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Extraction of phenol from aqueous effluent using triglycerides in supported liquid membrane

Vikrant Badgujar and Navin K. Rastogi*

Department of Food Engineering, Central Food Technological Research Institute, Council of Scientific and Industrial Research, Mysore 570 020, India Tel.: +918212513910; Fax: +918212517233; email: nkrastogi@cftri.res.in; nkrastogi@yahoo.com

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ABSTRACT

This research work focuses on the removal of phenol using a flat sheet supported liquid membrane impregnated with triglycerides (vegetable oils). The mass transfer of phenol was found to be dependent on various factors such as type of vegetable oil, support material, feed phase pH and concentration, stripping phase concentration and stirring speed. The phenol transport was found to be higher when PTFE membrane (pore size 0.45 µm) impregnated with coconut oil was used and mass transfer coefficient was found to be 3.50×10^{-6} m/s. The corresponding stirring speed, pH of feed solution, concentration of stripping (NaOH) solution were 350 rpm, 4.0 and 0.2 M, respectively. The 92.5% of phenol was extracted from feed phase to stripping phase in 20 h. The aqueous boundary layer thickness reduced with an increase in stirring speed up to a certain extent (350 rpm), beyond which, it resulted in turbulence leading to displacement of impregnated oil from membrane pores. Phenol can be transported through the membrane, when it is present in molecular or undissociated state in aqueous solution. Since the pKa value of phenol is 10, the phenol will be present in undissociated form when the pH of the feed solution was 4.0, which resulted in the highest membrane mass transfer coefficient. The extraction of phenol was found to be dependent on the composition of fatty acids (chain length and position of double bond) in triglyceride. It may be concluded that PTFE membrane impregnated with triglyceride from coconut can be successfully used for the extraction of phenol from aqueous feed.

Keywords: Phenol; Mass transfer; Supported liquid membrane; Vegetable oil

1. Introduction

Phenol and phenolic derivatives are chemical products found in aqueous effluents from various industries. Concentration of phenol present in the waste varies in the range of 2–3% [1]. Phenols are produced from common manufacturing processes including product of synthetic resins, dyes, paints,

wood products, antiseptics, pharmaceuticals. Maximum allowed concentration of phenol in non-chlorinated water, chlorinated water and for some water supplies are 0.1 mg/L, 0.001-0.002 mg/L and 1.0-2.0 ppb, respectively [2–4]. The allowable phenol concentration in drinking water is 1.0 µg/L [5]. Phenolic compounds in potable water emit an unpleasant odor and flavor in concentrations as low as 5.0 µg/L and are poisonous to aquatic life, plants and humans. Ingestion of phenols in concentrations from 10 to 240 mg/L

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^{*}Corresponding author

for long periods causes mouth irritation, diarrhea, and excretion of dark urine and vision problems [6]. Today most of the industries produce toxic chemicals in the processes, which are biologically nondegradable. So, it is necessary to treat wastewater before it is discharged into the environment [7].

On the other hand, phenolic compounds are valuable chemicals for industrial process and many techniques have been adopted to separate and recover them. Phenolic compounds are bioactive substances widely distributed in plants and are also important constituents of human diet. Phenolic compounds from plant sources comprise a great diversity of compounds such as flavonoids (anthocyanins, flavonols, flavones, etc.) and several classes of non-flavonoids (phenolic acids, lignins, stilbenes) [8]. The methods for the removal of phenol from waste water involve absorption [9], extraction [10], oxidation [11] and immobilization of polyphenoloxidase on alginate– SiO₂ hybrid gel [12], crosslinked β -cyclodextrin [13] or adsorption by activated carbon [14].

Liquid membrane processes are regarded as the most efficient method for the treatment of wastewater to extract phenol [15–19], o-nitrophenol [20] and *p*-nitrophenol [21–24]. The work on the liquid membrane was initiated by Li [25] and further investigated by many researchers for the recovery of metal ions [15] as well as organic compounds [26]. Emulsion liquid membrane system, supported liquid membrane system, bulk liquid membrane system are the most commonly used types of liquid membrane systems commonly used for the extraction [27,28].

The important features of supported liquid membrane include: (i) active transport, (ii) low energy consumption, (iii) high selectivity, (iv) minimal loss of extractant, (v) low membrane phase requirement and (vi) simple to operate and easy to scale up [29]. Major advantage of liquid membrane over conventional separation techniques is the simultaneous extraction and separation. In case of bulk liquid membrane extraction, it has its own set of demerits and thus it is rather difficult to upgrade the lab scale bulk liquid membrane to a pilot/commercial scale [30]. In case of emulsion liquid membrane extraction, many a time instability of the emulsion is observed due to swelling or change in the minute concentration of chemicals.

In case of supported liquid membrane, organic liquid is imbedded in the small pores of a polymer support and is retained by the capillary forces. The organic liquid separates aqueous feed and strip stream [31]. The component can move through this liquid membrane from one phase to other by diffusion process due to concentration gradient [30]. Supported liquid membrane combines the processes of extraction, diffusion, stripping and regeneration in a single step [15,32,33]. Most of the time solvent used for the separation is toxic, hazardous and expensive. Instead, nonhazardous, cheap and easily available vegetable oils can be used in case of supported liquid membrane. It has been demonstrated for the extraction of textile dye [34] and rhodamine [35]. A good amount of literature is available in this area, which speaks about its importance and continuous interest in the area among the research community. A few major works include extraction of metal ions [36-43], citric and lactic acids [44-46], natural organic molecules such as drugs [47-49], phenol [26,50], sugars [32,51–53], hydrocarbons [54-55]. Supported liquid membrane (SLM) was also used for the separation of citric and lactic acids in aqueous solutions [31].

The objective of the present work is to study the extraction of phenol form aqueous effluent using supported liquid membrane impregnated with different triglycerides (vegetable oils).

2. Theoretical considerations

During the extraction using SLM process, the feed and the stripping solutions are separated by a liquid membrane, which enables the separation of chemical species using a thin layer of organic solution (extractant) absorbed in the pores of polymeric support. The feed phase contains the species to be transferred and recovered from the strip solution. Both the processes of extraction and recovery processes are carried out simultaneously.

The feed containing aqueous solution of phenol is diffused from bulk to the feed side boundary layer, where the reaction of phenol takes place with triglycerides present in the membrane leading to the formation of phenol-triglyceride complex (Fig. 1) by hydrogen bonding or intermolecular interactions between them. In an acidic medium the phenol remains as unionized molecule (neutral). The extent of phenol available to form complex is dependent on the concentration of phenol present in the membrane phase, which is, in turn, dependent on the distribution coefficient of phenol between the aqueous and membrane phase (triglycerides). The difference in concentration of phenol in phases is due to difference in the solubility of phenol in liquid membrane and water. The distribution coefficient is defined as the ratio of concentration of phenol in triglyceride to that of in aqueous phase. In this way the diffusion of the unionized molecule into the membrane phase takes place [35].

Further, the stripping of phenol from the phenoltriglyceride complex takes place effectively on the other (stripping) side of the liquid membrane. The



Fig. 1. Mechanism of mass transfer of phenol through supported liquid membrane using vegetable oils. Dotted lines show the boundary layers on feed as well as stripping side. [PhOH] and [PhOH_i] are concentrations of phenol in bulk and feed side boundary layer, respectively. [PhOH_i.TG] and [PhOH_i.TG_i] are concentrations of phenol-triglyceride complex in liquid membrane and stripping side boundary layer, respectively. K_{f1} and K_{f2} are the rate of forward and backward reaction on feed side. K_{r1} is the rate of disappearance of phenol-triglyceride complex on stripping side, respectively. D is the distribution coefficient of phenol in aqueous and triglyceride phase.

phenol-triglyceride complex reacts with the aqueous sodium hydroxide solution leading to the formation of sodium phenolate and triglyceride molecules returns back to the liquid membrane to form complex with incoming phenol. This reaction was considered as irreversible and instantaneous [26,33]. The schematic presentation of the mechanism has been shown in Fig. 1.

3. Materials and methods

3.1. Materials

Commercially available three different kinds of vegetable oils (coconut oil, sunflower oil and palm oil) were procured a local super market and used in the present study. The fatty acid composition in coconut, palm and sunflower oil has been presented in Table 1 [56]. The chemicals used include phenol (Ranbaxy, India), methanol (Ranchem, Delhi, India), sodium hydroxide (Qualigens, India), sodium carbonate anhydrous, Folin and Ciocalteu's phenol reagent (FCP reagent, SRL, India). All the chemicals used were of analytical grade. Hydrophobic polytetrafluoroethylene (PTFE) membranes (dia 47 mm, pore size 0.45 μ m) obtained from M/s Sartorious, Bangalore was used.

3.2. SLM cell

The SLM cell consists of a polyacrylic cylindrical chamber (35 mm ID×110 mm length) fitted with a membrane with help of a flange and two rubber gaskets. In order to stir the feed solution, a magnetic bead was placed on the perforated platform just above the membrane surface. The cylindrical assembly was embedded in a bath (provided with magnetic bead) containing NaOH as stripping solution. Whole unit was placed on a magnetic stirrer (Fig. 2).

The effective volume of each cell was 100 ml and the contact area was 38.46 cm². The aqueous phenol and NaOH solutions were used as feed and stripping solutions, respectively. The feed and stripping phases were stirred using a magnetic stirrer at $27 \pm 1^{\circ}$ C to avoid concentration polarization at the membrane surfaces. The transport of phenol from feed phase to the receiving

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Table 1 Fatty acid composition (%) of triglycerides (vegetable oils) (Chow, 1992)

Fatty acids	Coconut oil	Palm oil	Sunflower oil
Saturated fatty acids			
C8:0 (Caprylic acid)	8.0	_	-
C10:0 (Capric acid)	6.4	-	_
C12:0 (Lauric acid)	48.5	0.3	_
C14:0 (Myristic acid)	17.6	1.1	_
C16:0 (Palmitic acid)	8.4	45.1	11.0
C18:0 (Stearic acid)	2.5	4.7	4.7
C20:0 (Arachidic acid	_	-	0.4
Unsaturated fatty acids			
Monounsaturated fatty ac	cid		
C18:1 (Oleic acid)	6.5	38.8	18.6
Polyunsaturated fatty acids			
C18:2 (Linoleic acid)	1.5	9.4	68.2
C18:3 (Linolenic acid)	-	-	0.5

phase was measured by taking samples from the feed solutions at regular time intervals and analyzed for the transport of phenol as per the procedure presented in the following section. All the experiments were carried out in triplicate and average values have been reported.

3.3. Preparation of SLM and stock solution

The membrane was dipped in vegetable oil for impregnation for 15 h before use [29,33,35,57]. Excess of the oil adhered to the surface of the membrane was removed gently with the help of a tissue paper. A stock solution of phenol (1,000 mg/L) was prepared by dissolving 1.0 g of the phenol in 1.0 l doubly distilled water and it was used for further studies by diluting it with water to the required concentrations. Molecular mass, density and solubility of phenol was 94.11 g/mol, density 1.07 g/mL and 8.3 g/100 ml, respectively.

3.4. Determination of mass transfer coefficient

The mass transfer coefficient (*K*) of the membrane for phenol transport is described as per the following equation [15,51]:

$$\ln\frac{C_t}{C_0} = -\frac{A}{V}Kt,\tag{1}$$

where C_0 is initial concentration of phenol in feed phase, C_t is concentration of phenol in feed phase at time t, A is the area of the membrane and V is volume of the feed solution.

3.5. Measurement of total phenol content

Total phenol content was determined calorimetrically using Folin-Ciocalteau reagent as described by Mohamed et al. [58]. Two hundred microliter of feed solution was mixed with 2.0 ml 50% methanol, 1.5 ml Folin-Ciocalteau reagent (diluted 10-fold with distilled water) and 1.5 ml sodium bicarbonate solution (60 g/ L). The mixture was allowed to stand at room temperature ($22 \pm 2^{\circ}$ C) for 90 min and absorbance was measured at 725 nm using spectrophotometer (Model UV 160A, M/ s. Shimadzu, Japan). The calibration curve using phenol was reported to be linear from 6 to 1,000 µg/1[59]. Hence, this technique was considered accurate in the above concentration range.

4. Results and discussion

4.1. Effect of different triglycerides as liquid membrane

Some of the triglycerides (vegetable oils) have the ability to dissolve phenolic substances. The extent of transport of phenols depends upon its solubility in these oils [51]. In the present work, three different types of oils such as coconut, palm or sunflower oils were used for the impregnation of membranes. The phenol concentration was kept at 1,000 mg/L. The unimpregnated membrane did not result in any transfer of phenol to the stripping side. The mass transfer coefficient for various vegetable oils was determined as per Eq. (1) for the transport of phenol (Fig. 3a). The values of mass transfer coefficient are presented in Table 2, which indicates that the coconut oil shows higher mass transfer coefficient (3.50 \times 10⁻⁶ m/s) as compared to other two oils, which is due to higher distribution coefficient of phenol. Hence, coconut oil was used for further studies.

The extraction efficiency is strongly dependent on the intermolecular interactions between the compound to be extracted and liquid membrane, which can form complex by hydrogen bonding or intermolecular interactions [33,53]. Higher interaction energy between compound to be extracted and liquid membrane phase indicates the stronger hydrogen bonds and the complex formed is more stable and the compound can be easily extracted. Jiang et al. [60] demonstrated that extraction efficiency of carboxylic acid with shorter hydrocarbon chains is higher than that with longer ones. Whereas in case of alcohols or amines longer hydrocarbon chains resulted in higher extraction efficiency. Coconut oil containing higher amount of lauric acid (C12:0) as compared to other two oils (palm and sunflower oils, Table 1) indicating that triglycerides present in membrane phase containing lower chain fatty acid can form stable complex with phenol leading



Fig. 2. Schematic design of supported liquid membrane (SLM) model.

to higher extraction efficiency. Further comparison of palm and sunflower oil indicated that extraction efficiency of sunflower oil was lower probably due to presence of saturated (Palmitic acid, C16:0) and monounsaturated fatty acids (Oleic acid, C18:1) in lower amount and polyunsaturated fatty acids (Linoleic acid, C18:2) in higher amount as compared to palm oil (Table 1).

4.2. Effect of various support material for SLM

The use of hydrophobic membrane as a support in SLM extraction processes results in lower mass transfer resistance than hydrophilic membranes [15]. It was reported that the PTFE membranes are much more robust and have significant extended durability [61]. Three types of hydrophobic membranes (PTFE membrane pore size 0.45 µm and PP (polypropylene) membrane pore sizes 0.22 and 0.45 µm) were impregnated with coconut oil and subsequently used for phenol extraction. The phenol concentration was kept at 1,000 mg/L. The extent of retention of phenol in feed is presented in Fig. 3b. A comparison of the mass transfer for the three hydrophobic membranes (Table 2) indicated that the mass transfer coefficient of PP membrane (pore size 0.2 μ m) was lowest (2.20 \times 10⁻⁶ m/s). Whereas, the mass transfer coefficient of the PTFE membrane (pore size 0.45 μ m) was highest (3.50 \times 10^{-6} m/s). The lowest mass transfer coefficient of PP membrane (pore size 0.22 µm) may be attributed to the highest resistance to mass transfer offered by PP support as compared to the other two membranes. Chakrabarty et al. [30] have also studied the effect of pore size and membrane thickness of various membranes and



Fig. 3. (a) Effect of different triglycerides (vegetable oils, PTFE, pore size 0.45 μm, feed pH 4.0, RPM 350, feed concentration 1,000 mg/L, strip concentration 0.2 M); (b) type of membranes (support material impregnated with coconut oil, feed pH 4, RPM 350, feed concentration 1,000 mg/L, strip concentration 0.2 M), (c) stirring speed (PTFE impregnated with coconut oil, feed pH 4, feed concentration 1,000 mg/L, strip concentration 0.2 M) and, (d) initial phenol concentration on the mass transfer coefficient of phenol (PTFE impregnated with coconut oil, RPM 350, Feed pH 4, strip concentration 0.2 M)

demonstrated that the PTFE membranes resulted in reduced mass transfer resistance. Hence, PTFE membrane (pore size 0.45 μ m) impregnated with coconut oil was used for further studies.

4.3. Effect of stirring speed

The increase of stirring speed not only enlarges the tangent velocity at the interface between the phases of the aqueous solution, but also increases the disturbance in the aqueous solution, which also in turn puts more shear force at the interface between the phases of the aqueous solution resulting in decrease in the thickness of boundary layer, which is essential for effective permeation [62,63]. The transport process through such type of membranes is limited by the boundary layer at very low stirring speed, however, the role of the boundary layer becomes of little importance at stirring speed since the thickness of this layer is reduced, thus the transport of phenol would be limited by the internal diffusion of the phenol through the membrane [64]. The effect of stirring in case of phenol extraction using SLM was evaluated by changing stirring speed from 250 to 550 rpm (Fig. 3c). The phenol concentration was kept at 1,000 mg/L. It was observed that the permeation of phenol was increased from 250 to 350 rpm and beyond 350 rpm, there was no appreciable increase in the mass transfer coefficient (Table 2). It may be explained based

Table 2 Effect of different variables on the mass transfer coefficient of phenol

	Mass transfer coefficient (m/s)
Effect of vegetable oils	
Coconut oil	$3.50~\pm~0.14~{ imes}~10^{-6}$
Sunflower oil	$1.53 \pm 0.29 \times 10^{-6}$
Palm oil	$1.94 \pm 0.10 imes 10^{-6}$
Effect of different membranes	
PTFE (pore size 0.45 μm)	$3.50 \pm 0.14 \times 10^{-6}$
PP (pore size 0.45 μm)	$2.98 \pm 0.13 \times 10^{-6}$
PP (pore size 0.22 μm)	$2.20 \pm 0.37 \times 10^{-6}$
Effect of initial feed concentration	
500	$2.25 \pm 0.40 \times 10^{-6}$
1,000	$3.50 \pm 0.14 \times 10^{-6}$
1,500	$3.90 \pm 0.19 \times 10^{-6}$
Effect of stirring speed (rpm)	
250	$2.14 \pm 0.94 \times 10^{-6}$
350	$3.50 \pm 0.14 \ge 10^{-6}$
550	$3.64 \pm 0.41 \ge 10^{-6}$

on the fact that the aqueous boundary layer thickness diminished continuously with increasing stirring speed up to 350 rpm and further increase in stirring speed resulted in turbulence leading to the displacement of impregnated oil from the membrane pores [15]. Hence, the stirring speed of 350 was kept for further studies.

4.4. Effect of initial concentration of phenol

The initial phenol concentration in the feed phase plays an important role in the transportation rate. In the present study the phenol concentration was maintained in the range of 500-1,500 mg/L. The effect of feed concentration on the transfer of phenol is shown in Fig. 3d and the mass transfer coefficient values are provided in Table 2. The values of mass transfer coefficient were found to increase from 2.25×10^{-6} to 3.90×10^{-6} m/s with an increase in feed concentration from 500 to 1,500 mg/L. It may be noted that the transportation rate is directly proportional to the initial concentration of feed side phenol. The increase in initial flux of phenol with an increase of the initial phenol concentration in the source phase was observed without membrane saturation phenomenon as demonstrated by Zidi et al. [33]. Similarly, Cichy and Szymanowski [65] observed an approximately linear relationship between the flux entering the receiving phase and the concentration of phenol in the source solution.

4.5. Effect of feed phase pH

The membrane mass transfer coefficient was found to decrease from 3.50 \times 10 $^{-6}$ to 1.69 \times



Fig. 4. (a) Effect of pH on the mass transfer coefficient of phenol (PTFE impregnated with coconut oil, RPM 350, feed conc. 1,000 mg/L, strip conc. 0.2 M); (b) effect of strip (NaOH) solution concentration on the mass transfer coefficient of phenol (PTFE impregnated with coconut oil, RPM 350, Feed pH 4, feed concentration. 1,000 mg/L).

 10^{-6} m/s with an increase in pH from 4.0 to 12.0 (Fig. 4a). The phenol concentration was kept at 1,000 mg/L. It may be explained based on the fact that the phenol can be transported through the membrane, when it is present in molecular or undissociated state in aqueous solution. Since the pK_a value of phenol is 10, the phenol will be present in undissociated form for the pH values less than 10 [29,61,66]. The extent of dissociation was found to be the least when pH of the feed was maintained at 4.0, which resulted in the highest membrane mass transfer coefficient (3.50 \times 10⁻⁶ m/s). It is evident from the following equation that the concentration of the molecular phenol decreases when the source pH increases, which in turn results in the transport efficiency of phenol [33]



Fig. 5. Comparison of experimental values with predicted values (using Eq. (1)) (PTFE impregnated with coconut oil, RPM 350, Feed pH 4, feed concentration 1,000 mg/L, strip (NaOH) solution concentration 0.2 M.

$$[PhOH]_{molecular} = \frac{[PhOH]_{total}}{1 + 10^{-pKa+pH}},$$
(2)

where [PhOH]_{molecular} and [PhOH]_{total} are the concentrations of molecular and total phenol, respectively. The concentration of total phenol refers to the concentration of molecular, undissociated and dissociated phenol.

4.6. Effect of stripping solution concentration

The NaOH solution in the present study was used as a stripping solution and the concentration was varied in the range of 0 to 0.6 M (Fig. 4b). When water was used as a stripping solution, it did not result in significant transfer of phenol. Whereas, the use of NaOH solution (0.2-0.6 M) as a stripping agent resulted in an increase in phenol transfer. The mass transfer coefficient was found to increase from 0.50×10^{-6} to 3.50×10^{-6} m/s with an increase in concentration up to 0.2 M. Further, increase in concentration from 0.2 to 0.6 M resulted in decrease in the mass transfer concentration from 3.50×10^{-6} to 2.03×10^{-6} m/s (Fig. 4b). The phenol is selectively dissolved in the SLM (impregnated oil) and pass through the porous membrane support, while concentration gradient acts as a driving force. As the phenol molecule reaches at the interface of the membrane on the side of stripping solution, it reacts with sodium hydroxide and converts into sodium phenolate, which cannot diffuse back through liquid membrane.

4.7. Comparison of experimental and predicted phenol concentration

The transportation of phenol from feed to the stripping solution side was studied for 20 h. The various parameters are actually involved in transport of phenol through supported liquid membrane like membrane pose size, membrane thickness, specific area, diffusion through membrane [67]. From the study, it was concluded that highest mass transfer coefficient was obtained when PTFE membrane impregnated with coconut oil used. The stirring speed, pH of feed solution, concentration of stripping solution (NaOH) were maintained at 350 rpm, 4.0 and 0.2 M, respectively, and the mass transfer coefficient obtained for this condition from the above study was found to be 3.50×10^{-6} m/s. The 92.5% of phenol was transported from feed phase to stripping phase in 20 h, when the initial concentration of phenol was 1,000 mg/L (Fig. 5). The experimental values were found to be in agreement with the predicted values ($R^2 = 0.97$).

5. Conclusion

SLM consisting of PTFE membrane (0.45 µm) impregnated into coconut oil was successfully used for the highest extraction of phenol. The PP membrane $(0.22 \ \mu m)$ offered higher resistance to mass transfer as compared to the other two membranes such as PP $(0.45 \,\mu\text{m})$ and PTFE $(0.45 \,\mu\text{m})$. The extraction efficiency was found to be strongly dependent on the type of triglyceride used as a liquid membrane phase. Triglycerides present in coconut oil contains higher amount of lower chain fatty acids, which form stable complex by hydrogen bonding or intermolecular interactions with phenol leading to higher extraction efficiency. The processing conditions such as stirring speed (350 rpm), pH of feed solution (4.0), concentration of stripping (NaOH) solution (0.2 M) resulted in highest mass transfer coefficient (3.50 \times 10⁻⁶ m/s), which resulted in 92.5% removal of phenol from the feed solution (1,000 mg/L) in 20 h. The study indicates that SLM impregnated with triglyceride from coconut oil can be successfully used for the extraction of phenol from the aqueous feed.

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