



# Performance evaluation of supported ionic liquid membrane for removal of phenol

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## ABSTRACT

This work evaluates the performance of ionic liquid in supported liquid membrane (SLM) for the removal of phenol from wastewater. Ionic liquids are organic salts entirely composed of organic cations and either organic or inorganic anions. Due to the fact that the vapor pressure of ionic liquid is not detectable and they are sparingly soluble in most conventional solvents, they can be applied in SLM as the organic phase. In this work, 1-*n*-alkyl-3-methylimidazolium salts,  $[C_n\text{MIM}]^+[\text{X}]^-$  have been investigated so as to determine an optimal supported ionic liquid membrane. The effect of operational parameters such as pH, stirring speed and the concentration of stripping agent has been studied, and an evaluation of different membrane supports were also carried out. With a minimal amount of the ionic liquid 1-Butyl-3-methylimidazolium hydrogensulfate, 85% phenol removal could be achieved by using polytetrafluoroethylene hydrophobic membrane filter in the SLM.

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## 1. Introduction

Phenol is considered an environmental pollutant due to its toxicity and carcinogenic effect, therefore, its elimination from industrial wastewater is of great importance. It is found in effluent of refineries, coking operations, coal processing, resin production, pulp and paper industries, wood product industries, paint and anti-septics [1–4], and its concentration in such effluents varies from 100 ppm to several percentages. It is used in the production of many chemicals such as dyes, adhesives, germicides, and chemical intermediates [5], so it is considered as a valuable chemical. Hence, the recovery of phenol results in achieving two objectives: prevention of environmental pollution and obtaining valuable phenolic compounds [6].

Supported liquid membrane (SLM) technique has acquired increasing attention among membrane methods. In this method, two aqueous phases are separated with a polymeric support which is impregnated with an organic phase containing a complexing agent. The solute can be transported from the feed phase to the strip solution through the supported membrane [7]. Combining the extraction and stripping processes in a single step and an insignificant amount of membrane liquid requirement propose some advantages such as possible usage of expensive carriers, high separation factors, easy scale-up, low energy requirements, low capital and operating costs [8,9]. SLM is an alternate approach to emulsion

instability in emulsion liquid membrane because the organic liquid phase is immobilized within a porous structure [10], as demonstrated in Fig. 1. Different configurations of membrane supports are available, such as plate and frame, spiral, tubular and hollow fibers [11] and among them, flat sheet supported liquid membrane (FSSLM) and hollow fiber supported liquid membrane (HFSLM) are the commonest. For a laboratory scale, a two-compartment cell is popular [9].

The most significant drawback of the SLM is lack of long term stability due to emulsification at the membrane–aqueous interfaces and another reason is that the osmotic pressure difference across the membrane displaces the organic solution from the micropores of the support. This can eventually lead to mixing of the feed and strip solutions and then to complete failure of the separation process. Attempts have been made by researchers to overcome this drawback by stabilizing SLM [12]. There are two characteristics attributed to the instability of SLM, i.e. the flux decreases with time because of the loss of the carrier and/or solvent from the support and leakage of the aqueous solution due to direct channeling of aqueous solutions between the feed and strip phases [13].

In a SLM process, phenol diffuses from the feed phase to the membrane phase, permeates through the membrane phase and reaches the stripping phase where it reacts with sodium hydroxide. The permeated phenol is converted into sodium phenolate which cannot diffuse back to the feed phase because of its insolubility in the membrane. The transport through the membrane is driven by concentration gradient of the solute across the membrane and results in permeate dissolution in the membrane and its diffusion

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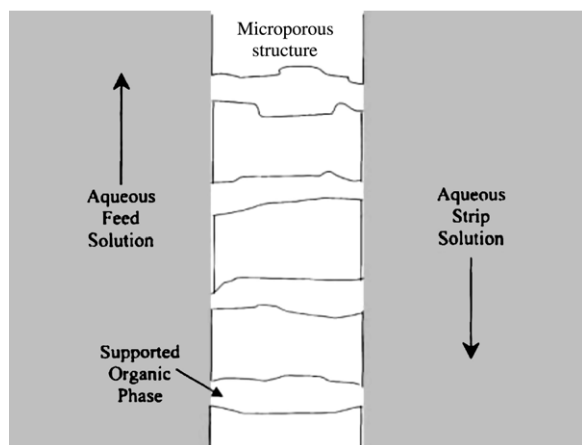


Fig. 1. Schematic of a supported liquid membrane [11].

through the membrane phase. The extraction will continue, as long as the concentration gradient is present and SLM operates with no equilibrium limitation [14–16].

Ionic liquids are organic salts entirely composed of organic cations and either organic or inorganic anions. Their melting point is under 100 °C and most of them have melting points around or less than ambient temperature which are called room temperature ionic liquids (RTIL) [17]. In fact, their vapor pressure is negligible so that they can be handled easily and this characteristic creates their “green” nature [18]. In fact, their vapor pressure is negligible so that they can be handled easily and this characteristic creates their “green” nature [18]. Their application is attractive due to minimization of solvent loss, less exposure to hazardous vapors and low toxicity [19,20].

Weingartner [18] also reported that ionic liquids are able to dissolve a considerable amount of a molecular solvent while their solubility in it is negligible. Furthermore, they cannot be mixed with nonpolar hydrocarbons and the hydrophobic types do not solvate polar solvents with ascending cohesive energy density such as water [18]. One of the alluring aspects of ionic liquids is tunability. The physical and chemical properties of ionic liquids such as density, melting point, viscosity and solubility in solvents can be controlled by choosing different anions and cations [21,22].

In consequence of having unique properties, ionic liquids have been investigated for various applications in industries. Wei et al. [23] claimed that liquid–liquid extraction can utilize hydrophobic and water immiscible ionic liquid to elicit hydrophobic substances. In this work, 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF<sub>6</sub>] as a solvent for heavy metal extraction.

Vasudeva Rao et al. [22] demonstrated the various prospective roles of ionic liquids such as extractant, diluent and electrolytic medium. Chakraborty and Bart [24] successfully utilized 1-methyl-3-octyl imidazolium chloride [OMIM]Cl in a bulk liquid membrane for the separation of toluene from *n*-heptane. In the extraction of rare earth elements, [Bmim][PF<sub>6</sub>] was found to be able to extract metal ions selectively and effectively in comparison to a common diluent such as *n*-dodecane [25]. However, liquid–liquid extraction demands a large amount of ionic liquids which are costly in comparison to the conventional organic solvents. As liquid membrane techniques require fairly less amount of ionic liquids as carrier whereas they could be good substitutes for extraction process [26–28]. Especially they can simply be recovered by washing or distillation process [29,30].

Due to the fact that the vapor pressure of ionic liquids is not detectable and they show diminished solubility with various kinds of solvents, their application as the organic phase in SLM seems very appealing [31,32]. Their high viscosities and interfacial ten-

sions and consequently the larger capillary force can reduce liquid displacement from micropores of the support and this improves the stability of SLM [33]. Ionic liquids also improve the mechanical stability of SLM because of their enhanced moisturizing properties [34]. Physicochemical properties of ionic liquids such as viscosity, water solubility in ILs and their solubility in water affect the transfer rate and the stability of the SLM. The supporting membrane material is another influential factor on the SLM stability [35]. It is also reported that a suitable selection of the cation and anion minimizes their solubility in the surrounding environment [36,37]. Additionally, other properties of ionic liquids such as high thermal stability, high ion conductivity and non-flammability favor their use in SLM [38].

Selective transport of organic compounds by Branco was the first application for ionic liquids in a SLM [39,40]. In more recent reports [38,41,42], there were more research on selective separation of organic compounds such as acids, alcohols, ketones, esters, amino acids and amines by supported ionic liquid membranes (SILM). Fortunato et al. [31] evaluated the use of ionic liquids, the 1-*n*-alkyl-3-methylimidazolium cation [c<sub>n</sub>mim][X] base in SLM for the separation of isomeric amines. Izák et al. [27] applied a hydrophobic IL, tetrapropylammonium tetracyanoborate [(C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N][B(CN)<sub>4</sub>], in a pervaporation process. The selective separation of substrates and products of a transesterification reaction was accomplished in SLM with ionic liquids based on 1-*n*-alkyl-3-methylimidazolium cation (*n*-butyl, *n*-octyl) and the hexafluorophosphate anion, as the liquid phase [41]. Aromatic hydrocarbons were successfully transferred through an ionic liquid used as a membrane liquid in a SLM without any carrier by Matsumoto et al. [43]. They claimed that ionic liquids improved the selectivity of aromatic compounds significantly rather than helping their permeation rate.

Many industrial applications have been prevised for ionic liquids but drawbacks such as cost, high viscosity and toxicity limit these applications. The unavailability of data for toxicity and physicochemical properties also restricts the use of ionic liquids in designing processes. Hence, generating these data can enhance their usage as green solvents [44]. Notwithstanding these drawbacks, ionic liquids have been used for the extraction of several phenolic compounds [19,45–47] but there is no published information on the removal of phenol by SILM. This work evaluates the performance of ionic liquid in SLM for the removal of phenol from wastewater. Several ionic liquids were investigated for the optimal use in SILM. Selection of a suitable ionic liquid, evaluation of different membrane supports, the effect of pH, stirring speed and the concentration of stripping agent have been discussed.

## 2. Experimental procedure

### 2.1. Reagents and membranes

Phenol was purchased from Merck, Malaysia and sodium hydroxide (NaOH) pellets (99%) were provided from R & M Chemicals, Malaysia. The ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF<sub>6</sub>], 1-Butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide [BMIM][NTF<sub>2</sub>], 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF<sub>4</sub>], 1-Hexyl-3-methylimidazolium hexafluorophosphate [HMIM][PF<sub>6</sub>], 1-Hexyl-3-methylimidazolium tetrafluoroborate [HMIM][BF<sub>4</sub>], 1-Ethyl-3-methylimidazolium hydrogensulfate [EMIM][HSO<sub>4</sub>], 1-Butyl-3-methylimidazolium hydrogensulfate [BMIM][HSO<sub>4</sub>], 1-Butyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate [BMIM][FAP], Trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide [PH<sub>3</sub>T][NTF<sub>2</sub>] and tri-*n*-octyl methyl ammonium chloride (TOMAC) were supplied by Merck, Malaysia. Deionized water was used for

preparing the chemical solutions. All of the chemicals were used as received. Fluoropore (FHP), Durapore (HVHP) and Mitex (LCWP) hydrophobic membrane filters were products of Millipore, Ireland. MS PTFE membrane filter was purchased from Membrane Solutions, China.

## 2.2. Analytical methods

The concentration of each sample was measured by UV–vis Spectrophotometer SECOMAM uviline 9400 at the wavelength of 270 nm for phenol and 288 nm for sodium phenolate. pH was measured with pH meter Cyber Scan pH300 and Rheintacho Rotaro Tachometer was used for stirring speed determination. Solutions were stirred mechanically by IKA Lab-Egg Overhead Stirrer RW11. AND Vibro viscometer was employed to measure viscosity of ionic liquids.

## 2.3. Preparation of supported liquid membranes

Hydrophobic microporous membranes were impregnated with a 100% solution of ionic liquids for at least 24 h before use. After the impregnation, the excess ionic liquid was wiped out from the surface of the membrane with a tissue paper. The cleaning procedure was done gently to assure that no ionic liquid was removed from the membrane pores. Then, the membrane was applied between the feed and strip cells as demonstrated in Fig. 2. A new supporting membrane was used in each experiment. The amount of ionic liquid loaded in the supporting membrane was determined by weighing the membrane before and after impregnation with the ionic liquid.

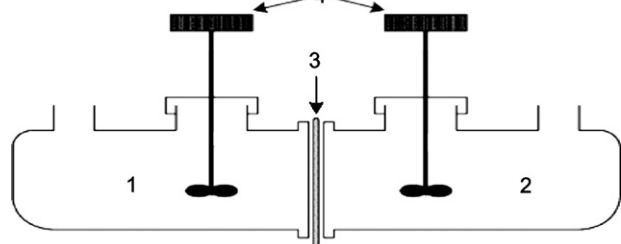
## 2.4. Experimental setup

Phenol removal in the SLM was evaluated at the ambient temperature using a glass diffusion cell with two separated compartments, as shown in Fig. 2. Each compartment contained 50 ml of the process solutions. The initial concentration of phenol in feed solution was 500 ppm. NaOH was used as a receiving phase and its concentration was varied according to each experiment. Both solutions were mechanically stirred to reach homogeneity. The sampling of the feed solution was accomplished at particular time intervals and in a defined period of time so as to observe phenol concentration change.

## 2.5. Transport studies

The phenol removal process was monitored through the change of solute concentration in the feed phase. The removal percentage was calculated using Eq. (1):

$$\text{Removal}(\%) = \frac{c_0 - c_1}{c_0} \times 100 \quad (1)$$



**Fig. 2.** Schematic illustration of the glass diffusion cell set up with two independent compartments used for experiments: (1) feed solution containing solutes; (2) receiving solution containing stripping solution; (3) supported liquid membrane; (4) stirrers.

where  $c_0$  is the initial and  $c_1$  is the final phenol concentration in the feed compartment.

## 3. Results and discussion

### 3.1. Selection of ionic liquids

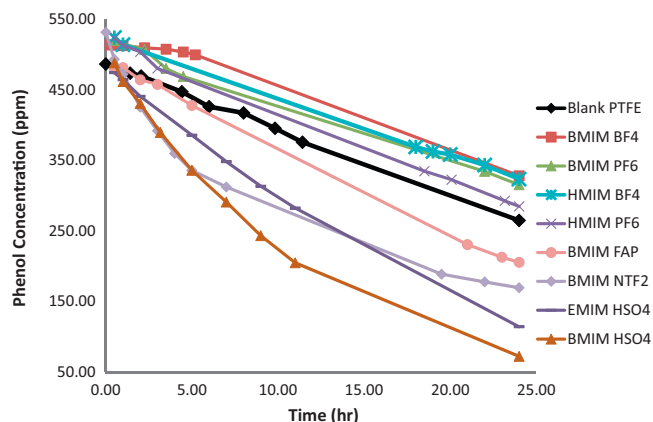
As illustrated in Fig. 3, the distinctive performance of each ionic liquid indicates that the choice of ionic liquid is important. Fan et al. [47] suggested that the hydrogen bonding and hydrophobic interactions between ionic liquid and phenols can ease the transfer of phenols from aqueous solution towards the ionic liquid phase, assisting phenol removal. In this regard, hydrogen bonding of anion and hydrophobic action of imidazolium cation play a significant role in phenol distribution ratio. Molecular form of phenol favors the hydrogen bonding interactions and consequently higher distribution ratio.

Zhao et al. [45] employed [BMIM][PF<sub>6</sub>] as an extractant for phenolic compounds. Additionally, [C<sub>n</sub>MIM][BF<sub>4</sub>] ( $n=1, 3, 6, 8, 10$ ) and [C<sub>n</sub>MIM][PF<sub>6</sub>] ( $n=6, 10$ ) were also introduced for the removal of phenol. Bis (trifluoromethylsulfonyl)imide (NTF<sub>2</sub>) anion is proposed by Poole and Poole [19] as an efficient phenol extractant. According to Merck Chemicals, [BMIM][FAP] has the most hydrophobicity among all the ionic liquids. Therefore, in this study its application in SILM for the removal of phenol was examined. BASF proposed an acidic ionic liquid [EMIM][HSO<sub>4</sub>] to extract phenol [48]. TOMAC is a typical extractant which has been used as a cation exchanger at low pH and as anion exchanger at high pH values [49].

The experiment with TOMAC was stopped after a few hours, due to the instant formation of a milky color in the feed compartment. It can be attributed to a reaction between TOMAC and the feed solution. Moreover, phenolate was measured in the feed side by UV analysis and this emphasized that the SLM with this ionic liquid was not stable. pH change of the feed solution is another parameter which can be considered as a failure for the process. Once the pH gets close to the one of stripping solution, it indicates leakage and direct channeling is occurring.

In comparison to the results for [BMIM][BF<sub>4</sub>], better removal was achieved using [HMIM][BF<sub>4</sub>]. This means that enlarging the length of alkyl chain in the cation can improve the performance of ionic liquid. The same conclusion can be achieved for [BMIM][PF<sub>6</sub>]/[HMIM][PF<sub>6</sub>] and [EMIM][HSO<sub>4</sub>]/[BMIM][HSO<sub>4</sub>]. This is also in close agreement with the research done by de los Ríos et al. [36].

Fig. 3 shows that ionic liquids with the same cation but various anions performed significantly different and this con-



**Fig. 3.** SLM performance comparison of different ionic liquids for phenol removal.

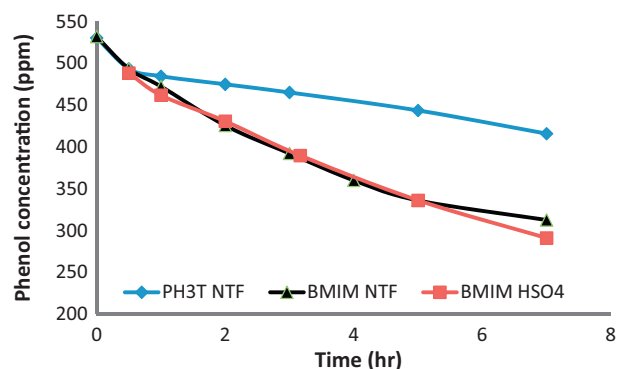


Fig. 4. SLM performance comparison for [BMIM][HSO<sub>4</sub>], [BMIM][NTF<sub>2</sub>] and [PH<sub>3</sub>T][NTF<sub>2</sub>].

Table 1  
IL loading on the solid support and its stability.

IL	BMIM NTF <sub>2</sub>	BMIM HSO <sub>4</sub>	Blank
IL loading (g)	0.08	0.02	–
Viscosity at 25 °C (mPa s)	78	4200	–
Phenol removal at 24 h	57	85	45
Stability time (h)	Less than 7	More than 24	More than 24

firmly that the role of anion is of principal importance. For the first 6 h of the process, [BMIM][NTF<sub>2</sub>] performed well in the extraction of phenol from the feed phase, but its performance diminished with time. Moreover, the stability of the liquid membrane lasted for around 6 h, and this was shorter than that of [EMIM][HSO<sub>4</sub>] and [BMIM][HSO<sub>4</sub>]. Stability failure was confirmed observing through the UV absorbance spectra showing phenolate and imidazolium cation peaks. Generally, ionic liquids containing HSO<sub>4</sub><sup>−</sup> anion showed both good performance and stability. Nevertheless, [BMIM][NTF<sub>2</sub>] and [BMIM][HSO<sub>4</sub>] were chosen for more elaborate inspection on their functionality. Phosphonium ILs were reported to be among the highly hydrophobic ILs [50] which enhance the stability of SILM. Therefore, [PH<sub>3</sub>T][NTF<sub>2</sub>] was selected to investigate its ability to provide stability with the NTF<sub>2</sub> anion. Fig. 4 illustrates performance of [BMIM][HSO<sub>4</sub>], [BMIM][NTF<sub>2</sub>] and [PH<sub>3</sub>T][NTF<sub>2</sub>]. The supported membrane impregnated with [PH<sub>3</sub>T][NTF<sub>2</sub>] exhibited low removal efficiency although good stability was achieved. Therefore, since the extraction behavior of [BMIM][HSO<sub>4</sub>] and [BMIM][NTF<sub>2</sub>] were similar, both were chosen for the next phase of the experiments. While the drawback of SLM with [BMIM][NTF<sub>2</sub>] was instability, different supports were tested for stability improvements and the results are discussed in Section 3.2.

For two ionic liquids with high removal efficiency, the amount of ionic liquid embedded in the pores of the support, the removal percentage and time of stability are listed in Table 1. With only 0.02 g of [BMIM][HSO<sub>4</sub>] phenol can be removed from an aqueous solution of 500 ppm up to 85% in 24 h. [BMIM][HSO<sub>4</sub>] is considerably more viscous than [BMIM][NTF<sub>2</sub>]. The more stable liquid membrane with [BMIM][HSO<sub>4</sub>] can be ascribed to the high viscosity. It is also worth considering that [BMIM][NTF<sub>2</sub>] can extract phenol up to 35% while

Table 3  
Different solid supports with their IL loading and stability.

IL	BMIM NTF <sub>2</sub>				BMIM HSO <sub>4</sub>			
	Durapore	Mitex	Fluoropore	MS	Durapore	Mitex	Fluoropore	MS
IL loading (g)	0.14	0.05	0.03	0.08	0.13	0.13	0.03	0.02
Removal at 7 h (%)	–	13	20	37	–	13	35	42
Stability time (h)	0	5	3	<7	0	<7	<7	26

Table 2  
Characteristics of the hydrophobic supports.

Membrane type	HVHP	LCWP	FHLP	MS
Trade name	Durapore	Mitex	Fluoropore	–
Material	PVDF	PTFE	PTFE	PTFE
Porosity (%)	75	60	85	85
Thickness (μm)	125	130	175	65
Pore Size (μm)	0.45	10	0.45	0.45

being stable in the support. However, 57% removal was observed in 24 h when it had lost its capability to stabilize SLM.

### 3.2. Selection of support membrane

Phenol is being separated on the basis of solubility difference between the aqueous and the organic phase. In comparison to the hydrophilic support, the hydrophobic polymeric support membrane impregnated with liquid membrane lessens the mass transfer resistance [1]. Thus, in his work four different hydrophobic membrane filters were tested, and their characteristics are as in (Table 2). All the filters were initially positioned in between the two cells without embedding any ionic liquid or carrier on them in order to check the stability. All these blank solid supports showed good stability for more than 24 h, while phenol transferred to the stripping side due to the concentration gradient. Following that, all were impregnated with [BMIM][HSO<sub>4</sub>] and [BMIM][NTF<sub>2</sub>] and then inserted in the SLM for phenol removal experiments.

Durapore filter instantly failed, because after a few minutes, phenolate was detected in the feed solution, and this was caused by NaOH transfer. It was observed that after contacting this filter with ionic liquid, its characteristics changed and it became transparent indicating that a reaction might have occurred between them. Subsequently, Durapore which was made of Polyvinylidene Fluoride (PVDF) was eliminated from the experiments due to its failure. Thus, polytetrafluoroethylene (PTFE) material was chosen as proper membrane support for the SLM experiments, as also suggested by Venkateswaran and Palanivelu [1,51].

From Table 3 was found that Mitex support impregnated with [BMIM][NTF<sub>2</sub>] could not perform as a stable supported liquid membrane, since it has the largest pore size among the three PTFE membrane supports. Larger pore size leads to higher mass transfer and more flux, but they cannot hold the liquid membrane for longer time, hence smaller pore size improves the stability of the membrane [13,52–54]. Generally, the pore size, thickness and hydrophobicity of the membrane support affect SLM stability [52]. Membranes with less thickness could improve the permeabilities [55], as greater thickness results in more mass transfer resistance [31].

High porosity is favorable because it can support the liquid membrane under hydrostatic pressure which increases the stability [56]. Moreover, it enhances the transport efficiency by providing more surface area [57]. As a result, MS membrane support demonstrated better performance and stability with smaller size, more porosity and less thickness. Table 3 indicates that in all experiments with [BMIM][HSO<sub>4</sub>] embedded on different membrane supports the stability is attained with an appropriate removal efficiency, so, it was selected for subsequent experiments.

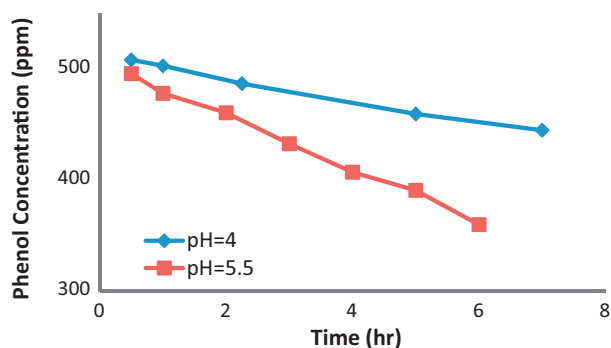


Fig. 5. Effect of pH on phenol removal.

### 3.3. The influence of pH on the removal efficiency

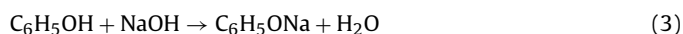
In high alkaline condition or basic solutions, phenol does not exist as a molecular form, so the hydrogen bonding and hydrophobic interactions between imidazolium cation of ionic liquid and phenol vanishes and this decreases the distribution of phenol in the ionic liquid [47]. It indicates that phenol cannot transfer to the ionic liquid and then to the stripping phase. Therefore, an acidic ambient was examined to investigate the removal process. In this particular section, for the set of experiments for the influence of pH, EMIM HSO<sub>4</sub> was used. The initial pH of the fresh feed phase was in the range of  $6 \pm 0.1$  and it was adjusted to 4 by adding hydrochloric acid (HCl) solution. Fig. 5 illustrates that the acidic pH of the feed phase did not have a positive effect on phenol removal. Increasing the acidity of the feed phase did not improve the phenol separation to the organic phase and this finding supported that of Shen et al. [55]. According to Reis et al. [3], up to pH value less than 8, the partition data of phenol in the organic phase were independent of the acidity of the feed phase and above this value, the extraction decrease due to the increase in the dissociation of phenol.



In Eq. (2), the backward reaction is fortified by lowering the pH [58]. According to several researchers, [5,19,47], in pH range of less than 7, phenol remains in the neutral form and this favors the extraction from the aqueous phase. Therefore, in the present work, the pH of the feed phase was not adjusted for the following experiments, since it was already less than 7. Once the pH of the feed phase rose gradually, there was a sign of failure due to the reverse movement of sodium phenolate from stripping phase to the feed phase.

### 3.4. Effect of NaOH concentration on phenol removal by SLM

Phenol diffuses from the feed phase to the membrane phase and then it permeates through the membrane to the stripping phase where it reacts with NaOH to produce sodium phenolate, according to Eq. (3). The new form of phenol cannot permeate back to the membrane phase, because it cannot be absorbed.



To investigate the effect of concentration of the stripping agent, the concentration of sodium hydroxide was varied from 0 to 1 M. Fig. 6 illustrates the phenol removal percentage at these concentrations for the experiments of 2, 5 and 7 h showed that the concentration of NaOH is not a very significant factor for phenol removal, i.e. the high amount of NaOH was unnecessary, and this is in agreement with Venkateswaran et al. [1].

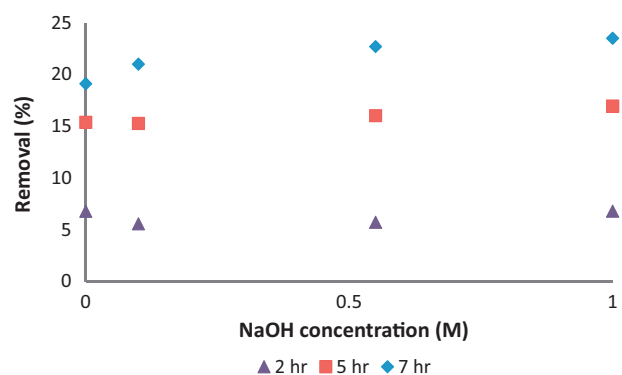


Fig. 6. Effect of concentration of NaOH at 450 rpm; after 2 h, 5 h and 7 h.

### 3.5. Effect of stirring speed

Stirring of both aqueous phases is to attain homogeneous mixing and to maintain a minimum thickness of aqueous diffusion boundary layer and to minimize the resistance to aqueous mass transfer [59].

As illustrated in Fig. 7, the phenol removal was independent of the stirring speed above 200 rpm and this demonstrates that the thickness of aqueous boundary layer had reached a minimum constant value. Further, at maximum stirring speed of 1000 rpm, a question of stability arose due to the high turbulence which brought about the displacement of carrier from the support. This finding is in agreement with the observations by Zha et al. [13], i.e. membrane loss is faster at higher speed and an increase in linear velocity of aqueous solutions shortens the SLM lifetime. A comparison between Figs. 8 and 9 indicates that at low NaOH concentration,

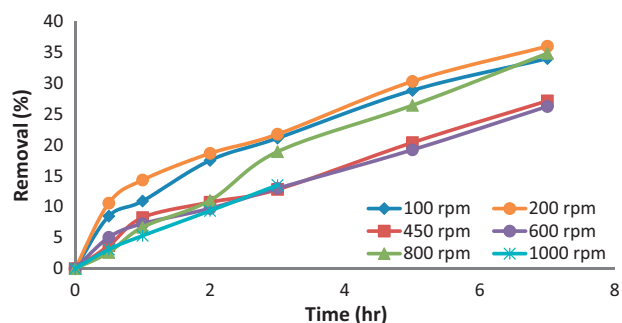


Fig. 7. Effect of stirring speed (concentration of NaOH: 0.55 M).

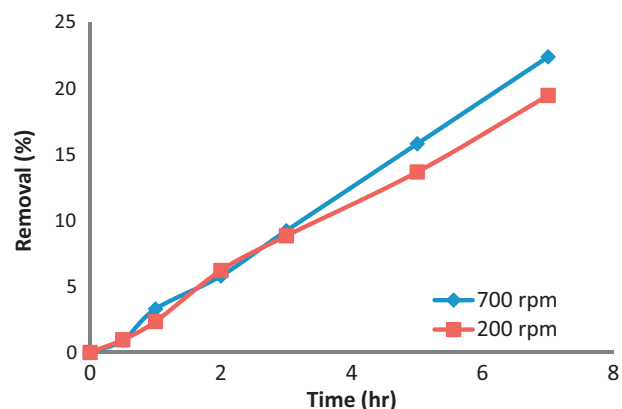


Fig. 8. Effect of stirring speed (concentration of NaOH: 0.23 M).

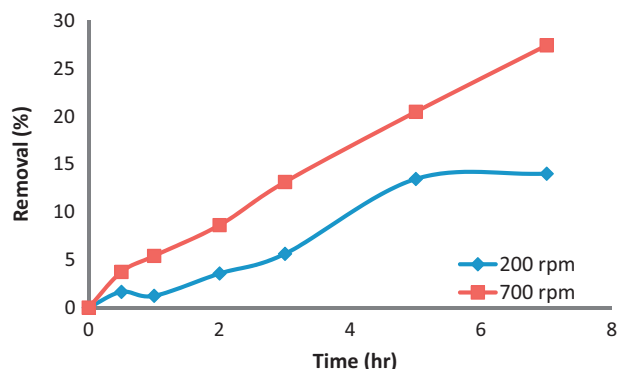


Fig. 9. Effect of stirring speed (concentration of NaOH: 0.87 M).

the stirring speed is insignificant although it becomes noteworthy at higher concentrations.

### 3.6. Effect of membrane preparation method

Owing to the high viscosity of ionic liquids, the SILM preparation method can affect the stability significantly. The preparation methods include applying pressure above atmosphere [36,37], vacuum technique [31,37] and immersion technique. The more common method is of the support in the liquid [60,61]. Hernández-Fernández et al. [37] recommended immobilizing low viscous ionic liquids under vacuum which is an easier method as well. However, for high viscous ionic liquids, applying pressure is to make sure that as much membrane pores as possible are filled with the liquid. In the present study, [BMIM][HSO<sub>4</sub>] being a high viscous ionic liquid, pressure method was employed for the purpose of comparing the performance and also the stability of the liquid membrane with the immersion technique. A two bar nitrogen pressure was applied to compel the flow of the ionic liquid into the pores, but no obvious difference in the performance was observed while applying pressure, in comparison to the immersion technique, as illustrated in (Fig. 10). It implies that in the immersion method, pores were filled properly due to sufficient soaking time and adequate amount of liquid. The stability of liquid membrane in the case of the pressure technique did not last long, and this can be attributed to water solubility of [BMIM][HSO<sub>4</sub>]. Direct channeling might have taken place through the membrane.

### 3.7. Stability

Stability is the principal limitation of the application of SLM. Liquid membrane solubility in aqueous phases, wetting of the support

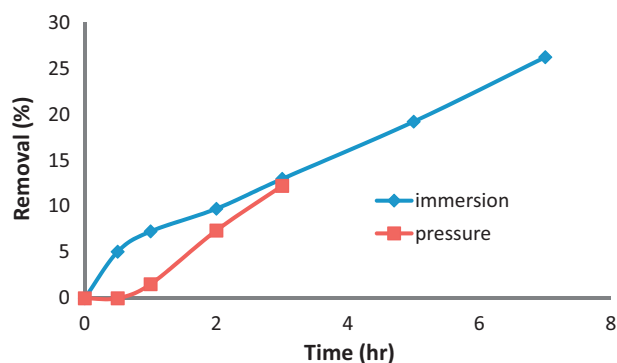


Fig. 10. Effect of membrane preparation method.

pores, osmotic pressure gradient or pressure difference over the membrane, shear induced phenomena and blockage of the pores are proposed by different researchers as the SLM instability mechanisms [62,63,12]. However, these mechanisms are not in the same level of influence and significance. Osmotic pressure mechanism is a controversial mechanism. According to Fabiani et al. [64] and Danesi et al. [65], osmotic pressure gradient could reduce the stability of the SLM, but the idea was first challenged by Neplenbroek et al. [66]. He explained that by an increase in osmotic pressure SLM stability improves and the water transport is not a reason but a cause of SLM instability and that is in contrast to the osmotic pressure mechanism. In the instability investigation for removal of phenol by Zha et al. [13] the same result was obtained and they claimed that the osmotic pressure difference was not the cause of SLM degradation. Moreover, in a recent research on phenol removal by Zheng et al. [67], the mechanisms of solubility and osmotic pressure are proved not to be important instability mechanism, although they are also contributed to the loss of ML. Emulsification is claimed to be the main mechanism of instability [13,63,67]. To improve the stability it is suggested to choose: low stirring speed, supports with smaller pore size and high hydrophobicity and also to reduce the factors which are favorable for the formation of emulsions such as high HLB (hydrophile–lipophile balance) value or water solubility [13,62,65]. In this study, a hydrophobic support with small pores was chosen. The membrane phase only contained ionic liquid and no surfactant was added. In the experiment with ionic liquid [BMIM][HSO<sub>4</sub>], no sodium phenolate was detected in the feed side for over the experimental run of more than 24 h and no proton leakage was observed in this time. Imidazolium cation was detected in the feed phase at the same time of phenolate detection. It can be attributed to the membrane solubility. Further investigation must be done to determine the dominant mechanism in the supported ionic liquid membrane systems.

## 4. Conclusion

In this study on SLM, it was demonstrated that up to 85 percent of phenol can be removed from wastewater by using the ionic liquid [BMIM][HSO<sub>4</sub>] with PTFE membrane filter. A stable SILM comprising of [BMIM][HSO<sub>4</sub>] and the hydrophobic PTFE support was achieved for over the experimental run of more than 24 h. The immersion technique with a sufficient amount of ionic liquid provides a stable membrane for the process. Although, NaOH concentration was not a significant parameter, it was required as the stripping agent to remove phenol efficiently. With a homogeneous mixing was achieved at stirring speed of 200 rpm, whereby there was no resistance to mass transfer.

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