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Performance Of Ionic Liquid As Bulk Liquid Membrane For Chlorophenol Removal

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Abstract: The emerging interest on room temperature ionic liquids (RTIL) as an alternative to conventional organic solvents is mainly due to their properties of negligible volatility, low vapor pressure and thermal stability. An experimental study on the extraction performance of ionic liquids for removal of chlorophenol was carried out in a bulk liquid membrane system. Three different ionic liquids with high hydrophobicity were used to study the removal efficiency for chlorophenol. The effects of extraction parameters, namely pH, concentration of the feed and concentration of NaOH were also investigated. The preliminary study shows that high chlorophenol extraction and stripping efficiencies of 98.10% and 78.5% respectively were achieved by ionic liquid membrane with a minimum membrane loss which offers a better choice to organic membrane solvents.

Keywords: Chlorophenol, Ionic Liquid, Liquid Membrane, Extraction efficiency, Stripping efficiency.

1. Introduction

Chlorophenolic compounds are often found in the waste discharges of many industries including petrochemical, oil refinery, plastic, pulp and insulation material[1-3]. Chlorophenols are used as bacteriacide, fungicide and preservative. According to the Environmental Health Criteria 93[4], chlorophenols are toxic and have a carcinogenic effect on human and aquatic lives when released to the environment. Fish kills have resulted from chlorophenol spills due to exposure to large quantities (0.1 – 5 ppm) of chlorophenols[4]. This gives adverse effect like impaired reproduction, impaired flavor of fish, reduced production of zooplanktons and thus disrupting the aquatic ecosystem balance. Chlorophenols has been included in the EPA National Priorities List (NPL) and maximum chlorophenol discharge concentration was set to 1 ppm[5]. Thus, finding out an effective method for the treatment of wastewater containing chlorophenol has become very essential.

In the recent years, liquid membrane has attracted the attention from the many industries. The liquid that serves as semi-permeable liquid which forms a barrier between the feed phase and the stripping phase and it transports the targeted solute selectively from one phase to another is termed as Liquid membrane[6,7]. This method combines the extraction and stripping processes in a single stage, thus providing lower capital and operating cost, technical simplicity, and independency on the transport equilibrium limitation[8-12]. Applications of liquid membranes in separation field have been reported by a number of researchers, mainly for the separation of organic compounds[7,9,13,14] and metal ions[11,16]. However, the utilization of organic membrane solvents such as hydrocarbons and chloroalkanes[7,9-11,13-15] have their drawbacks as they are usually volatile, flammable and often toxic, thus restricting their applications in the industries.

Room temperature ionic liquids are very simply molten salts. They are a group of low melting point salts that consist of organic cations and organic/inorganic anions. They have negligible vapor pressure, low flammability and are thermally stable. These unique properties serve them as an option to replace the volatile organic solvents. In the present study, imidazolium based ionic liquids were chosen as their physical and chemical properties are more readily available in comparison to other ionic liquids.[16-19] In fact, studies on liquid-liquid extraction of chlorophenol by imidazolium ionic liquids with [BF_4^-] and [PF_6^-] anions have solvents in terms of extraction efficiency. The effects of several parameters such as pH, operating temperature and volume ratio of ionic liquid/water on the extraction efficiency have also been evaluated[20-23].

Despite the favorable chlorophenol extraction efficiency in liquid–liquid extraction, the utilization of imidazolium based ionic liquid membrane for chlorophenol removal is less studied. Instead, they are some published information on the separation of other organic compounds such as toluene[24], aromatic hydrocarbons[25], trans-esterification products[12,26] and selective separation of 1-butanol, 1-propanol, cyclohexanol, 1,4-dioxane, cyclohexanone, morpholine and methyl-morpholine[27] by these ionic liquids. These works show that imidazolium based ionic liquid membranes provide selective transport with good stability. However, Fortunato et al[28,29]. and Matsumoto et al[30]. reported that the selectivities of ionic liquid membrane diminished when contacted with aqueous phase. According to them, this was mainly caused by the significant water solubility of these ionic liquids. The formation of water microenvironment path in imidazolium based ionic liquids with [BF_4] and [PF_6] anions reduced the membrane selectivities during the transport of water soluble compounds such as tritiated water, NaCl, amino acid, amino acid esters[28,29] and penicillin G[30].

In the present work, the technical feasibility of hydrophobic ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate [BF_4], 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim] [PF_6], 1-butyl-3-methylimidazolium chloride [Cl] when applied as bulk ionic liquid membranes for phenol removal was discussed. Bulk liquid membrane system was chosen as its simple configuration enabled the observation on the effect of ionic liquids on the phenol extraction and stripping efficiencies. The effect of different types of anion and hydrophobicity of the ionic liquids on the phenol extraction and stripping efficiencies were investigated.

2. Experimental

2.1. Materials

The chlorophenol crystals, ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim-BF_4], 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim-PF_6], 1-butyl-3-methylimidazolium chloride [Bmim-Cl] were supplied by Sigma Aldrich, hydrochloric acid and sodium hydroxide were supplied by SRL. Chlorophenol absorbance measurement was accomplished using UV–Vis Spectrophotometer (SL 159&150 Elico), laboratory stirrer was used for stirring speed determination and pH meter (LI 127&120 Elico) were also used in the experiments, mainly for pH measurement.

2.2. Preparation of solutions

Chlorophenol solutions were prepared by dissolving the theoretical amount of chlorophenol crystals into distilled water with different concentrations in a calibrated volumetric flask. Each solution was stirred for approximately 10 min to ensure the complete dissolution of chlorophenol. The same procedure was applied for the preparation of NaOH solution from the pellets. HCl solution was prepared by diluting the concentrated HCl with distilled water in a volumetric flask. The solution was stirred to ensure a well mixed solution.

2.3. Bulk ionic liquid membrane experiment

The experiment was carried out in a U-tube glass vessel with an inner diameter of 10 cm. The left limb of the U tube is feed compartment and the right limb is considered as stripping compartment. A volume of 10mL of ionic liquid was weighed and transferred into the cell above the bottom clearance. After that, 10mL each of 100 ppm chlorophenol solution and 0.5 M NaOH solution was transferred into the feed compartment and stripping compartment, respectively, where both phases were bridged by the ionic liquid. The aqueous phases were stirred by lab stirrers at 250 rpm at both the limbs, while the membrane phase was stirred by a magnetic stirrer at a fixed speed of 200 rpm. The duration of each experiment was 2 h. At different time interval, 1 mL of sample was taken from the feed phase and stripping phase using a pipette. The samples were then analyzed by UV–Vis Spectrophotometer, both extraction and stripping efficiencies were calculated, as discussed in Section 2.4.2. The experiments were repeated and the results obtained were within an experimental error of 5%.

2.4. Analytical method

2.4.1. Dilution of samples

The samples were diluted before analysis to make sure that the absorbance of the samples can be measured within detectable range of the UV–Vis Spectrophotometer. The feed samples were provided with an acidic environment by diluting it with 0.5 M HCl solution, thereby making the chlorophenol exist only in molecular form. The stripping samples were diluted with 0.5 M NaOH solution, thereby chlorophenol exists only in the form of cholorophenolate ion (sodium chlorophenolate). The chlorophenol absorbances were measured in wavelength of 270 nm in the feed samples and 288 nm for chlorophenolate ion detection in the stripping samples. The concentrations of chlorophenol and chlorophenolate in the samples were obtained by their absorbance–concentration calibration curves.

2.4.2. Determination of extraction and stripping efficiencies in bulk ionic liquid membrane

Chlorophenol extraction and stripping efficiencies were determined by the concentration of chlorophenol in each phase. The extraction efficiency was calculated using Eq. (1):

$$\textbf{Extraction Efficiency, \%} = \frac{\text{Initial Concentration} - \text{Concentration of feed samples}}{\text{Initial Concentration}} \times 100 \qquad (1)$$

The Stripping efficiency was calculated using Eq. (2):

$$\textbf{Stripping Efficiency, \%} = \frac{\text{Chlorophenol concentration in stripping samples}}{\text{Initial Concentration} - \text{Concentration of feed samples}} \times 100 \qquad (2)$$

The amount of sodium chlorophenolate in the stripping phase was converted to the theoretical amount of chlorophenol that should be present in the stripping phase for the determination of chlorophenol in stripping phase, based on the mole balance from Eq.(3).

$$ClC_6H_4OH + NaOH \rightarrow ClC_6H_4ONa + H_2O \qquad (3)$$

2.5. Reuse of ionic liquids

Ionic liquid used as liquid membrane was regenerated in line with the method that was published by Fan et al[22]. The ionic liquid was mixed vigorously for 30 min with equal volume of 0.5 M NaOH solution, the stripping agent was used to remove chlorophenol. The aqueous sample after phase separation was analyzed for sodium chlorophenolate concentration using the UV–Vis spectrophotometer. This procedure was repeated until there was no significant sodium chlorophenolate was detected in the NaOH solution. The ionic liquid was then washed with distilled water until a pH of 6.5–7.5 was obtained. The excess moisture in the recovered ionic liquid was removed by heating at 75 °C for 2 days[22]. Ionic liquid was then stored in a desiccator before it was being reused.

3. Results and discussion

3.1. Effect of different types of ionic liquids as membrane solvents

The performance of bulk ionic liquid membrane by different types of ionic liquids was evaluated in terms of chlorophenol extraction efficiency and stripping efficiency.

3.1.1. Extraction efficiency

In the current study, ionic liquids [Bmim][BF_4], [Bmim][PF_6] and [Bmim][Cl] were utilized as membrane solvents Fig. 1 shows that the extraction efficiency of bulk ionic liquid membrane is in the order of [Bmim][BF_4] > [Bmim][PF_6] > [Bmim][Cl]. The present work chlorophenol extraction efficiency increases due to the ionic liquids' hydrophobicity and hydrogen bond basicity[22]. Among the ionic liquids studied, [Bmim][BF_4] was the most hydrophobic ionic liquid showing the maximum extraction efficiency. The extraction efficiency was found to be more dependent on the strength of the hydrogen bond basicity of the ionic liquids, in the sequence of [Bmim][BF_4], [Bmim][PF_6] , [Bmim][Cl] [15,33,34].

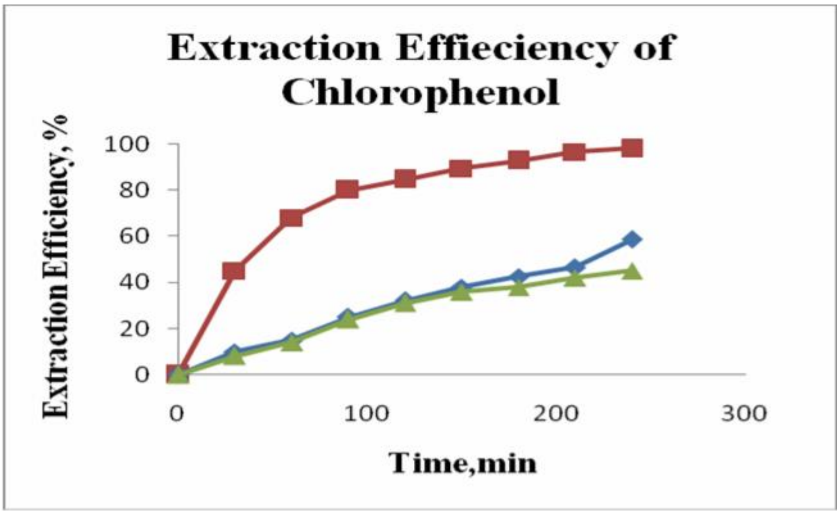

Fig.1. Extraction efficiency of phenol by bulk ionic liquid membrane
(Feed phase pH: ≈ 6.5; Feed concentration: 300 ppm; NaOH concentration: 0.5 M).

3.1.2. Stripping efficiency

Fig. 2 shows that the chlorophenol present in the ionic liquid membrane is effectively stripped down by NaOH. It was found that the efficiency of [Bmim][BF_4] was greater than [Bmim][PF_6] which was the same as [Bmim][Cl]. In bulk liquid membrane process, due to the high membrane thickness, the viscosity of the membrane solvent was significant on governing the stripping rate. [Bmim][BF_4] had the highest stripping efficiency among the ionic liquids studied as its viscosity was the lowest. It was also found that ionic liquid membranes of [Bmim][PF_6] and [Bmim][Cl] had similar chlorophenol stripping efficiencies even though the viscosity of [Bmim][Cl] was much lower than [Bmim][PF_6].

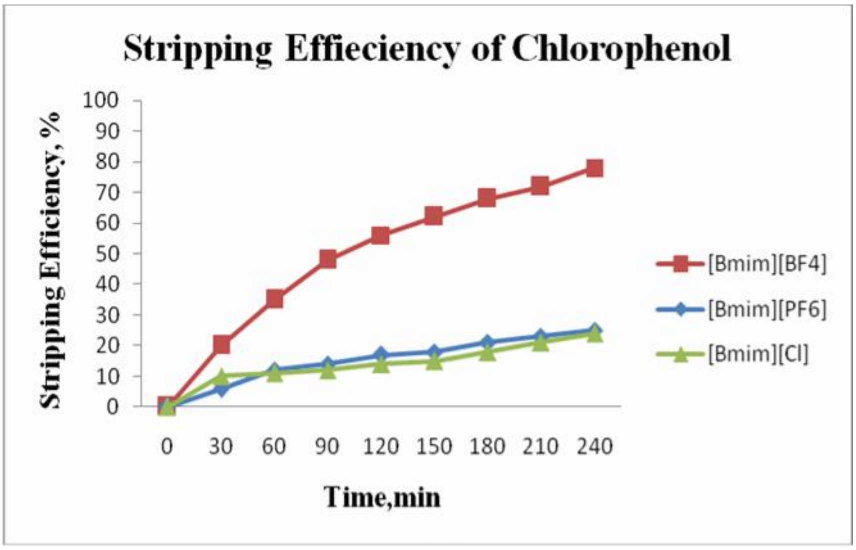

Fig.2. Stripping efficiency of phenol by bulk ionic liquid membrane (Feed phase pH: ≈ 6.5; Feed concentration: 300 ppm; NaOH concentration: 0.5 M).

3.2. Behavior of ionic liquid as bulk liquid membranes for phenol removal

The results in Section 3.1 show that ionic liquid membrane based on [Bmim][BF_4] gives higher extraction and stripping efficiencies than [Bmim][PF_6] and [Bmim][Cl]. Hence, the effect of feed phases pH, feed concentration and NaOH concentration on extraction efficiency and stripping efficiency on the performance of ionic liquid membrane was further studied.

3.2.1. Effect of feed phase pH

The pH of the feed phase was adjusted using NaOH and HCl solutions before the experiment. The form of chlorophenol present in the feed phase strongly depends upon the pH of the feed phase. Fig. 3 shows that when the feed phase pH is held below 6.5, the extraction efficiency of chlorophenol by [Bmim] [BF_4], [Bmim] [PF_6] , [Bmim] [Cl] based liquid membrane remains constant. However, there was a drastic decrease in the extraction efficiency when the pH was increased from 6.5 to 8 and 12.

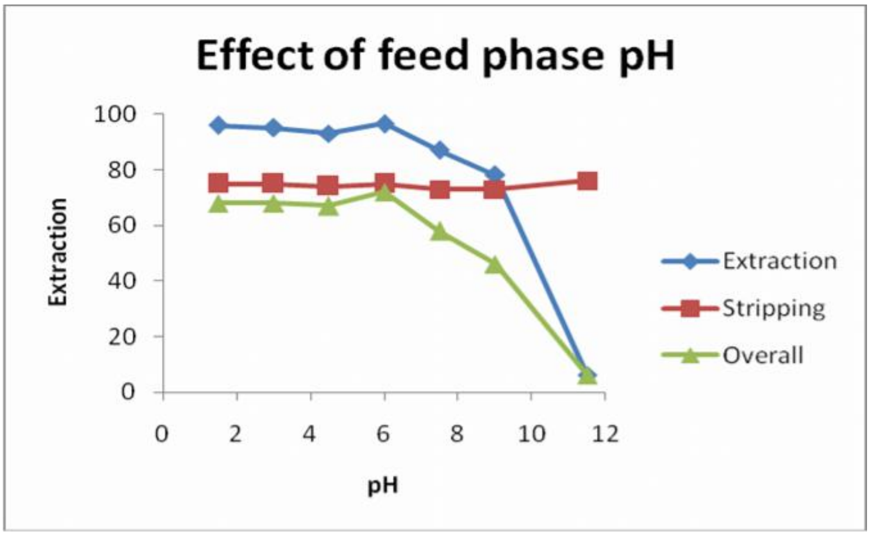

Fig.3. Effect of feed phase pH on the performance of bulk ionic liquid membrane (Feed concentration: 300 ppm; NaOH concentration: 0.5 M).

3.2.2. Effect of feed concentration

Fig.4 illustrates the feed concentration has less effect on the extraction efficiency. The feed concentration was increased from 250 to 5000 ppm, the final extraction efficiency remained 95%. This may be due to the high chlorophenol dissolving capacity of the ionic liquids, in addition to the simultaneous stripping process which prolonged the time required for saturation of the membrane. This leads to the undisturbed extraction efficiency.

Fig.5 illustrates the feed concentration's effect on stripping efficiency. High extraction rate was observed in high feed concentration due to the high capacity for the chlorophenol extraction in the ionic liquid membrane phase. The uneven high extraction and low stripping rates caused the increase of chlorophenol concentration in the membrane phase. This chlorophenol can be effectively made to get distributed to the stripping phase by effective stirring using magnetic stirrer. Thus, the stripping efficiency was increased as the feed concentration was increased from 1000 to 5000 ppm.

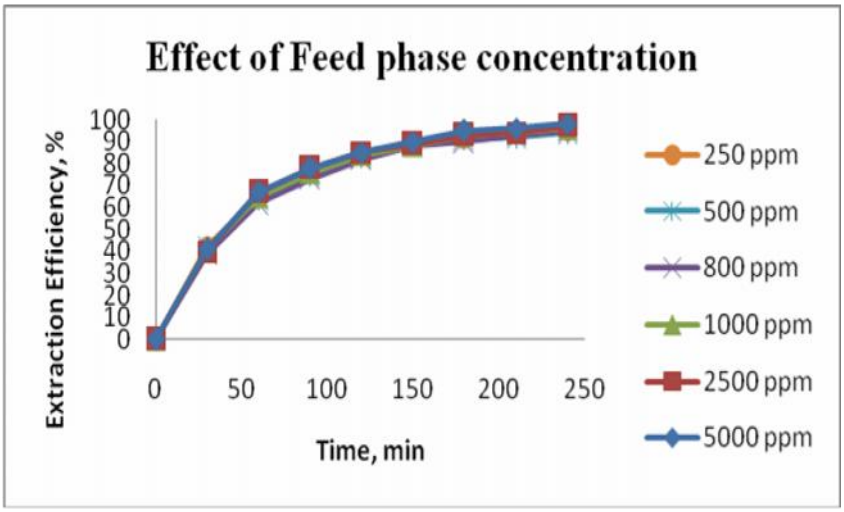

Fig.4. Extraction efficiency of phenol by bulk ionic liquid membrane at different feed concentrations (Feed phase pH: ≈ 5.8–6.5; NaOH concentration: 0.5 M).

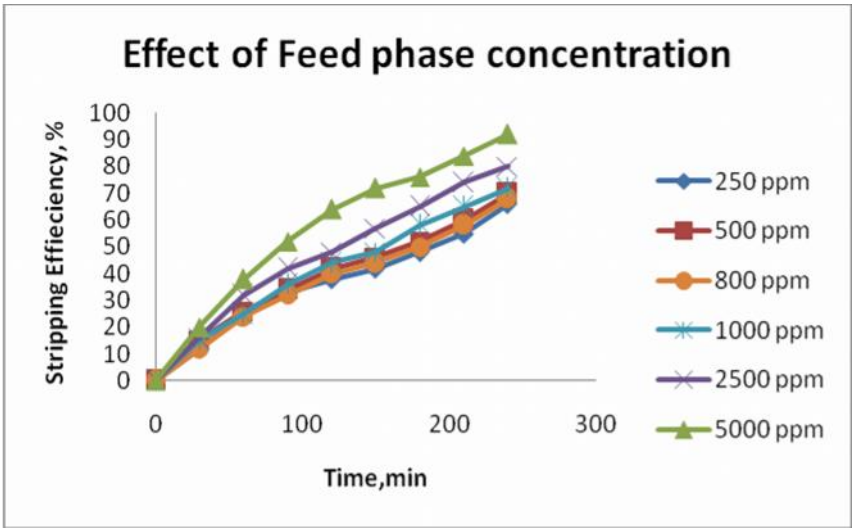

Fig.5. Stripping efficiency of phenol by bulk ionic liquid membrane at different feed concentrations (Feed phase pH: ≈ 5.8–6.5; NaOH concentration: 0.5 M).

3.2.3. Effect of NaOH concentration

Fig. 6 illustrates that the concentration of NaOH has less effect on the extraction efficiency of bulk ionic liquid membrane. A final extraction efficiency of 95% was achieved for the NaOH concentration range of 0.05–0.5 M while they had significant influence on the stripping efficiency of the system. Fig. 7 shows that the stripping efficiency increases in the following order: 0.05 M, 0.1 M, 0.15 M, 0.25 M, 0.5 M. In this study, NaOH concentration of 0.15 M (pH ≈11.7) was observed to be adequate to maintain the high stripping efficiency and beyond this concentration, the stripping efficiency remained the same. The activity of molecular phenol in the stripping phase is suppressed, as Chlorophenol reacts with NaOH in the stripping phase to form sodium chlorophenolate. The activity of unreacted molecular chlorophenol slowed down the stripping process by reducing the concentration gradient between membrane and stripping phases under low NaOH concentration, thus reducing the stripping rate and efficiency.

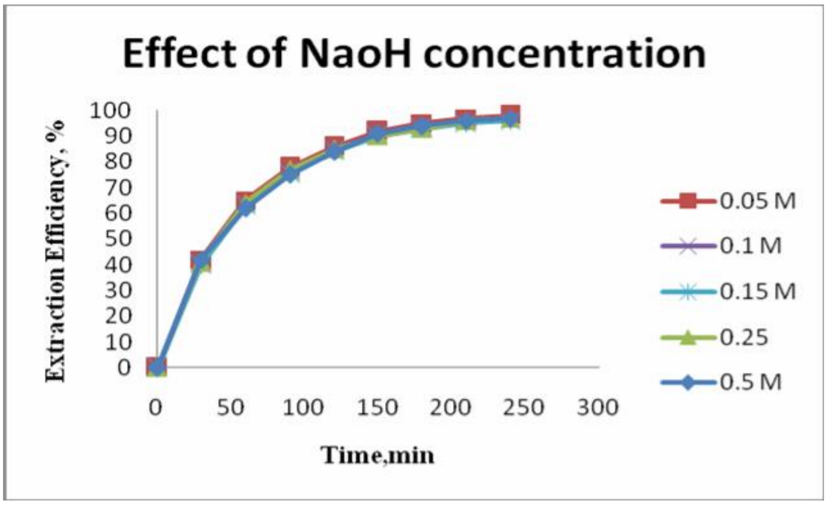

Fig.6. Extraction efficiency of phenol by bulk ionic liquid membrane at different NaOH concentrations

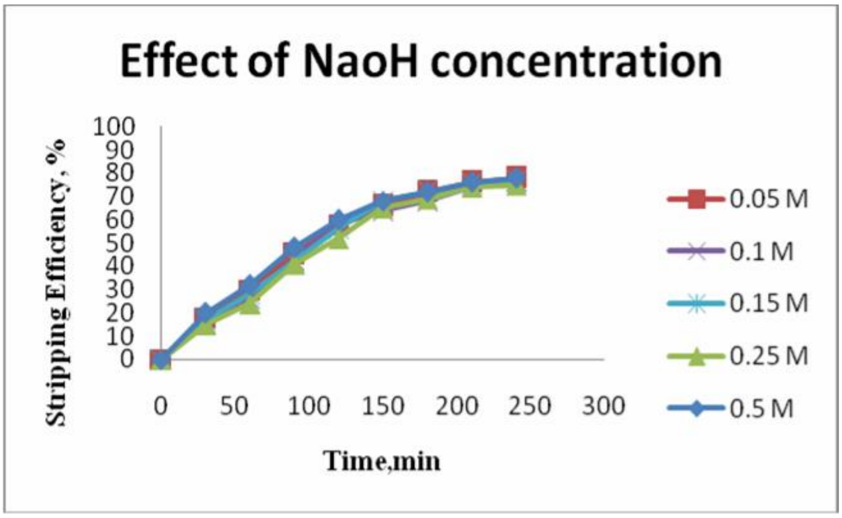

Fig.7. Stripping efficiency of phenol by bulk ionic liquid membrane at different NaOH concentrations

$$NaOH + ClC_6H_4OH_{aq} \longleftrightarrow ClC_6H_4OH_{IL} \longrightarrow ClC_6H_4ONa + H_2O \quad (4)$$

Pertraction of molecular chlorophenol in bulk ionic liquid membranes consists of two major processes extraction and stripping

i. Molecular chlorophenol dissolves in ionic liquid membrane due to its high distribution coefficient between ILs and water. The extraction process is reversible which is governed by equilibrium extraction of chlorophenols between the ionic liquid membrane and the feed phase which is similar to liquid–liquid extraction.

ii. Chlorophenol travels via the ionic liquid membrane to reach membrane/stripping interface. Due to the concentration gradient difference between the phases, the molecular chlorophenol diffuses into the stripping phase. Under high OH^- concentration stripping phase (high pH), the weak acid chlorophenol ionizes into chlorophenolate ion and hydrogen ion. These ions react with sodium ion and hydroxide ion in the stripping phase, respectively to yield sodium chlorophenolate and water. Back stripping of chlorophenol is prevented, as chlorophenolate ion is insoluble in ionic liquid membrane. Moreover, chlorophenol's activity in the stripping phase is suppressed by NaOH present in it and by maintaining concentration gradient between membrane phase and stripping phase. Thus, one way stripping process is achieved.

4.Conclusions

- The best extractant of chlorophenol was found to be [Bmim][BF_4]. This due to its effective negative charge than other two ILs. The strength of hydrogen bonding between [BF_4] anion and the chlorophenol was much stronger, resulting higher extraction efficiency.
- The maximum chlorophenol extraction and stripping efficiencies were contributed due to the low viscosity and high hydrogen bond basicity strength of [Bmim][BF_4] when compared with [Bmim][PF_6] and [Bmim][Cl].
- A good membrane stability and reusability of the ionic liquids were achieved for all the ionic liquids tested.
- The hydrophobicity of the ionic liquids did not have much effect on the results but contributed significantly in the membrane recovery whereby the increment in the hydrophobicity reduces the ionic liquid membrane loss.
- The effect of feed phase pH, feed concentration and NaOH concentration showed that [Bmim][BF_4] based liquid membrane showed better behavior when compared with organic liquid membranes. The transport of chlorophenol was stable for [Bmim][BF_4] liquid membrane.
- A high extraction and stripping efficiencies of 98.10% and 78.5% respectively were achieved using [Bmim][BF_4]. Hence, [Bmim][BF_4] offers a best choice as it gives the maximum chlorophenol extraction and stripping efficiencies with a stable transport process and lower solvent loss.

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