Treatment of cyanide wastewater by bulk liquid membrane using tricaprylamine as a carrier

Guoping Li, Juanqin Xue, Nina Liu and Lihua Yu

ABSTRACT

The transport of cyanide from wastewater through a bulk liquid membrane (BLM) containing tricaprylamine (TOA) as a carrier was studied. The effect of cyanide concentration in the feed solution, TOA concentration in the organic phase, the stirring speed, NaOH concentration in the stripping solution and temperature on cyanide transport was determined through BLM. Mass transfer of cyanide through BLM was analyzed by following the kinetic laws of two consecutive irreversible first-order reactions, and the kinetic parameters ($k_1$, $k_2$, $R_m$, $t_{max}$, $J_{max}$, $J_a$, $J_d$) were also calculated. Apparently, increase in membrane entrance ($k_1$) and exit rate ($k_2$) constants was accompanied by a rise in temperature. The values of activation energies were obtained as 35.6 kJ/mol and 18.2 kJ/mol for removal and recovery, respectively. These values showed that both removal and recovery steps in cyanide transport is controlled by the rate of the chemical complexation reaction. The optimal reaction conditions were determined by BLM using trioctylamine as the carrier: feed phase: pH 4, carrier TOA possession ratio in organic phase: 2% (V/V), stripping phase concentration of NaOH: 1% (W/V), reaction time: 60 min, stirring speed: 250 r/min. Under the above conditions, the removal rate was up to 92.96%. The experiments demonstrated that TOA was a good carrier for cyanide transport through BLM in this study.

Key words | bulk liquid membrane, cyanide wastewater, transport kinetics, tricaprylamine

INTRODUCTION

Cyanide, an environmentally significant pollutant in many industrial wastewaters, is generated on a large scale for use in gold and silver extraction, electroplating, synthetic fiber production, coal cooking, coal conversion effluents, organic chemical and other industries (Dvořák et al. 2014; Shen et al. 2014). Cyanide is highly toxic to humans and aquatic organisms. To preserve human and environmental health, wastewater containing cyanide has to be treated in a viable process for removal of cyanide before being released into the environment (Moussavi et al. 2015). A considerable number of methods have been investigated for treating cyanide-containing wastewater, including active carbon adsorption, ferrate oxidation process, photo-catalytic oxidation, membrane method, ion exchange method, solvent extraction, electrolysis and so on. Although these methods for treating cyanide have a certain effect, there are still insufficient in some aspects. Electrolytic method is suitable for wastewater containing high concentration cyanide, but the current efficiency is low, and higher current density increases the cost (Scarazzato et al. 2015). Photo-catalytic oxidation has high chemical stability, non-toxicity and high oxidation power, but it is suitable for low concentration cyanide wastewater (Khakpash et al. 2011; Pala et al. 2015).

Ultimately, a simple, cost effective and safe alternative for removal and recovery of cyanide from wastewater is required. Liquid membrane technologies have acquired a prominent role for their use in separation, purification or analytical application in various areas, such as biomedicine, ion selective electrodes, effluent treatment and hydrometallurgy (Muthuraman et al. 2010). In recent years, a remarkable increase of application of liquid membranes in separation processes has been observed, not only because of its outstanding characteristics such as ease of installation, high preconcentration, high selectivity, high fluxes, reusability and low energy consumption, but also it helps for understanding the principles, driving force and main factors influencing the transport (Alonso et al. 2006; Panja et al. 2012; Biswas et al. 2015; Lopez et al. 2015).
Liquid membranes can be generally classified into three types: bulk, emulsion and supported liquid membranes. Among liquid membrane technologies, bulk liquid membrane (BLM) is one of the simplest, lowest costing and most efficient types of liquid membranes. BLMs constitute the cheapest separation techniques because of their relatively small inventory and low capital cost. A relatively thick layer of immiscible fluid is used to separate the feed and stripping phase in a BLM. There is no means of support for the membrane phase and it is kept apart from the external phases only by means of its immiscibility. BLMs consist of three phases: two aqueous phases as a donor and an acceptor, and one organic phase in which a carrier is dissolved. The cyanide transport from an aqueous donor phase through an organic membrane phase to an aqueous stripping phase (Belova et al. 2014).

BLM shows excellent performance in terms of separation and enrichment. With the thick film, stable interface boundary area, and a steady-state migration process, BLM has a strong advantage for the study of thermodynamics and kinetics, and the constants of thermodynamics and kinetics which have theoretical guidance significance for the extraction process (Alizadeh & Memar-bashi 2012; Szczepański & Wódzki 2013). BLM separation technology has been widely used in the separation of metal ion extraction (Dalali et al. 2012; Koter et al. 2013; Pinto et al. 2015), and less research for the separation of aromatic compounds (Akin et al. 2012; Szczepański et al. 2014), separation of amino acid (Ma et al. 2002), separation of antibiotic (Ren et al. 2009), separation of enzymes (Nishii et al. 2002), separation of chiral drug (Hu et al. 2008) and separation of anion (Lamb et al. 2008).

The large number of publications concerning BLMs were focused on systems in which metal ions are being removed mainly for economical reasons and also carried out to determine the transport mechanism. There are hundreds of publications on cation separation in the literature but only a few examples are known for the separation of anions, especially for the separation of cyanide wastewater.

In the present work, cyanide transport through a BLM containing tricaprylamine (TOA) in kerosene was studied which aimed at investigating the ability of TOA as a mobile carrier for the simultaneous bulk liquid transport of cyanide and emphasizing the kinetic model as well as the application of the technique for the treatment of cyanide wastewater. The influence of cyanide concentration in the feed solution, TOA concentration in the organic phase, stirring speed, NaOH concentration in the stripping solution and temperature were investigated, and optimization of the parameters was obtained. The transport kinetics of cyanide through BLM were examined at various temperatures in the range of 278–308 K. The transport mechanism was analyzed according to coupled non-steady-state kinetics of two consecutive irreversible first-order reactions, and the pseudo-first-order apparent rate constants, k1, k2 and the apparent activation energy values of interfacial transport of extraction and back extraction have been determined. The aim of the present work was to perform a treatment of the BLM extraction, which might provide a potential method for the removal of cyanide from wastewater and evaluate the prospects of its application in hydrometallurgy.

**EXPERIMENTAL**

**Reagents and materials**

All the reagents such as tricaprylamine, kerosene, sodium hydroxide, p-dimethylaminobenzalrhodanine, ethylenediaminetetraacetic acid (EDTA), silver nitrate, phosphoric acid, and acetone used in the present work were of analytical grade. All chemical reagents were dissolved by deionized water. The wastewater came from gold smelter in Henan Province, China, and the chemical properties of the cyanide wastewater are listed in Table 1.

**Procedure**

A BLM cell (Figure 1(a)) was used in all experiments. Before each experiment, the membrane phase (250 mL) was prepared by dissolving TOA (1–5 w%) in kerosene. Then, it was homogenized by mixing this solution and shaking the organic phase. Two portions of aqueous donor (150 mL, wastewater) and acceptor solutions (150 mL, NaOH) were located at the bottom of the glass cell and the membrane solution was carefully added on the top. The donor phase, the stripping phase and the organic phase were stirred at a constant speed by a stirrer (Pudong JJ-1). After a certain time, samples were taken and determined by Silver Nitrate

**Table 1** The chemical properties of the cyanide wastewater

<table>
<thead>
<tr>
<th>Feed phase</th>
<th>pH</th>
<th>Cyanide concentration/ (mol/L)</th>
<th>Cu²⁺/ (mol/L)</th>
<th>Zn²⁺/ (mol/L)</th>
<th>Fe³⁺/ (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanide wastewater</td>
<td>4.0</td>
<td>1,800</td>
<td>255.8</td>
<td>45.9</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Titration Method (GB/T 7486-87), whereas the extraction percentage was calculated using the following equation:

$$E\% = \left(\frac{C_0 - C}{C_0}\right) \times 100\% \quad (1)$$

where $C_0$ and $C$ were the initial and final concentrations of cyanide in aqueous solution before and after extraction, respectively. The corresponding change of cyanide concentration in the membrane phase was determined from the material balance between the phases. For practical reasons, dimensionless reduced concentrations ($R$) were used:

$$R_d = \frac{C_d}{C_{d_0}}, \quad R_m = \frac{C_m}{C_{d_0}}, \quad R_a = \frac{C_a}{C_{d_0}} \quad (2)$$

$$R_d + R_m + R_a = 1 \quad (3)$$

where $R_d$ was the dimensionless reduced concentration of cyanide in the donor, $R_m$ that in the membrane, and $R_a$ that in the stripping phase.

**Transport process**

With TOA as the mobile carrier, kerosene as a membrane solvent, the transfer process of cyanide in the system can be roughly divided into the following processes.

1. Firstly, cyanide of feed phase pass through the aqueous diffusion layer between the feed phase and the membrane phase, cyanide and carrier (TOA) occurs complexation reaction as follows:

$$nH^+ + nCN^- + TOA_{org} = [TOAH_n]CN_n \quad (4)$$

where the subscript $f$ is aqueous phase, the subscript $org$ is membrane phase and $n$ is the coordination number.

2. Cyanide-carrier generated complexes diffuse from the aqueous diffusion layer to membrane phase, then continue to diffuse in the membrane phase, and occurs reaction with desorption agent on the phase interface between the membrane phase and stripping phase:

$$[TOAH_n]CN_n + nNa^+ + nOH^- = nNaCN_s + TOA_{org} + nH_2O \quad (5)$$

where $s$ is stripping phase, the stirring effect provides fully contact opportunity cyanide-carrier generated complexes and desorption agent, which ensure the process of extraction and re-extraction continuing, and improve effectively the transport rate of the cyanide.

Considering the reaction equations of (4) and (5), as long as the driving force of concentration difference between the two sides of the membrane, the process will...
repeat, and cyanide can achieve eventually the separation from feed phase. Stop stirring, and stand a while, then the stripping phase containing high concentration cyanide will automatically separate with membrane phase, which is convenient for concentrated treatment.

**RESULTS AND DISCUSSION**

**Kinetics cyanide transport process**

Variation with time of the reduced concentrations of cyanide in the donor, membrane and stripping phase is shown in Figure 1(b) (experimental conditions: feed phase 120 mol/L at pH 4.0; stripping phase: 1% NaOH solution; membrane phase: 2% carrier TOA possession ratio in kerosene; stirring speed: 250 r/min). The experimental results revealed that $R_d$ decreased exponentially with time, accompanied by a simultaneous increase of $R_a$, whereas $R_m$ presented a maximum at intermediate times and decreased slowly with time to reach a constant value. Complexation was primary in 20 min while decomplexation was supplemented; with the reducing of cyanide concentration in feed phase after 20 min, decomplexation was given priority to the whole process, which led to the decreasing of cyanide concentration in the membrane phase and increasing in the stripping phase. It could be seen that $R_d$ versus time yielded a mono-exponentially decreasing curve, while $R_a$ followed an increasing sigmoid curve. $R_m$ was initially increased, then it reached a maximum and was slowly decreased with time to reach a constant value. When $R_d$, $R_m$ and $R_a$ values are inspected, the results suggest that the cyanide transport obeys the kinetic laws of two consecutive irreversible first-order reactions according to the kinetic scheme:

$$C_d \xrightarrow{k_1} C_m \xrightarrow{k_2} C_a$$ (6)

where $k_1$ and $k_2$ are the pseudo-first apparent rate constants of the extraction and the re-extraction, respectively. The change of carrier concentration and other factors affect cyanide concentration in the feed phase, membrane phase and strip phase, which results in a change in $k_1$ and $k_2$ values. The kinetic scheme for consecutive reaction systems can be described by considering the reduced concentrations as follows:

$$\frac{dR_d}{dt} = -k_1R_d \equiv J_d$$ (7)

$$\frac{dR_m}{dt} = k_1R_d - k_2R_m \equiv J_a$$ (8)

where $J$ represents the flux, when $k_1 \neq k_2$, integrating Equations (7)–(9), gives the following expressions:

$$R_d = \exp(-k_1t)$$ (10)

$$R_m = \frac{k_1}{k_2 - k_1} \left[ \exp(-k_1t) - \exp(-k_2t) \right]$$ (11)

$$R_a = 1 - \frac{1}{k_2 - k_1} \left[ k_2 \exp(-k_1t) - k_1 \exp(-k_2t) \right]$$ (12)

The kinetic parameters $k_1$ and $k_2$ are obtained by Equations (10)–(12). Then, the maximum values of $R_m$ (when $dR_m/dt = 0$) and $t_{max}$ can be written as follows:

$$R_{max} = \left( \frac{k_1}{k_2} \right)^{-k_2/(k_1 - k_2)}$$ (13)

$$t_{max} = \left( \frac{1}{k_1 - k_2} \right) \ln \left( \frac{k_1}{k_2} \right)$$ (14)

By considering the first-order time differentiation of Equations (10)–(12) at $t = t_{max}$ one obtains the following equations:

$$\left. \frac{dR_d}{dt} \right|_{t_{max}} = -k_1 \left( \frac{k_1}{k_2} \right)^{-k_2/(k_1 - k_2)} \equiv J_{d_{max}}$$ (15)

$$\left. \frac{dR_m}{dt} \right|_{t_{max}} = 0$$ (16)

$$\left. \frac{dR_a}{dt} \right|_{t_{max}} = k_2 \left( \frac{k_1}{k_2} \right)^{-k_2/(k_1 - k_2)} \equiv J_{a_{max}}$$ (17)

when $t = t_{max}$ the system is in a steady state because the concentration of cyanide in the membrane does not change with time (Equation (16)). As a result, the exit and entrance fluxes are equal and have opposite signs:

$$-J_{d_{max}} = J_{a_{max}}$$ (18)
BLM experiments

Effect of feed concentration

The effect of feed concentration on the extraction process was tested at various initial concentrations of cyanide in the range of 30–220 mg/L, and the results are shown in Figure 1(c) (experimental conditions: feed phase 30–120 mol/L at pH 4.0; stripping phase: 1% NaOH solution; membrane phase: 2% carrier TOA possession ratio in kerosene; reaction time: 60 min; stirring speed: 250 r/min). Figure 1(c) reveals a sudden increase in the cyanide extraction percent at concentrations from 30 to 120 mg/L value for which it attained maximum. This rapid enhancement might be explained by the fact that with increasing concentration, the contact between cyanide and TOA was increased, and at concentration 120 mg/l, TOA get saturated and attains a maximum extraction percent, whereas at higher concentration, carrier became fully saturated and could not transport cyanide much efficiently from the aqueous to the organic phase. This indicated that the number of moles transported through the membrane per unit area of the membrane per unit time were determined by the concentration of TOA, since the effective area of membrane and time were fixed, which meant there was not enough carriers to transport cyanide proportionally (Reddy et al. 2013; Khani et al. 2015). Therefore, 120 mg/l concentration was suitable for the transport of cyanide using TOA through BLM.

Effect of the carrier concentration

The carrier which is the important component of BLM removes the active component from donor phase by complexing with it and after subsequent diffusion into organic phase; it discharges that component into the stripping phase (Memon et al. 2014). In order to investigate the effect of carrier concentration on the transport of cyanide, the experiments were run at five different carrier concentrations: 0.5–4.0% (v/v) (experimental conditions: feed phase 120 mol/L at pH 4.0; stripping phase: 1% NaOH solution; membrane phase: 0.5–4.0% carrier TOA possession ratio in kerosene; stirring speed: 250 r/min). The results (Figure 2(a)) demonstrated that transport of cyanide through BLM was improved with an increase in carrier concentration.
concentration up to a certain concentration and then decreased. Maximum transport occurred at the carrier concentration of 2.0%. Because the transport of cyanide was jointly controlled by chemical reaction and diffusion dynamics, which was a dynamic equilibrium process (Du et al. 2004). When the carrier concentration was low, the whole process was controlled by chemical reaction (Wu et al. 2014). According to the principle of chemical equilibrium, increasing the concentration of reactants was in favor of forming carrier complexes, so removal rate of cyanide increased rapidly, but when the carrier concentration reached a certain value, interfacial concentration close to saturation, diffusion process would play a decisive role. While continuing to increase the carrier concentration, the viscosity of the membrane phase would become bigger, and the membrane pore might be blocked up, which reduced the diffusion coefficient of the complex, so the removal rate of cyanide decreased (Ma et al. 2001).

**Effect of the concentration of stripping phase**

In any extraction processes, it is imperative to back extract the extracted cyanide from the organic phase and allow recycling of the organic phase without loss of efficiency (Muthuraman & Ibrahim 2013; Soniya & Muthuraman 2015). The effect of concentration in the strip phase on transport efficiency of cyanide through BLM is presented in Figure 2(b) (experimental conditions: feed phase 120 mol/L at pH 4.0; stripping phase: 0.25–5.00% NaOH solution; membrane phase: 2% carrier TOA possession ratio in kerosene; stirring speed: 250 r/min). When the NaOH concentration was 0.25–1%, with the increase of NaOH concentration, the migration power of cyanide compounds from wastewater phase to stripping phase increased, and an excess amount of the stoichiometric NaOH could be used to convert CN (I) to NaCN in order to trap them in the stripping phase. A further increase of NaOH concentration decreased the efficiency to some extent. Because higher NaOH concentration produced more strength of the solution which resulted in a lower activity coefficient for hydroxyl ions and reduced less active hydroxyl ions to decompose the [TOAH_n]CN_n complex (Madaeni et al. 2011).

**Effect of stirring speed**

The influence of the stirring speed on cyanide transport was studied in order to optimize uniform mixing of the solution and to minimize thickness of aqueous boundary layers (Safi et al. 2006). The effect of stirring speed in the range of 150–350 rpm on the cyanide transport efficiency were studied (Figure 2(c)) (experimental conditions: feed phase 120 mol/L at pH 4.0; stripping phase: 1% NaOH solution; membrane phase: 2% carrier TOA possession ratio in kerosene; stirring speed: 150, 250, 350 r/min). With the gradual increasing of stirring speed from 150 to 250 rpm, more and more cyanide in wastewater combined with carrier, and stirring could increase the liquidity of the liquid membrane, which minimized concentration polarization in the feed phase and provided better penetration of cyanide into the stripping phase. When the liquid membrane flow increased, liquid membrane mass transfer efficiency and cyanide migration power also increased gradually. A further increase of stirring speed decreased the efficiency to some extent, because the interfaces between the phases were deformed at higher stirring speeds and even drops of the stripping phase were transferred mechanically to the donor phase. There was not a negligible amount of loss of carrier during the transport process due to its partitioning by mass transport into one or both external phases, reducing the transport efficiency.

**Effect of temperature**

The effect of temperature on the transport of cyanide across the BLM was tested at 278 K, 288 K, 298 K and 303 K, respectively. Table 2 presents the cyanide transport from the feed phase to stripping phase as a function of temperature. It was obvious that the efficiency of the uptake ($k_1$) from the feed phase as well as the release ($k_2$) of cyanide into the solution enhanced with temperature in the range of 278–303 K. The fitted regression equations were ‘$y = -4.27907x + 10.56791$’ for $k_1$ and ‘$y = -2.18605x + 2.80814$’ for $k_2$, respectively. It was quite obvious that the kinetic parameters: $t_{\text{max}}$ decreased, which meant the time needed reaching maximum concentration of cyanide in the membrane decreased, and the maximum concentration ($R_{\text{m}}^{\text{max}}$) of cyanide increased, as well as $J_{\text{f}}^{\text{max}}$ and $-J_{\text{d}}^{\text{max}}$ increased with an increase in the temperature. The transport was stirring controlled so the effects might be pronounced

<table>
<thead>
<tr>
<th>T/K</th>
<th>$k_1 \times 10^{-2}$</th>
<th>$k_2 \times 10^{-2}$</th>
<th>$t_{\text{max}}$/min</th>
<th>$R_{\text{m}}^{\text{max}} \times 10^{-2}$/min</th>
<th>$J_{\text{f}}^{\text{max}} \times 10^{-2}$/min</th>
<th>$-J_{\text{d}}^{\text{max}} \times 10^{-2}$/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>278</td>
<td>0.78</td>
<td>0.65</td>
<td>140.2</td>
<td>0.402 0.261</td>
<td>-0.261</td>
<td></td>
</tr>
<tr>
<td>288</td>
<td>1.45</td>
<td>0.72</td>
<td>95.9</td>
<td>0.500 0.360</td>
<td>-0.360</td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>2.55</td>
<td>1.02</td>
<td>59.9</td>
<td>0.543 0.541</td>
<td>-0.541</td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>2.77</td>
<td>1.28</td>
<td>51.8</td>
<td>0.554 0.659</td>
<td>-0.659</td>
<td></td>
</tr>
</tbody>
</table>
especially at higher temperature. Thus, cyanide were rapidly transported into the membrane phase and less accumulation appeared in the membrane. The results could be interpreted as the effect of temperature on the diffusion of the transported species through liquid membrane; due to the temperature dependency of the membrane, viscosity was another effect of temperature on the transport process. However, the dependency of the distribution of the carrier on temperature should also be taken into account for describing the experimental results.

The activation energy values were obtained from the Arrhenius equation by using the \( k_1 \) and \( k_2 \) values at different temperatures:

\[
\ln k = \ln A - \frac{E_a}{RT}
\]

(19)

Figure 2(d) shows that the effect of temperature was higher on \( k_1 \), while it is relatively lower on \( k_2 \), and the Arrhenius-type plot was also followed. The values of the activation energies (\( E_a \)) for removal and recovery were obtained from an Arrhenius type plot as \( 35.6 \text{ kJ/mol} \) and \( 18.2 \text{ kJ/mol} \), respectively. Because of the stronger influence of the temperature on the rate constant, \( E_a \) for diffusion-controlled processes were much lower (<5 kJ/mol), than that for chemical-controlled processes (>10 kJ/mol) (Kobya et al. 1997). Therefore, \( E_a \) obtained from the transport process could serve as an indicator as to whether diffusion or chemical reaction was the rate controlling step (Lazarova & Boyadzhiev 1995). Thus, the calculated \( E_a \) indicated that transport of cyanide was controlled by the rate of the chemical complexation reaction.

**Transport reproducibility**

Under optimum conditions (experimental conditions: feed phase 120 mol/L at pH 4.0; stripping phase: 1% NaOH solution; membrane phase: 2% carrier TOA possession ratio in kerosene; reaction time: 60 min; stirring speed: 250 r/min) the reproducibility of cyanide transport was investigated, the transport rate of cyanide using five replicates of BLM was found to be 92.1 ± 1.5%. The relative standard deviation was found to be 1.5%.

**CONCLUSION**

Cyanide could be effectively transported through a BLM containing tricaprylamine, and the highest transport rate was found to be 92.96% by using 2% carrier in the kerosene membrane, 1% NaOH in stripping phase, 60 min of reaction time, and 250 r/min of stirring speed, respectively. The influences of the kinetic parameters (\( k_1, k_2, R_m, t_{max}, J_{max}, f_{max} \)) for the various temperatures in the system were calculated. With increasing the temperature, \( R_m \) increased, \( t_{max} \) decreased, and cyanide was rapidly transported into the membrane and less accumulation appeared in the membrane. The values of activation energies were obtained as 35.6 kJ/mol and 18.2 kJ/mol for removal and recovery, respectively. These values showed that both removal and recovery steps in cyanide transport was controlled by the rate of the chemical complexation reaction.

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