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Performance of different ionic liquids to remove phenol from aqueous solutions using supported liquid membrane

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ABSTRACT

An experimental study was carried out for the removal of phenol from aqueous solutions using supported liquid membranes containing ionic liquid (IL) as the carrier solvent. The commercial grade ILs namely: [CYPHOS® 101], [CYPHOS® 102], [CYPHOS® 103], [CYPHOS® 104], [Aliquat 336®], and [C_8MIM][PF_6] were used as membrane phase in this work. The effect of various parameters such feed phase pH, operation time, and stirring speed on the removal of phenol has been investigated using the six different ILs. Supported ionic liquid membrane (SILM) through vacuum immobilization method was used for the removal of phenol. The maximum permeation rate of 75.63% was achieved over an experimental run of 24 h at pH 4. High permeation rate was obtained by [CYPHOS® 104] among all the six ILs studied. The order of the permeation rates followed: [CYPHOS® 104] > [CYPHOS® 103] > [CYPHOS® 102] > [CYPHOS® 101] > [C_8MIM][PF_6] > [Aliquat 336®]. The operational stability and performance of the supported liquid membranes were studied via characterization techniques such as scanning electron microscopy, energy dispersive X-ray, and FTIR analysis. The mechanism of phenol transport through SILM was also proposed.

Keywords: Ionic liquid; Phenol removal; Liquid membrane; Wastewater treatment

1. Introduction

The contamination of environment is a major global problem. Industries such as chemical, automobile, oil refinery, pharmaceutical, bulk drug, health care, and personnel care products are the major industries contributing to the pollution in a severe manner. Among the various pollutants, phenol (C_6H_5OH) is one of the major organic pollutants. Organic compounds such as phenol, alcohol, and ether are the basic compounds for the formation of detergents, antiseptics, and fragrances, respectively. Trace amounts of phenolic compounds present in water and wastewater are the most difficult to remove. Phenol is a non-steroidal anti-inflammatory drug and is raw material for several polymers (nylon, bakelite, epoxy resins, and other plastics), pharmaceuticals, drugs, and herbicides.

Phenol removal from wastewater is widely studied by several researchers; the employed methods such as solvent extraction [1], evaporation [2], biosorption [3], and extraction [4] are notable. These methods concern with their own inherent limitations such as formation of emulsion, requirement of more energy, labor intensive process, low reproducibility, sensitive operating conditions, generation of toxic sludge and high capital, and operating costs.

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It has been reported that membrane-based separation has the ability to overcome some of these inherent problems. Apart from these, membrane-based separation processes are getting appreciable attention due to easy scaling up, capability of integration with other process (hybrid processes), and adjustable characteristics of the membrane. Liquid membranes in general have certain advantages such as generation of large surface area in small equipment, simultaneous extraction, and stripping in single step and high selectivity [5]. Supported liquid membranes are especially better in terms of the stability problem associated with liquid membranes [6].

Extractants used in liquid membranes are mainly organic solvents such as aromatic and aliphatic hydrocarbons, amines, esters, ethers, ketones, and nitrated or chlorinated hydrocarbons. Most of these solvents are carcinogens as recognized by NIOSH, volatile at room temperature, non-biodegradable and are flammable. Search for better and greener solvents ends with room temperature ionic liquids (ILs), which have numerous advantages over the traditional organic solvents. ILs are composed solely of organic cations and organic or inorganic anions [7]. They have favorable properties such as negligible vapor pressures, tunable viscosities, high thermal and chemical stability, and high thermal conductivity and polarity [8]. ILs having technological applications includes electrochemical cells, Li-ion batteries, ultracapacitors and sensors, fuel cell membranes, and synthesis reactions such as epoxidation, hydrogenation, and hydroformulations [9,10]. Solvent extraction of organic pollutants using ILs was reported earlier [11,12]. A detailed discussion on this area was described in a recent review by Schlosser et al. [13]. It has been proved that ILs provides better stability to the supported liquid membranes [14]. Removal of organic compounds and heavy metals from aqueous phase has been reported by several earlier researchers [15–18]. The preparation of supported ionic liquid membrane (SILM) requires a small amount of IL (as a membrane carrier) which is required to fill the pores of the supporting membrane, thereby the process becomes economical.

The objective of the present study was to study the separation of phenol from aqueous solution using SILM. The parameters such as membrane weight loss, permeation rate, stirring speed, and effect of pH with respect to time were studied. The mechanism of phenol permeation through the SILM was also proposed. Further, scanning electron microscopy (SEM) was used to study the morphology of the SILM before and after transport experiments.

2. Experimental

2.1. Chemicals and materials

The chemicals used in this study were purchased from Sigma Aldrich (Germany) until unless stated. Trihexyltetradecyl phosphonium chloride [CYPHOS® 101], trihexyltetradecyl phosphonium bromide [CYPHOS® 102], trihexyl (tetradecyl) phosphonium decanoate [CYPHOS® 103], trihexyl (tetradecyl) phosphonium bis(2,4,4-trimethylpentyl) phosphinate [CYPHOS® 104], methyltrioctyl ammonium chloride [Aliquat 336®], and [C_8MIM][PF_6] were ILs used in this work. [C_8MIM][PF_6] was synthesized according to the reported literature [11]. The synthesis procedure was given in next section. Physical characteristics of ILs are given in Table 1. The pH of the aqueous solutions was adjusted using H_2SO_4 and NaOH. Chemicals such as HCl, H_2SO_4, NaOH, and phenol (C_6H_5OH) were procured from Merck, Germany. Polyvinyldene fluoride (PVDF) membrane (Durapore, Millipore Co. India) was used as polymeric support throughout this work. All the chemicals were used as received without further treatment.

2.2. Synthesis of [C_8MIM][PF_6]

[C_8MIM][Cl] was transferred to a 2 L glass beaker followed by the addition of 500 mL deionized (Millipore India) water. An aqueous solution of 60% $NaPF_6$

Table 1
Physical characteristics of ILs

Name of IL used	CAS number	Molecular formula	Mol. wt. (g/mol)	Density (g/cm^3)
[CYPHOS® 101]	258864-54-9	$C_{32}H_{68}ClP$	519.31	0.894
[CYPHOS® 102]	654057-97-3	$C_{32}H_{68}BrP$	563.76	0.952
[CYPHOS® 103]	465527-65-5	$C_{42}H_{87}O_2P$	665.11	0.883
[CYPHOS® 104]	465527-59-7	$C_{48}H_{102}O_2P_2$	773.27	0.887
[C_8MIM][PF_6]	304680-36-2	$C_{12}H_{23}N_2PF_6$	340.29	1.234
[Aliquat 336®]	63393-96-4	$CH_3N[(CH_2)_7CH_3]_3Cl$	404.16	0.884

was prepared in a separate glass beaker and was then added to the first beaker in a 1.1:1 molar ratio. As $NaPF_6$ was added, two phases were formed, where $[C_8MIM][PF_6]$ was the bottom phase and NaCl was the top phase. The top phase was decanted and 500 mL of deionized water was added followed by vigorous shaking and thorough mixing. As the mixture settled, the top aqueous phase was decanted and more deionized water was added. This procedure was repeated till the pH of the top phase was 7.0. The synthesized $[C_8MIM][PF_6]$ was stored in contact with water and is referred to as water equilibrated or "wet."

2.3. Method of preparation of SILM

A porous hydrophilic PVDF membrane was used as the support and the IL was used as a carrier in this membrane. The PVDF membranes were used by many researchers' for the separation effluents and industrial gases [19]. Detailed specifications and properties of the PVDF membrane were given in Table 2. Method of preparation of SILM can have a significant role on the membrane performance, because of relative higher viscosities of ILs. Commonly used methods for the preparation of SILMs are direct immersion, pressure, and vacuum immobilization methods [19–21]. In this work, vacuum immobilization method was followed for the preparation of SILM. PVDF membrane was submerged in a Petridish containing IL until membrane was wetted. Petridish having membranes were then sealed with paraffin tape and allowed to stand for 24 h. This was followed by the removal of any residual solvent from the surface using soft tissue paper. In the next step, membrane was dried completely and kept in the vacuum desiccator for a period of 24 h to dry off the excess IL remaining on the membrane. This vacuum drying leads to displacing the air from the membrane pores filled with IL [19,20].

Weights of the SILMs were noted before and after the transport experiments. Table 3 describes the noted weight of membranes before transport experiment and % weight loss of ILs after the transport experiment and also the rate of permeation of phenol for different ILs. The data from Table 3 indicates that loss of IL from the membrane pores over a period of 24 h is around ~5%. This confirms that the ILs are not easily removed from the pores of the polymer support under a cross-membrane pressure difference, since IL was immobilized by the high van der Waals forces. This was also due to their higher viscosities as explained earlier [22,23]. The % wt. loss of the membrane was calculated by the following Eq. (1).

$$\%\ \text{Wt. loss} = \left(\frac{\text{Wt. of membrane before experiment} - \text{Wt.of membrane after experiment}}{\text{Wt. of membrane before experiment}}\right) \times 100 \quad (1)$$

2.4. Preparation of standard stock solution

Required amount of phenol crystals were dissolved in deionized (Millipore, India) water to obtain a standard stock solution with a concentration of 1,000 mg L^{-1}. The stock solutions were stored in refrigerator at

Table 2
Specifications and properties of PVDF membrane by the supplier

Description	Specification
Refractive index	1.42
Pore size (μm)	0.45
Filter diameter (mm)	90
Thickness (μm)	125
Water flow rate (mL/min × cm^2)	29
Gravimetric extractables (%)	0.5
Air flow rate (L/min × cm^2)	4
Chemistry	Hydrophilic PVDF
Maximum operating temperature (°C)	85
Porosity (%)	70
Wettability	Hydrophilic
Filter color	White
Filter surface	Plain
Bubble point at 23°C	≥1.55 bar, air-with water
Filter type	Screen filter
Trade name	Durapore

Table 3
Weight of membrane before and after the transport experiment, and rate of permeation of different ILs

		Weight of membrane (g)		
S. no.	Name of the IL	Before expt.	After expt.	Loss (%)
1	[C8MIM][PF6]	0.982	0.933	4.9
2	[Aliquat-336]	0.898	0.86	3.8
3	[CYPHOS-101]	0.893	0.868	2.5
4	[CYPHOS-102]	0.889	0.867	2.2
5	[CYPHOS-103]	0.888	0.867	2.1
6	[CYPHOS-104]	0.879	0.855	2.4

25 ± 1°C. Stored stock solutions were diluted into required working solutions for further use. Working solutions were prepared daily from the standard stock solution.

2.5. Method of analysis

The analysis of phenol was done by UV–Vis Spectrophotometer (Varian, Model Cary 50 Bio) at the wavelength of 500 nm using 4-aminoantipyrine method. Solution pH was measured with pH meter (Eutech pH spear). SEM and EDAX analysis was done using LEO, Model 1430VP electron microscope.

2.6. Permeation experiments

Experimental setup of permeation cell is illustrated in Fig. 1. It is an assembly of two separate glass diffusion cells (*M/S ab Chemicals and Instruments, Guwahati*). The volume of each glass cell is about 100 mL and they are separated by a membrane having an effective contact area of 12.5 cm^2. Both the compartments were separately stirred with magnetic spinbars. Initial feed phase concentration of phenol was kept at 100 $mg\,L^{-1}$. A solution of 0.1 N NaOH was used as a receiving phase and its concentration was kept constant for all experiments. Both the compartments having phenol and 0.1 N NaOH solutions were mechanically stirred. The experiments were carried out with and without pH control from feed side. Concentrated HCl was used to control the feed pH. The changes in phenol concentration were observed by taking sample of the feed and permeate at particular time intervals and in a defined period of time. It was reported in literature that temperature had little effect on the extraction of organic compounds [12]. Considering this, all the SILM transport experiments were conducted at room temperature (25 ± 1°C). Each experiment was performed three times and less than 5% error was observed.

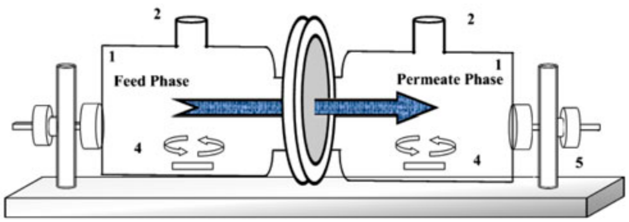


Fig. 1. Experimental setup of permeation cell: (1) glass cell, (2) glass cell lid, (3) supported IL membrane, (4) magnetic sipnbars, (5) support clamps, and (6) magnetic stirrer.

2.7. Selection of ILs

A key characteristic of IL is that their phenomenal properties can be designed by judicious selection of cation, anion, and substitutes. Previously, Seddon and his group [24] furnished some common procedure on the effect of anion choice on the miscibility of ILs and water. Thus, the water solubility of the IL can be assured by the nature of the R-group. Increase in the alkyl chain length of the cation, increases the hydrophobic nature of IL, thereby reducing water solubility. In addition, physical and chemical properties can be varied considerably by the choice of anion, such as halide [Cl^-, Br^-, I^-], nitrate [NO_3^-], acetate [$CH_3CO_2^-$], tetrafluoroborate [BF_4^-], hexafluorophosphate [PF_6^-], and bis(trifluoromethyl-sulfonyl)imide [$(CF_3SO_2)_2N^-$] [14]. In the present work, six ILs were chosen which are hydrophobic in nature.

3. Results and discussion

The effects of concentration of phenol in feed phase with time, effects of concentration of phenol in stripping phase with time, rates of permeation of phenol with different ILs, and rate of permeation of phenol at different pH conditions were studied and the results are discussed in this section.

3.1. *Effect of time on phenol concentrations in feed and stripping phase for different ILs*

The change in concentration of phenol in feed phase and stripping phase with respect to time is shown in Figs. 2 and 3. The initial feed concentration of phenol was fixed at 100 mg L^{-1}. Fig. 2 shows the effect of feed phase concentration with time for different ILs at feed phase pH of 5.6 (natural pH of the feed). From Fig. 2, it can be seen that the concentration of phenol decreased very sharply in feed side within 12 h of transport experiment, while reaching a steady state at around 24 h. Thereafter, no variation was observed with operating time. Out of the six ILs used, approximately 53.2 mg L^{-1} (73.63%) of phenol present in the feed phase was transported to permeate side within 24 h via SILM consisting of [CYPHOS® 104] at feed pH of 5.6. Table 4 gives the complete details of the different IL membranes used and their corresponding feed concentration and % rate of permeation after 24 h of transport experiment.

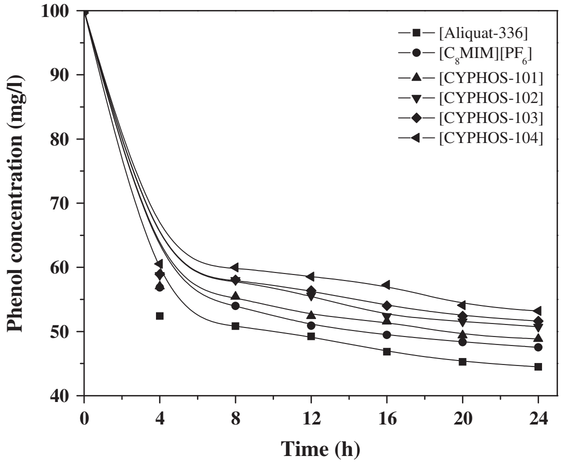


Fig. 2. Variation of feed phase concentration with time for different ILs for SILM transport experiment (conditions: initial feed phase concentration: 100 mg L^{-1}, pH: 5.6, stirring speed: 300 rpm and temperature: 25 ± 1˚C).

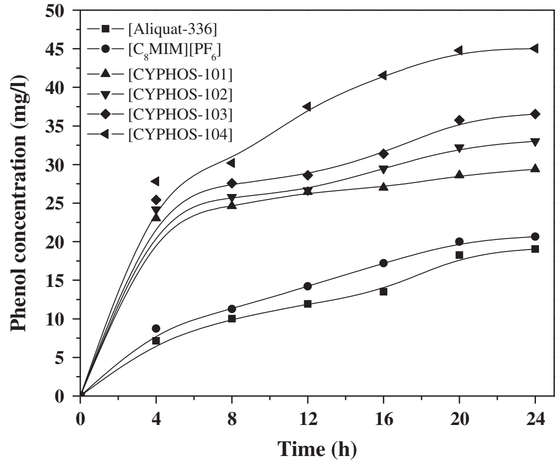


Fig. 3. Variation of stripping phase concentration with time for different ILs for SILM transport experiment (conditions: initial strip phase concentration: 100 mg L^{-1}, pH: 5.6, stirring speed: 300 rpm and temperature: 25 ± 1˚C).

For phosphonium-based ILs, it was observed that the concentration of phenol decreased with time with an increase in the length of alkyl chain on the cation of the phosphonium IL. The anion bis(2,4,4-trimethylpentyl) phosphinate gave better separation than that of chloride anion. This was due to stronger hydrogen bonding between bis(2,4,4-trimethylpentyl) phosphinate and phenol compound. The chloride anion gave very poor separation, may be due its high solubility in water.

The order the permeation rate of ILs for a given phenol concentration at feed pH of 5.6 was as follows: [CYPHOS® 104] > [CYPHOS® 103] > [CYPHOS® 102] > [CYPHOS® 101] > [C$_8$MIM][PF$_6$] > [Aliquat 336®] under the same experimental conditions. On the other hand, Fig. 3 shows the effect of phenol concentration in stripping side with respect to time for the six different ILs used. 0.1 N NaOH was used as stripping agent. The concentration of phenol in the stripping phase increased with increasing time (Fig. 3). It was observed that the concentration of phenol in the stripping phase increased sharply within first 8–12 h of transport experiment, thereby slowly reached to equilibrium. Hence, the phenol present in the feed phase was transported to the permeate side after 24 h of the transport experiment. As mentioned above highest rate of permeation of (at pH 5.6) was observed for [CYPHOS-104].

Among the six ILs used, [CYPHOS-104] gave the highest extraction of phenol (53.21 mg L^{-1}) from feed phase, whereas [Aliquat-336]'s performance was poor (44.47 mg L^{-1}) when compared with phosphonium-based ILs. Marták et al. [25] reported that phosphonium-based ILs were highly hydrophobic, which ultimately improves the stability of SILM. More details about the stability of the supported liquid membranes were reported elsewhere [26].

3.2. *Rate of permeation and membrane flux*

The permeation rate was calculated as per the following formula:

$$\text{Rate of permeation }(\%) = \frac{C_{R,24\,\text{h}}}{C_{F,0}} \times 100 \qquad (2)$$

Table 4
Weight of membrane before and after the transport experiment, and rate of permeation of different SILMs used

S. no.	Name of the IL	Feed con. after 24 h of expt.	Rate of permeation (%) at pH 5.6
1	[Aliquat-336]	44.47	32.43
2	[C8MIM][PF6]	47.53	35.11
3	[CYPHOS-101]	48.84	50.00
4	[CYPHOS-102]	50.75	54.23
5	[CYPHOS-103]	51.62	59.74
6	[CYPHOS-104]	53.21	73.63

where $C_{R,24\,\mathrm{h}}$ is concentration of phenol in receiving phase after 24 h, $C_{F,0}$ is initial concentration of phenol in feed phase.

The rate of permeation of phenol in different ILs through the SILM is presented in Fig. 4(A). [CYPHOS-104] was observed to give better permeation, whereas other ILs such as [Aliquat-336] and [C_8MIM][PF_6] did not give good permeation as compared to phosphonium ILs. Lowest rate of permeation of phenol was given by Aliquat-336 and [C_8MIM][PF_6] with corresponding values of 32.43 and 35.11%, respectively. The permeation rates followed the order: [CYPHOS® 104] > [CYPHOS® 103] > [CYPHOS® 102] > [CYPHOS® 101] > [C_8MIM][PF_6] > [Aliquat 336®]. From the literature [27], important observations made for the rate of permeation are: (i) permeation is independent of pressure; (ii) increase in temperature lead to decrease in penetrant solubility, but made the membrane more permeable; (iii) prolonged exposure to elevated temperature affected the retention capacity of the membrane, and (iv) variation in membrane thickness altered the permeation rate but not the separation characteristics of the polymer.

The membrane flux measures the number of moles or amount of substance diffusing per unit time and unit effective contact area of the membrane. The flux can be calculated by the following equation.

$$J = -\left(\frac{V}{A}\right) \times \left(\frac{dC}{dt}\right) \tag{3}$$

where V is the stripping phase volume in m^3; A is the contact area of the membrane in m^2; C is the concentration of phenol in the receiving phase in mol L^{-1}, and t is the time elapsed in s. The SI unit of membrane flux is mol m^{-2} s^{-1}. The membrane fluxes were measured every time with fresh membrane feed in stripping solutions, so that the same driving force for each flux measurement can be obtained. [CYPHOS-104] IL was used as the membrane phase for flux measurements. Fig. 4(B) describes the variation of permeate flux with operation time. The initial feed phenol concentration used was 100 mg L^{-1}. 0.1 N NaOH was used as the stripping phase and the feed phase pH was 5.6. From Fig. 4(B), it can be seen that

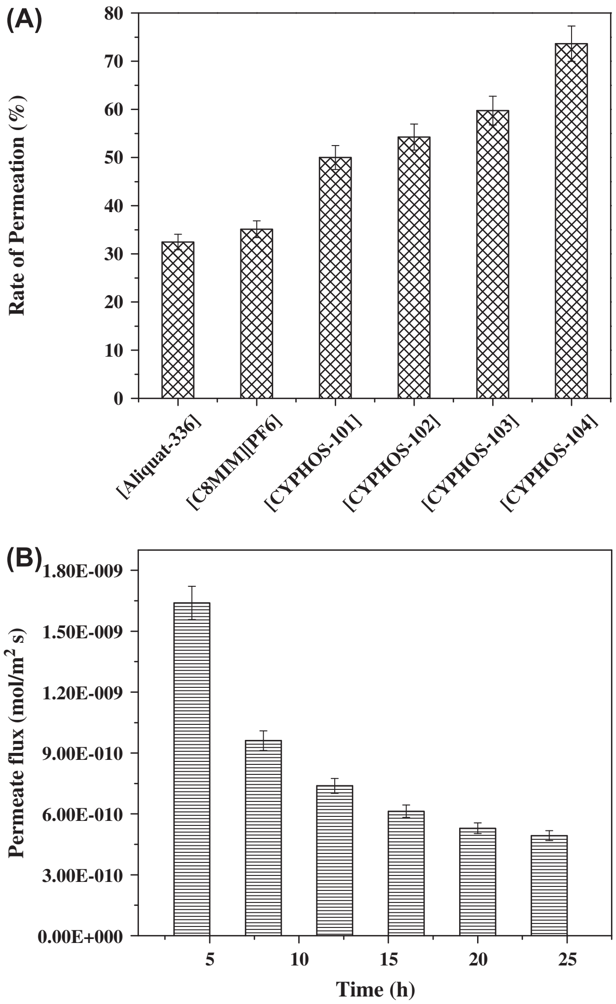


Fig. 4. (A) Rate of permeation of different ILs (conditions: initial feed concentration: 100 mg L^{-1}, stripping phase concentration: 0.1 N NaOH, pH: 5.6, stirring speed: 300 rpm, and temperature: 25 ± 1℃). (B) Plot of permeate flux vs. time (conditions: initial feed concentration: 100 mg L^{-1}, stripping phase concentration: 0.1 N NaOH, pH: 5.6, temperature: 25 ± 1℃, and [CYPHOS-104] IL was used).

the permeate flux decreased sharply within 10 h of operation and later on reached a steady state. Severe flux decline was observed which could be due to the membrane fouling. Vigorous membrane fouling may thus require cleaning or replacement of membrane.

3.3. Effect of stirring speed

The rotation speed of the magnetic spinbars in feed phase and stripping phase compartments of the permeation cell was controlled by magnetic stirrer. The concentration polarization at the interface of the IL membrane can be avoided by continuous mechanical stirring of the feed as well as stripping phase. Stirring speed was varied from 100 to 400 rpm (Fig. 5) to find out the optimum stirring speed that permits effective diffusion of phenol through the SILM. Permeability was increased when the stirring speed was increased from 100 to 300 rpm. This shows that the aqueous boundary layer thickness decreased by increasing the stirring speed. For stirring speed above 300 rpm, the permeation rate started to decrease. This was due to the high speeds that lead to the displacement of IL from pores of the support. The optimum rotation speed reduces the mass transfer resistance and due to this reason 300 rpm was chosen as the optimum rotation speed throughout the investigation. Thus, the mass transfer rate from feed to permeate side will be affected by solubility and the diffusivity of the phenol in the immobilized IL phase. The separation rate is also influenced by the properties of solid support such as porosity of the membrane, thickness of the membrane, and tortuosity of the membrane pores [28].

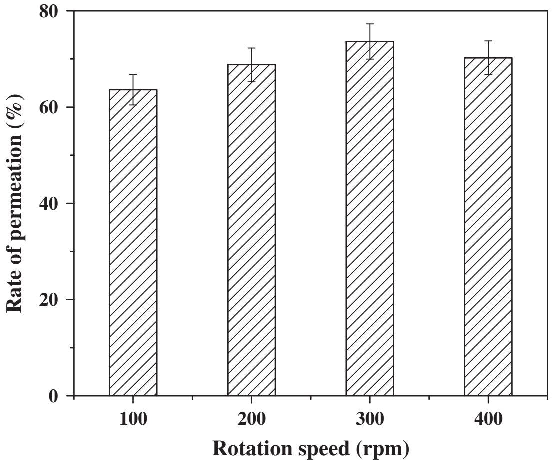


Fig. 5. Effect of stirring speed (conditions: initial feed concentration: 100 mg L^{-1}, stripping phase concentration: 0.1 N NaOH, pH: 5.6, temperature: 25 ± 1℃, and [CYPHOS-104] IL was used).

3.4. Effect of feed phase pH on rate of permeation

Fig. 6 shows the effect of feed phase pH on the performance of SILM. In this experiment, the feed phase pH was varied from 4 to 7.5 by adjusting with 1 M HCl or 1 M NaOH solution, 0.1 N NaOH was used as a stripping agent as mentioned above. From Fig. 6, it was noted that the pH of feed phase did not have much positive effect on the removal of phenol. The highest permeation rate of 75.70% was achieved by [CYPHOS-104] at pH 4. Similarly, at pH 7.5 the rate of permeation was 69.86% for the same IL. It was found that phenol permeation rate was increased only by ~6% when the feed phase pH was varied from 4 to 7.5. Phenol exists in two different forms in aqueous phase depending on its pK_a value. The pK_a value of phenol is approximately within 9.2–9.6 as reported elsewhere [12]. If the pH of the solution containing phenol is higher than the pK_a value, then phenol dissociates to form phenolate ions ($C_6H_5O^-$) and below its pK_a value, phenol exists in its molecular form [29]. It was reported earlier by several researchers that at pH ≥ pK_a, there

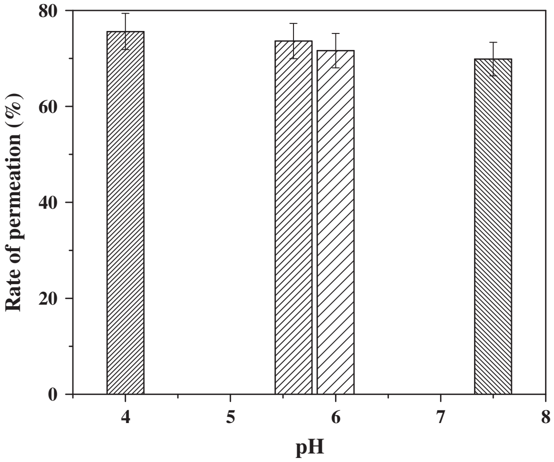


Fig. 6. Effect of feed phase pH on performance of SILM.

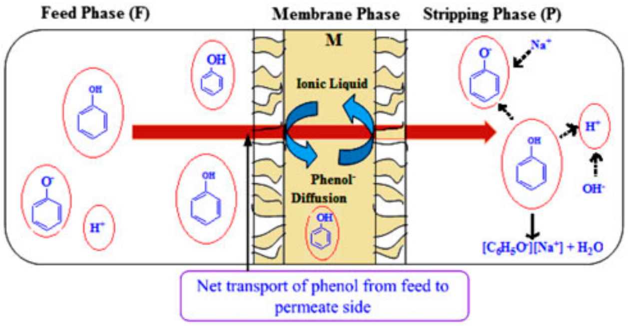


Fig. 7. Transport mechanism of phenol from feed to permeate side.

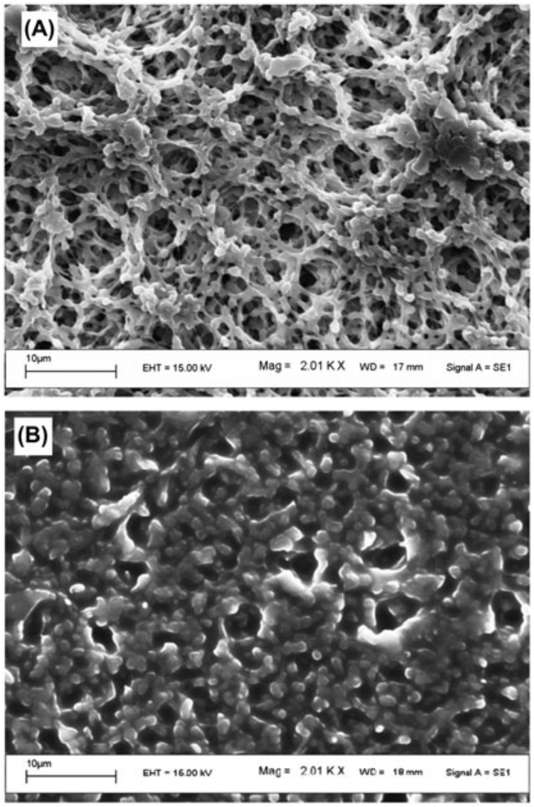
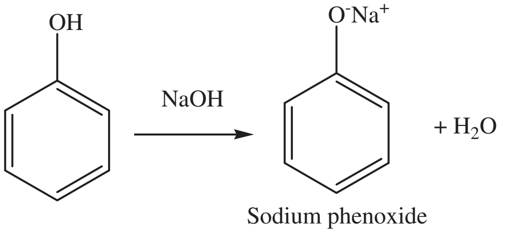


Fig. 8. (A) Scanning electron micrographs of the blank PVDF membrane. (B) Scanning electron micrographs of the PVDF membrane impregnated with $[C_8MIM][PF_6]$.

was drastic decrease in phenol removal. That is why in this work, feed phase pH was varied from 4 and 7.5. Shen et al. [30] have come up with similar conclusion for the phenol recovery with tributyl phosphate in a hollow fiber membrane contactor. The extraction process decreased because of the increase in the dissociation of phenol at $pH > pK_a$, which is in agreement with the results reported by Reis et al. [31]. Similar kind of phenomenon was also observed by Fan et al. [12], Vidal et al. [32], and Khachatryan et al. [1].

3.5. Phenol transport mechanism

Fig. 7 illustrates the detailed transport mechanism of phenol in SILM. It was envisaged that diffusion of phenol from feed phase to stripping phase through SILM occurred via simple permeation process. From the previous section, it was confirmed that phenol remains in its molecular form under $pH < pK_a$; hence, phenol in molecular form was transported via SILM. The proposed mechanism (Fig. 7) consists of molecular form of phenol dissolved in SILM due to its high distribution coefficient between trihexyl(tetradecyl) phosphonium bis(2,4,4-trimethylpentyl)phosphinate ([CYPHOS® 104]) and water. The extraction of phenol depends on formation of H-bonding between the molecular phenol and the anion of the IL. The IL here may act as H-donor. Molecular phenol in the feed solution diffused towards the interface. The formation of a complex between phenol and IL takes place, which then permeates through the membrane to the receiving phase due to the concentration gradient, where it reacts with 0.1 N NaOH to produce sodium phenolate ($C_6H_5O^-Na^+$) (Eq. (4)). In most cases, the phenolic compounds have very weak tendencies to lose the H^+ ions from the hydroxyl group, leading to the formation of sodium phenolate ion and water [29]. Since sodium phenolate is insoluble in membrane phase, it was trapped in the stripping phase and under the present experimental conditions, it cannot diffuse back to the feed phase.



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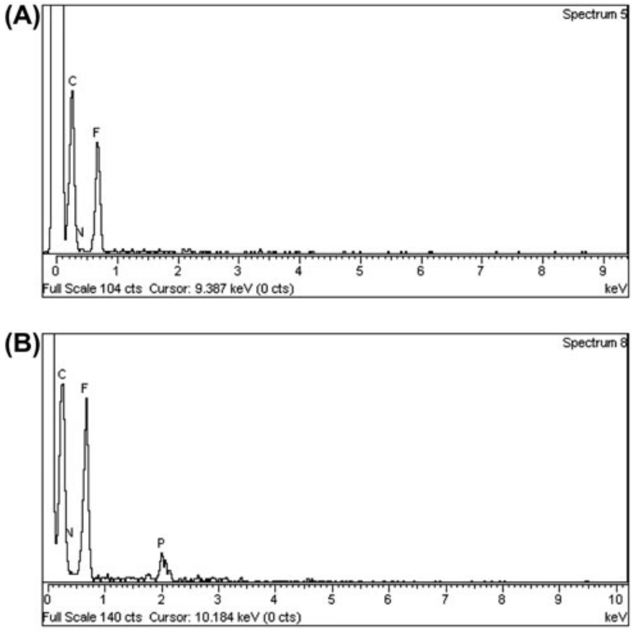

Fig. 9. (A) EDX spectra of the PVDF membrane without IL and (B) EDX spectra of the PVDF membrane impregnated with $[C_8MIM][PF6]$.

Sodium hydroxide concentration (stripping phase) was varied from 0 to 0.5 N to study the effect of concentration of the stripping agent. The phenol removal percentage at these concentrations for the experimental run of 4–10 h showed that the concentration of NaOH is not a significant factor for phenol removal. This agrees well with the findings of Wang and Hu [33] and Venkateswaran and Palanivelu [16].

3.6. Characterization of PVDF membrane

Characterization of the membrane surface morphology was done by SEM (*LEO, Model 1430VP*) and energy dispersive X-ray (EDX) analysis. The characterization of membrane was used to study the influence of the vacuum immobilization method on the SILMs performance [34]. SEM micrographs gave the morphological information of the distribution of the IL within the membrane pores, where as the EDX spectra gave elemental composition of the membrane. Fig. 8(A) and (B) shows examples of SEM micrographs of a blank PVDF membrane and supported liquid membranes based on [C$_8$MIM][PF$_6$], respectively. From Fig. 8(A), it can be observed that pores of the PVDF membrane were completely unfilled and no material was present inside the pore. Fig. 8(B) shows the morphological study of membrane after vacuum immobilization technique with [C$_8$MIM][PF$_6$]. The surface morphology study showed that the IL was homogeneously distributed within the smaller pores of the membrane, whereas the larger macropores were partially filled with IL. From Fig. 8(B), it can be seen that a small amount of excess IL was found to settle on the external surface of the membrane. The ILs are predominantly viscous in nature, which is the reason that some amount of IL accumulated and settled on the surface of the membrane. In this case, low viscous ILs are more desirable as they can completely fill the pores of the membrane but do not settle on the surface of the membrane. Nevertheless, low viscosity ILs suffer from mechanical stability.

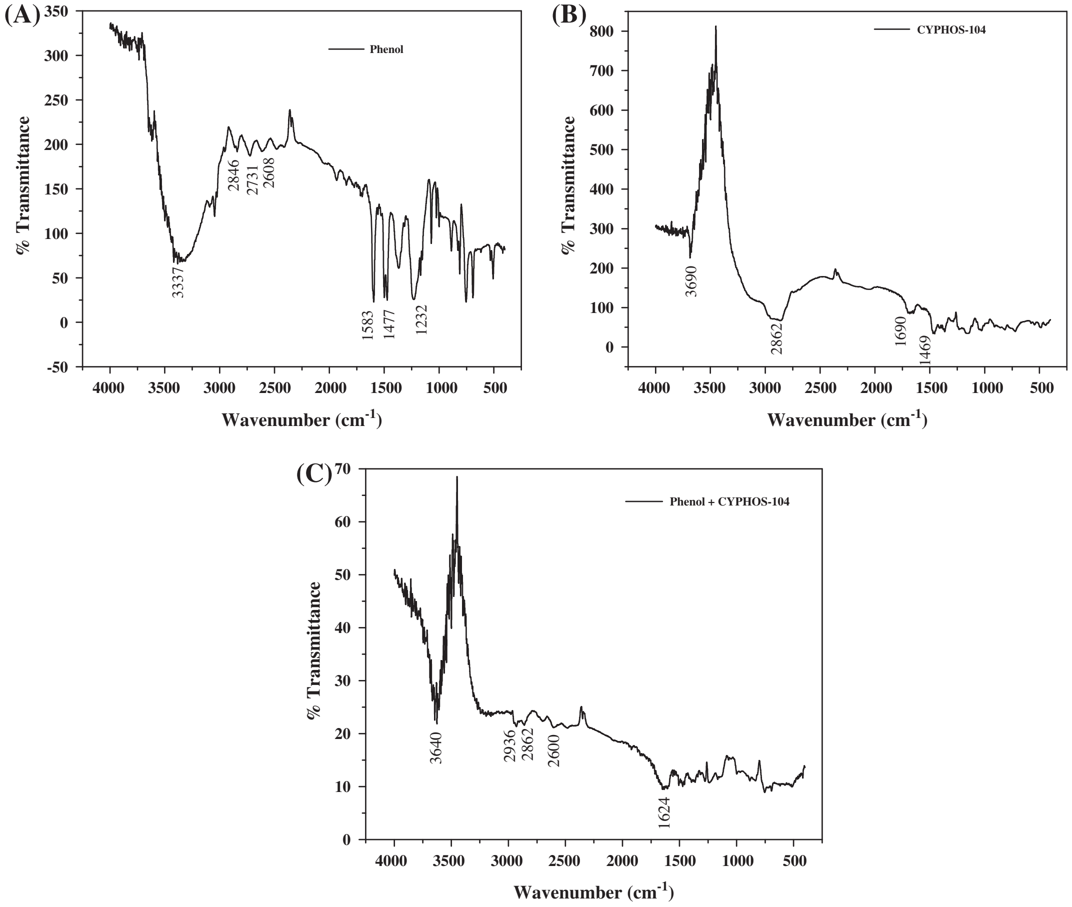

Fig. 10. (A) The IR spectra of pure phenol. (B) The IR spectra of pure IL (CYPHOS-104). (C) The IR spectra of mixture of phenol and CYPHOS-104.

The EDX spectrum of the PVDF membranes was analyzed before and after immobilization with the IL as shown in Fig. 9(A) and (B), respectively. The EDX comparison study of SILMs was based on the selection of characteristic elements of interest in IL. In case of Fig. 9(A), identified elements were C and F, where as F is common in both the spectra, since membrane is made of the fluorosurfactant perfluorononanoic acid. From Fig. 9(B), it was clear that elements P and N were observed as it originated from [C_8MIM][PF_6] composed of sodium hexafluorophosphate and 1-octyl-3-methylimidazolium chloride as discussed in synthesis section.This confirmed that the IL remains in the pores of the PVDF membrane support throughout the experimental run of 24 h.

Fig. 10(A)–(C) shows the IR spectra (Shimadzu, Japan, model: IRAffinity-1) of pure phenol, pure IL (CYPHOS-104), and mixture of phenol and IL. All the IR peaks of phenol (Fig. 10(C)) are broadened and shifted from their parent positions because of the solubility of phenol in IL. There is also large change in intensities of IR peaks. Some additional bands appeared in the spectra of combination of phenol and CYPHOS-104 (Fig. 10(C)) compared with individual spectra's of phenol (Fig. 10(A)) and CYPHOS-104 (Fig. 10(B)) such as stretching band at 3,640, 2,936, 2,600, and 1,624 cm^{-1}, which indicated the presence of O–H (H-bonded), =C–H, =CH_2, and substituted C–O. The additional peaks observed were due to the impurities present.

4. Conclusions

The present study confirmed that the phosphonium-based ILs were alternative greener solvents for the removal of phenol from the aqueous solutions using supported liquid membrane technique. Initial feed concentration of 100 mg L^{-1} of phenol was used for all the experiments. SILM was prepared through vacuum immobilization method. Effect of time on the concentration of phenol in both feed and stripping phase for different ILs was analyzed. About 73.63% of the phenol present in the feed phase was transported to stripping phase within 24 h at feed phase of pH 5.6 using [CYPHOS® 104]. By adjusting the feed pH to 4, [CYPHOS®104] gave the maximum permeation rate of 75.70% over an experimental run of 24 h. It was noteworthy that the effect of feed phase pH on phenol removal using SILM was negligible. The stirring speed of 300 rpm was found to be optimum for highest rate of permeation. [CYPHOS® 104] gave highest permeation rate among the six different ILs used. The concentration of NaOH used as stripping agent was found to be insignificant. The operational stability and performance of the supported liquid membranes was studied. Superior operational performance was found and results of this study indicated that the designed SILM may be used in future separation processes for removal of organic compounds.

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