods of demulsification [13-14].

The ELM's allow faster permeation rates of metals due to a large specific interfacial area. Compared to conventional process, liquid emulsion membrane process has certainly some attractive features e.g. simple operation high efficiency, extraction and stripping in one stage, larger interfacial area, scope of continuous operation etc. Studies on extraction of metal ions by emulsion liquid membranes using bi-functional surfactant were considered [15]. Surfactant adds stability to the emulsion but at higher concentration lowers extraction rate. Some surfactants, known as bi-functional surfactants, have dual properties of an extractant and an emulsifier. Use of such surfactant may eliminate the addition of an extractant to ELM system.

EXPERIMENTAL PROCEDURE

Membrane (emulsion) was prepared by mixing extensively the definite amount of organic phase (containing oil soluble emulsifier span 80) and aqueous phase generally the same amount of both the phases. It is stirred at very high speed by blender in a glass beaker. As organic substance being volatile, the beaker was covered with a cover in order to prevent the loss of the same during the emulsification.

The blending speed was 3000 rpm for 15 minutes and thus the milky white water in oil emulsion was obtained. Emulsion thus prepared was added after curing for 30 min, to the external aqueous phenolic feed phase in necessary amounts as per the requirements. Stirring rate was kept

constant so that the uniform distribution of the emulsion was attained. Samples for analysis were withdrawn from the external aqueous phase at regular time intervals. Mixing was stopped after a time span of 30 min in which the maximum extent of separation was achieved. Emulsion phase undergoes stage wise settling immediately after stopping the mixing. The membrane phase used is a homogeneous mixture of commercial grade kerosene/toluene as organic solvent, span 80 (sorbitane mono oleate) as surfactant, and aqueous solution of sodium hydroxide as internal stripping solution. The external phase (feed) is prepared using phenol solution. The organic chemicals for analytical purposes used were of AR grade and the water used was distilled.

Emulsion preparation

The ELM used in this study was water-oil-water (w/o/w) type of emulsion formed by emulsifying aqueous solution of base (strip phase) with an organic phase (membrane phase). The membrane consists of fixed proportions of non ionic surfactant (span 80) and diluent kerosene/toluene. The solution containing surfactant and the diluent is stirred at 3000-4000 rpm for 15 min with the addition of strip phase (aqueous solution of Sodium hydroxide) to form a w/o emulsion. Thus a milky white and stable (12 min) w/o emulsion is obtained. When the stirring is stopped, the multiple emulsion coalesces i.e., the continuous phase (aqueous solution of phenol) separates from the w/o emulsion phase. The later can be broken down thermally/electro-statically. The mass transfer direction can be from strip phase to continuous phase or in the reverse direction.

Extraction procedure

Extraction is carried out in a one litre beaker. The w/o emulsion is dispersed in feed phase containing aqueous solution of phenol. Stirrer with larger diameter operating at variable (200-350) rpm is used for stirring during extraction operation. The emulsion phase is separated from feed phase by simple gravity separation using separating funnel and finally the demulsification process is carried out for the analysis of strip phase. Emulsion phase undergoes stage wise settling immediately after stopping the mixing. Samples of about 5 ml are withdrawn from the extractor at different intervals of time and are filtered through a sintered glass plug to separate emulsion and aqueous feed phase. At the end, the emulsion phase is separated from feed phase by simple gravity separation using a separating funnel and finally the demulsification processes are carried out for the analysis of strip phase. The samples were analysed by colorimeter to find optical density of the phenol concentration at 490 nm. The final concentration of phenol is mixed with diazide solution (sulphanalinic acid, sodium nitrate, concentrated sulphuric acid in the ratio of 5:1:5) and with sodium hydroxide of 0.25 M and analysed at 490nm in the visible range. For a series of known concentrations, absorbances (O.D) are measured and plotted against concentration. We get a straight line passing through origin, which is known as calibration curve. The concentration of the unknown can be determined. The

percentage recovery of the solute is defined as the ratio of difference in initial and final solute concentration to the initial concentration.

RESULTS AND DISCUSSIONS

The extraction of phenol in the ELM investigated in this work is represented by subsequent graphs and is accessed critically here with.

Effect of kerosene as solvent

Kerosene as solvent

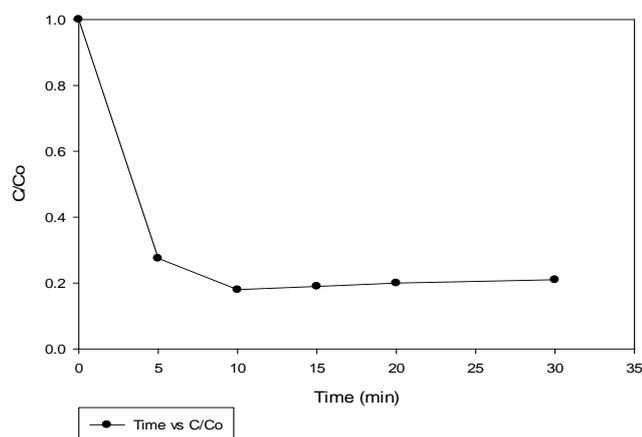


Fig. 1: Plot showing ratio of initial to final concentrations vs. time by taking kerosene as solvent

The samples were analysed to obtain phenol concentration of samples taken at regular time intervals. Dimensionless ratio of the sample concentration to the initial concentration thus obtained is plotted vs. time as shown in fig.1. Maximum removal is obtained at 10 min. One thing which is remarkable is that all curves tend to flatten after 10 minutes showing that the equilibrium has been received between drop and feed phase.

Effect of treating ratio

Treat ratio

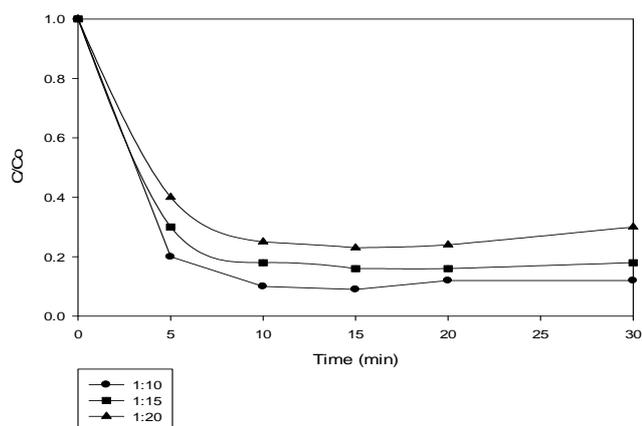


Fig.2 Plot showing ratio of initial to final concentrations vs. time by taking treat ratio

In batch reactive extractive system, change in the treat ratio implies change in molar ratios of the reactive components as well as change in phase ratios of the two heterogeneous

phases. To distinguish the influence of change of phase ratio independent of molar ratio. Runs were carried out with constant molar ratio of NaOH to phenol. While changing the treat ratio (as shown in fig.2) shows the effect of change of treat ratio at constant NaOH to phenol molar ratio. It is seen that when treat ratios were high, initial rate of extraction were more because of large surface areas formed. These runs were carried out at treat ratio of 1:10, 1:15 and 1:20 keeping all parameters constant and results were obtained as shown in figure 2. As it is evident from figure that as the treat ratio increases, the rate of extraction and extent of extraction also increases in the emulsion phase of the system.

On comparing the treat ratio of 1:20 to 1:10, we observe that increase in treat ratio which means more amount of emulsion globules in system leads to large increase in initial rates and almost 87% of phenol is removed in 15 minute compared 76% with the treat ratio of 1:15 and only 66% with the treat ratio 1:20.

Effect of Membrane to Internal phase ratio

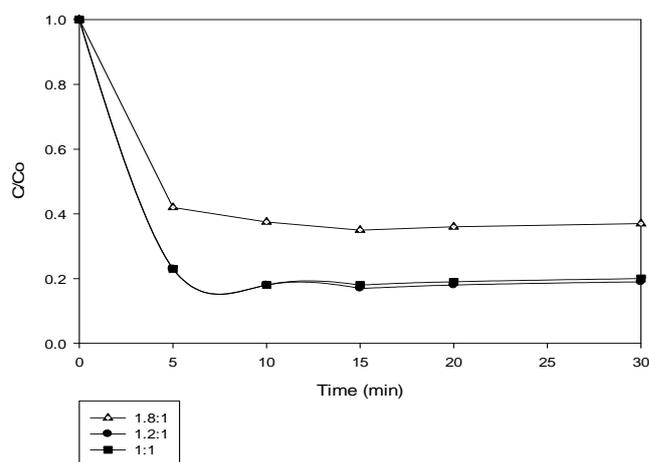


Fig.3 Effect of variation of membrane to internal phase ratio.

Figure 3 shows the effect of variation of membrane to internal reactive phase volume ratio; it was observed that as the volume fraction of the internal phase decreases, rates of extraction also decreases. Drop breakage appears to be very severe when membranes to internal phase ratios were high (i.e. 3:1). In these cases the viscosity of the emulsion was comparable to that of pure solvent.

A number of runs were carried out by varying the internal phase/ external phase ratio. When membrane phase / internal phase ratio was changed from 1.2:1 to 1:1, it was observed that the initial rates of extraction were higher when the ratio membrane phase/ internal phase ratio was 1.2:1, however after 4 min both the curves merged together. It is likely that since internal phase volume has increased; the internal droplet size could be larger initially leading to the lower rates of extraction. When the ratio is increased to 1.8:1, the extent of extraction was less. This could be attributed to the fact that the molar ratio of NaOH/ phenol is substantially decreased.

Effect of stirring speed

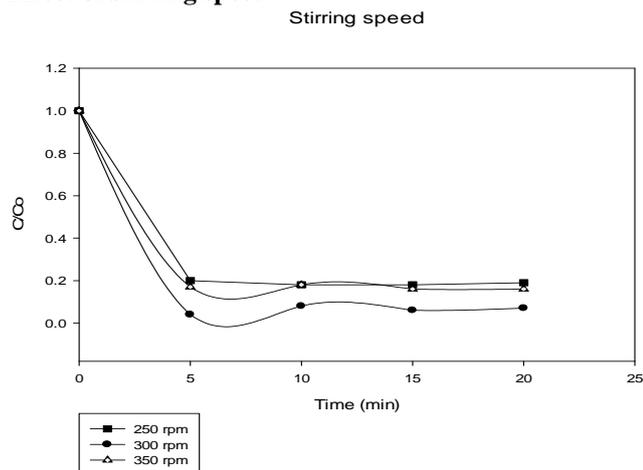


Fig.4 Effect of agitator speed on percentage phenol removed

Figure 4 shows the effect of agitator speed on percentage phenol recovered from external phase. The stirring speed influences the rate of extraction, because by increasing the speed of stirring large membrane surface area may be generated due to fine dispersion of emulsion in the continuous phase and a layer of emulsion rested on the fluid mass.

As a result of increase in speed from 200 to 300rpm, emulsion globules distributed uniformly in continuous phase. It is observed that as the speed was increased from 200 to 300rpm, the percentage solute recovered from external phase increased and decreased keeping all other parameters constant. Further on increasing the speed to 350, it was observed that although the initial rate of extraction was rapid but there was significant drop breakage with time which leads to reduction in the membrane efficiency.

The speed at 300rpm is found to be most effective one as it recovers about 87% of solute at 1:1 ratio. The reason for the drop in percentage solute extracted from external phase beyond 300rpm is due to either de-emulsification induced by higher shear of the impeller or due to leakage from internal stripping phase. This is due to the interfacial area of contact between external phase and emulsion decreases due to high intensity of micelle concentration, nothing but the dense micelle interfacial layer formed at the membrane phase which resists the solute transfer.

Effect of Surfactant concentration

The concentration of surfactant determines the stability of emulsion and also on the rate of extraction as shown in fig. 5. As the initial concentration of span 80 increases, the initial rate of extraction increases. The emulsion was not stable below span 80 concentration of 3% w/w of oil phase because of the sharp increase in the breakage in the emulsion phase with time of agitation. Most stable emulsions were obtained when span 80 concentration was 3% w/w and 5% w/w.

Surfactant concentration

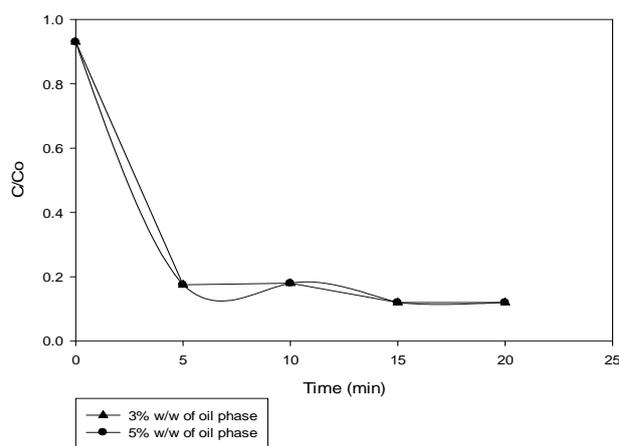


Fig.5 Effect of surfactant concentration on rate of phenol extraction

Internal phase concentration

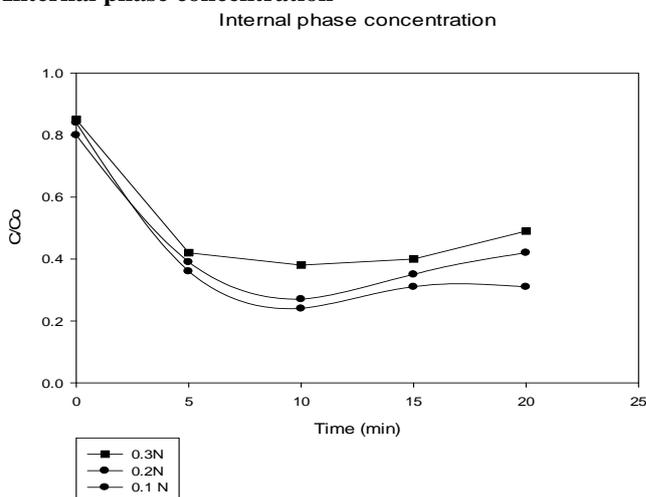


Fig.6 Effect of NaOH concentration on phenol extraction

Increase in NaOH concentration leads to greater removal of phenol. Increase in NaOH concentration leads to an increase in NaOH to phenol molar ratio. The molar requirement of NaOH to phenol is 1:1 and for initial phenol feed of 500rpm (0.00532M) and treat ratio T=1:15, the NaOH concentration in the internal phase should be 0.178M to maintain stoichiometric equivalence of 1:1 molar. Thus increase in the extent of extraction can be attributed to increase in NaOH to phenol molar ratio as shown in fig. 6.

Effect of initial phenol concentration

Variation of phenol concentration in continuous phase while keeping all other system parameters Constant results in change in molar ratio. For decrease in phenol concentration, the initial rate of concentration is likely to increase because of increase in NaOH to phenol mole ratio as shown in fig. 7. When phenol concentration in continuous phase is decreased but simultaneously the NaOH to phenol molar ratio is kept constant.

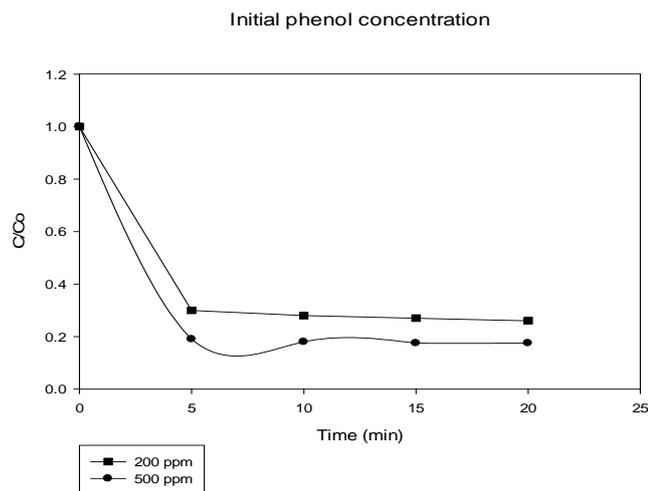


Fig. 7 Effect of initial phenol concentration on rate of extraction

Comparison of two solvents

Comparison of kerosene with toluene as solvent

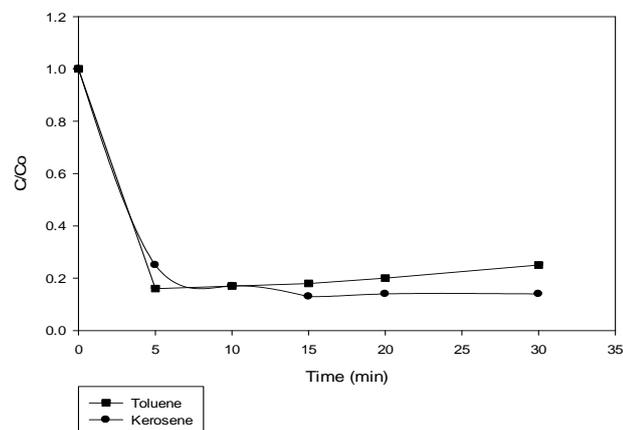


Fig. 8 Rate of extraction comparing with two solvents

ELM prepared with kerosene was compared with ELM prepared with toluene. One thing which was observed that toluene based ELM did not retain their dimensional stability throughout the run and droplet globule sizes were not so uniform. Moreover, as is evident from the figure 8, that the plots for kerosene based ELM tends to flatten out and do not show an excessive rising trend, even after 20-25 minutes of agitation. This indicates that the droplet breakage is not significant in kerosene. But toluene based ELM was broken after 9-10 minutes.

It is evident from this figure that rates of extraction are very rapid in case of emulsion membrane made of toluene in comparison with that of the kerosene. While the maximum extraction in toluene based membranes occur in 9 minutes, the maximum extraction in 15 minutes. This behavior could be explained by the fact that phenol being an aromatic in nature is more soluble in toluene phase than in kerosene phase. The effective diffusivity of the phenol in the toluene is $1.5319 \times 10^{-9} \text{ m}^2/\text{s}$ [17]. While effective diffusivity of phenol in kerosene is 1.06×10^{-9} [18]. The large effective diffusivity of phenol – toluene based ELM is responsible for the rapidity of the extraction process.

Effect of Temperature

Comparison of temperatures

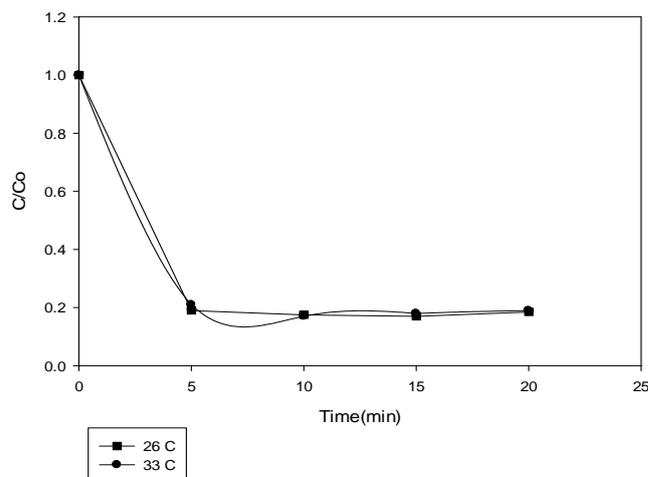


Figure. 9 Effect of temperature on the extraction of phenol.

When temperature is 26°C , the viscosity of emulsion phase was observed as 5.7 cp, while at 33°C the viscosity was 3.4 cp. increasing viscosity leads to easier and more uniform dispersion of emulsion in continuous phase as shown in 9. The enhanced extraction of phenol at lower temperature is attributed to better emulsion globule stability.

CONCLUSIONS

ELM based on kerosene is stable one. ELM based on kerosene being slow in removal compared to ELM based on toluene due to more diffusivity of phenol in the toluene. Demulsification is easy for ELM based on toluene. Treat ratio being the crucial factor in economy, by reducing the emulsion required /waste water; cost of removal can be significantly and efficiently reduced. The rate of agitation is also a major parameter which affected the dispersion of the emulsion in the continuous phase, although high speeds of agitation was detrimental for extraction process because of excessive rupture of emulsion due to agitator shear. Lower temperatures favoured the rates as well as the extent of the extraction as it appears that the increase in viscosity due to lowering of temperature leads to formation of more stable membranes. Separation and purification by emulsion liquid membrane processes inexpensive and less time consuming process.

ACKNOWLEDGEMENTS

Authors wish to thank Vignan's University for providing laboratory facilities to carry out this work.

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