Characterization of a supported ionic liquid membrane used for the removal of cyanide from wastewater
Juan Qin Xue, Ni Na Liu, Guo Ping Li and Long Tao Dang

ABSTRACT
This work evaluated the performance of ionic liquids (ILs) in supported liquid membranes in the removal of total cyanide from wastewater. Membranes were characterized by scanning electron microscopy and contact angle measurements to study the membrane morphology and wetting ability. In particular, the effects of operational parameters such as membrane immersion time, feed-phase concentration, and pH on cyanide removal were investigated. ILs are organic salts that are entirely composed of organic cations and either organic or inorganic anions. Since their vapor pressure is negligible, they can be handled easily; this characteristic gives rise to their ‘green’ nature. In this study, a hydrophobic IL, 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF6), was immobilized in the pores of a solid polymeric support made of polyvinylidene fluoride. The optimal conditions were as follows: 1 hour membrane immersion time, 312.24 mg/L feed-phase concentration, a feed-phase pH of 4, 3% NaOH solution, and 1 hour stirring time. The cyanide removal was 95.31%. The treatment of cyanide using supported ionic liquid membrane (SILM) technology is a method with potential applications in industry.

Key words | characterization, cyanide wastewater, supported ionic liquid membrane

INTRODUCTION
Cyanides are toxic compounds that have a strong tendency for complexation (Shen et al. 2014; Li et al. 2015). Many industrial activities such as mining, pharmaceutical manufacture, and electroplating use cyanides in their operation processes, thus also generating cyanides as an undesirable byproduct (Hanela et al. 2015). Cyanides are extremely hazardous because they rapidly combine with cytochrome, thus interfering with tissue respiration (Bhardwaj & Singh 2013). In addition, any discharge of cyanide wastewater is deleterious to the environment (Xie & Dreisinger 2009).

Several techniques have been used for the removal of cyanide from wastewater, such as alkaline chlorination/oxidation and chemical precipitation (Moussavi & Talebi 2012). However, these methods have several drawbacks, including the requirement for chemicals and their harmful effects on the environment (Chen et al. 2008). Therefore, a novel treatment method for the removal cyanide from wastewater is imperative.

Supported liquid membrane (SLM) technology has been found to be a potential method for the removal of toxic metal ions (Kedari et al. 2013; Bhatluri et al. 2014, 2015; Swain et al. 2015), weak acids, and bases from wastewater (Malik et al. 2011), as well as for the separation hydrocarbons (Molinari et al. 2009), gaseous mixtures, (Castro-Dominguez et al. 2013; Shimoyama & Neha 2014), and multicomponent mixtures (Chakrabarty et al. 2010).

In the SLM process, two aqueous phases are separated with a polymeric support that is impregnated with an organic phase (Nosrati et al. 2011). The solute can be transported from the feed phase to the strip solution through the supported membrane (Huang et al. 2014). The stability of SLM, however, is one of the main drawbacks of this technique. In this study, therefore, a high-viscosity ionic liquid (IL), 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF6), was used to make the SLM more stable. In contrast to traditional volatile organic solvents, ILs have fascinating physical and chemical properties: negligible vapor pressure (low volatility), good thermal stability, and high chemical stability. ILs can be used as organic phase to prepare a supported ionic liquid membrane (SILM) from an SLM (Lozano et al. 2011). SILM technology has many advantages such as high selectivity, small requirement for solvents,
easy scale-up, and low energy consumption (Dahi et al. 2014). Moreover, SILM technology combines the extraction and stripping process in a single step (Dai et al. 2016).

This study evaluated the performance of ILs in SILM in the removal of cyanide from wastewater. Because of the hydrophilicity of the feed and strip phase (NaOH), using a hydrophobic IL, [Bmim]PF}_6, in the membrane, as well as a hydrophobic polymer, polyvinylidene fluoride (PVDF), prevents the outflow of ILs from membrane pores. Experimental parameters such as membrane immersion time, feed-phase concentration, and pH were studied to optimize the conditions for cyanide removal.

MATERIALS AND METHODS

Reagents and materials

All chemicals used in this study were of analytical grade. Aqueous solutions were prepared by using Millipore (USA) deionized water. [Bmim]PF}_6 was purchased from DB (China). The physical properties of the ILs used are shown in Table 1. PVDF membranes (hydrophobicity, 0.2 μm pore size, 65 μm thickness, 75–80% porosity) were purchased from YD (China). All other chemicals such as kerosene, sulfuric acid, and disodium edetate were obtained from WL (China). Cyanide wastewater was derived from a gold smelter.

Analytical apparatus

A digital pH meter (PHS-3C, China) was used for the measurement of pH. The membrane morphology was studied by using a field emission scanning electron microscope (Zeiss Sigma). The membrane surface contact angle was measured using a contact-angle-measuring instrument (SL200A, China).

Membranes preparation

SILMs were typically prepared through the impregnation method by immersing a porous support membrane in the membrane solvent for a certain time. PVDF membranes were immersed in membrane solvent ([Bmim]PF}_6 in kerosene at a certain concentration) for 1 hour. During immersion, the ILs filled the pores of the support membrane under capillary force. The membranes thus obtained, SILMs, were subsequently removed and blotted with filter paper to dry.

Membrane transport experiments

The SILM transport process was carried out in a two-compartment cell made of organic glass, both sides (feed and strip phase) of which have a maximum capacity of 500 mL. The effective area of the membrane is 2,450 mm\(^2\). To prevent leakage of ILs, the prepared SILMs were firmly fixed with a seal sheet in the middle of the cell. The experimental setup is shown in Figure 1. A predetermined concentration of equal volumes of feed and strip solutions were then poured into the two separate sides of the cell. The feed phase was obtained by diluting the wastewater containing cyanide to a certain concentration, and then by adding sulfuric acid dropwise to the solution until its pH reached 4. Solutions in the two compartments were stirred at 250 rpm with the help of mechanical stirrers (JJ-1, China). All experiments were carried out at room temperature i.e., 25.0 ± 1 °C. The total concentration of cyanide was determined through silver nitrate titration (National Environmental Protection Agency 1987). The removal efficiency of total cyanide (% removal) were calculated using the following formula:

\[
\% \text{ removal} = \left(1 - \frac{c_0 - c_1}{c_0}\right) \times 100
\]

where \(c_0\) is the initial concentration of total cyanide in the feed phase (mg/L); \(c_1\) is the total cyanide concentration in the feed phase after the transport process (mg/L).

Membrane characterization

Loss rate of membrane

ILs may flow out of the membrane pores during a transport process. The loss rate of the membrane is described by the

Table 1 | Physical properties of the IL used in the experiment

<table>
<thead>
<tr>
<th>ILs</th>
<th>Molecular formula</th>
<th>Density (g·mL(^{-1}))</th>
<th>Viscosity (Pa·s)</th>
<th>Melting point (K)</th>
<th>Thermal decomposition temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Bmim]PF}_6</td>
<td>C(<em>8)H(</em>{15})N(_2)F(_6)P</td>
<td>1.38</td>
<td>0.312</td>
<td>279.65</td>
<td>373.15</td>
</tr>
</tbody>
</table>
following equation:

$$\varepsilon = \frac{m_1 - m_2}{m_1 - m_0} \times 100\%$$  \hspace{1cm} (2)$$

where $\varepsilon$ is the loss rate of the membrane, $m_0$ is the mass of the PVDF membrane, $m_1$ is the mass of the SILM, and $m_2$ is the mass of the SILM after the transport process (g).

Membrane immobilization capacity

The membrane immobilization capacity ($F_c$) is the mass of IL immobilized per unit volume of membrane. The membrane immobilization capacity was estimated using the following equation:

$$F_c = \frac{m_1 - m_0}{(\pi/4)D^2 \delta} \text{ (g/cm}^3\text{)}$$  \hspace{1cm} (3)$$

where $D$ is the membrane diameter ($\mu$m); $\delta$ is the membrane thickness ($\mu$m).

Scanning electron microscopy

SILMs with good appearance (i.e. no obvious defects and brittle fractures) were exposed to low temperature using liquid nitrogen and were then sprayed with a thin layer of gold atoms under vacuum. The surface morphology of the SILMs were subsequently observed.

Contact angle

The surface hydrophobicity of the SILMs can be represented by the contact angle at room temperature. A droplet of purified water was applied to a SILM, and a static image of the droplet with the membrane surface at equilibrium was taken. To ensure accuracy, measurements were performed at three different locations, and the average value was regarded as the contact angle.

RESULTS AND DISCUSSION

Preparation of the SILM

Effect of membrane immersion time

ILs are generally immobilized in the support pores by capillary forces. The duration for which the support membrane was immersed in the membrane solvent is the membrane immersion time. This time was varied from 0.25 to 3 hours to investigate its effect on the % removal. Figure 4(a) and 4(b) show that both the % removal and amount of ILs lost increases as the immersion time increases. When the immersion time was 1 hour, % removal was 86.87% (30%ILs). This result can be explained by the fact that ILs in the membrane pores reach saturation as the immersion time increases. Moreover, loss of ILs through the membrane pores may be due to the high transmembrane pressure difference ($\Delta p$) under the capillary forces that the membrane can sustain. When the membrane pore size was small or the feed-phase flux was large, the transmembrane $\Delta p$ might be substantial. The maximum $\Delta p$ that a SILM can resist is related to the maximum pore size of the membrane, the pore structure, the interfacial tension of the membrane liquids, and the contact angle (Zhao et al. 2015). Hence, 1 hour was considered to be the optimal membrane immersion time; further studies were conducted at 1 hour.

Membrane morphology

To study the impact of ILs on the microstructure of the PVDF membrane, scanning electron microscopy (SEM) was used to characterize the membrane surface morphology. These membranes were analyzed after impregnation to ensure sufficient immobilization and homogeneous distribution of ILs in the membrane pores. Figure 2(a)–2(f) show SEM micrographs of the PVDF membranes impregnated with [Bmim]PF$_6$. Figure 2(a), 2(c) and 2(e) show that the PVDF membranes have a spongy structure and that micropores are well distributed on the uniform membrane surface (Zhao et al. 2015). After the PVDF membranes were immersed,
the ILs were distributed in the membrane micropores (0.22 μm) homogeneously, but large macropores (5–10 μm) were partially filled. A similar phenomenon was observed by Lozano et al. (Lozano et al. 2011). The images also show the excess ILs adsorbed onto the membrane surface, when the IL concentration was greater. Because of the small losses of ILs, the membrane pores became exposed and the membrane surface was rough, as shown in Figure 2(b), 2(d) and 2(f).

Membrane immobilization capacity and loss rate of the membrane

In contrast to conventional SLMs, SILMs have a high capacity and low membrane loss, which demonstrate the advantages of using ILs in an SLM system (Table 2). The IL in the liquid membrane phase stabilizes SLMs because it has negligible vapor pressure (minimal loss via volatilization) and relatively high viscosity (Dai et al. 2016).
Moreover, the loss of IL may be attributed to membrane compression and extrusion from large pores (Malik et al. 2014).

Membrane wetting ability

Figure 3 shows the wetting ability of PVDF and SILMs. The surface water contact angles of PVDF and SILMs with 30% IL and 100% IL are 114.80°, 123.15°, and 130.14° respectively. Meanwhile, when [Bmim]PF6 entered the membrane pores, both the SILM contact angle and membrane hydrophobicity increased. Loss of ILs from membrane pores caused the SILM contact angle (after the removal process) to slightly decrease relative to that of the impregnated SILMs. Consequently, the membrane hydrophobicity decreased slightly. The reduction of the contact angle was relatively small, indicating retention of the ILs in the SILM pores after removal.

SILM separation process

Effect of concentration of feed phase

The effect of feed-phase concentration on cyanide removal in the range of 46.84 to 468.36 mg/L was studied. The removal efficiencies and loss rates of the membrane at various feed-phase concentrations are shown in Figure 4(c) and 4(d). The cyanide removal rate (92.6% of 30% IL; 91.5% of 100% IL) increased quickly as the feed-phase concentration increased to 312.24 mg/L and then slowly because of the formation of an effective contact area between the feed phase and membrane. However, the feed concentration further increased and reached a limit on the membrane interface, thus decreasing the cyanide removal efficiency. The reduction of cyanide removal efficiency can also be attributed to the lack of ILs in the membrane pores. The SILM separation performance mainly depended on the characteristics of the imbedded ILs rather than on the support membrane. Thus, a feed-phase concentration at 312.24 mg/L was used in subsequent experiments.

Effect of feed-phase pH

The feed-phase pH is an important factor that strongly influences cyanide removal efficiency. The feed-phase pH was 12 ± 0.2, which was adjusted to the range of 2 to 6 by adding sulfuric acid solution. Figure 4(e) shows that the removal efficiency initially increases, and then slowly declines at a pH of approximately 4. This indicates that any deviation from a pH of 4 hinders cyanide removal. After acidification of the feed phase, H+ migrates through SILMs from the feed-phase side to the strip-phase side in the transport process (de los Ríos et al. 2015). The feed-phase pH slightly decreased, but it still remained low during the mass-transfer process. This result confirms that cyanide transport through the SILMs takes place because of a pH difference between the feed and strip phases. In addition, the membrane loss rate increased significantly when the pH was higher than 5 (Figure 4(f)). This increase may be attributed to the solubility of ILs in an acidic solution.

Table 2 | Membrane immobilization capacity and loss rate of membrane in different membrane liquids used in this work

<table>
<thead>
<tr>
<th>Membrane liquid</th>
<th>Membrane immobilization capacity (g/cm³)</th>
<th>Loss rate of membrane (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLMs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% kerosene</td>
<td>0.2744</td>
<td>61.32</td>
</tr>
<tr>
<td>100% TOA</td>
<td>0.2901</td>
<td>40.58</td>
</tr>
<tr>
<td>100% N503</td>
<td>0.2583</td>
<td>56.25</td>
</tr>
<tr>
<td>SILMs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30%[Bmim]PF6 and kerosene</td>
<td>0.9001</td>
<td>22.21</td>
</tr>
<tr>
<td>100% [Bmim]PF6</td>
<td>1.1051</td>
<td>17.68</td>
</tr>
</tbody>
</table>

Conditions: initial cyanide concentration, 312.24 mg/L; pH of feed, 4; membrane immersion time, 1 hour; strip solution, 3% NaOH; stirring time, 1 hour.

TOA: Tri-n-octylamine, N503: a high-efficiency extractant.

Figure 3 | Water contact angles of PVDF and SILMs (‘*’ represents the membrane after the removal process). Conditions: cyanide concentration, 312.24 mg/L; pH of feed, 4; membrane immersion time, 1 hour; strip solution, 3% NaOH; stirring time, 1 hour.
Figure 4  Effect of operational parameters on the removal efficiency of total cyanide and loss rate of membrane using SILM: (a) and (b) membrane immersion time (conditions: cyanide concentration, 312.24 mg/L; pH of feed, 4; strip solution, 3% NaOH; stirring time, 1 hour); (c) and (d) concentration of feed phase (conditions: membrane immersion time, 1 hour; pH of feed, 4; strip solution, 3% NaOH; stirring time, 1 hour); (e) and (f) pH of feed phase (conditions: membrane immersion time, 1 hour; cyanide concentration, 312.24 mg/L; strip solution, 3% NaOH; stirring time, 1 hour); (g) and (h) concentration of NaOH (conditions: membrane immersion time, 1 hour; cyanide concentration, 312.24 mg/L; pH of feed, 4; stirring time, 1 hour); (i and j) stirring time (conditions: membrane immersion time, 1 hour; cyanide concentration, 312.24 mg/L; pH of feed, 4; strip solution, 3% NaOH).
Effect of strip-phase concentration

The effect of strip-phase (NaOH) concentration on the removal of cyanide is presented in Figure 4(g). Batch experiments were performed by changing NaOH concentration of the strip solution from 1 to 5% (wt%) while keeping the feed-phase concentration at 312.24 mg/L. The cyanide removal efficiency marginally increased as the NaOH concentration increased to 3%, subsequently decreasing as the NaOH concentration continued to increase. The cyanide removal efficiency decreased from 88.12% (3% NaOH) to 69.37% (5% NaOH). This result may be explained by the reduced stability of SILMs. Loss of ILs from the SILM surface to the strip phase with the increase in the NaOH concentration led to a decline in the removal efficiency. A higher concentration of NaOH is disadvantageous to cyanide removal, in agreement with studies of the groups of Nosrati and other investigators (Nosrati et al. 2011; De San Miguel et al. 2014). Moreover, a higher concentration would inevitably increase treatment costs. The loss rate of the membrane increased as the NaOH concentration increased (Figure 4(h)). Hence, 3% was considered as the optimum NaOH concentration in the strip phase.

Effect of stirring time

In the SILM process, ILs reacts with the feed phase, and the stripping reaction with the strip phase occurs simultaneously, forming a product. Theoretically, it is reasonable to keep the stirring time long and the mass transfer process more complete to obtain a high removal efficiency. Figure 4(i) shows that the stirring time changed from 0.25 to 2 hour and the cyanide removal increased, but the latter declined at approximately 1 hour (% removal: 86.87%). Meanwhile, the loss rate of the membrane remained relatively stable and low. These responses may be attributed to the loss of ILs due to the stirring shear force in the cell, which reduces the cyanide removal efficiency. Analysis and descriptions of the above-mentioned hypothesis is consistent with the trend shown in Figure 4(j).

CONCLUSIONS

In this research, the removal of cyanide from wastewater using SILM technology was studied by optimizing various parameters for maximum cyanide removal. The parameters are a 1 hour membrane immersion time, 312.24 mg/L concentration of feed phase, a feed-phase pH of 4, 3% NaOH solution, and 1 hour stirring time. The removal efficiency under the optimum conditions was as high as 95.31%. The IL homogeneously distributed in the membrane pores, and the SILMs have a high capacity and low IL loss.

The study demonstrated that PVDF membranes with [Bmim]PF₆ have promising performances in the removal of cyanide from wastewater. The results also provide a theoretical basis for industrial applications. However, technical challenges such as decreasing loss of ILs from membrane pores still hinder practical applications.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (No. 51478379, No. 51278407, No. 51408468).

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First received 1 November 2016; accepted in revised form 20 July 2017. Available online 5 September 2017