Study of cyanide wastewater treatment by dispersion supported liquid membrane using trioctylamine and kerosene as liquid membrane
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ABSTRACT
A certain amount of cyanide is present in wastewater of various industrial processes, such as wet extraction of gold, coal processing, electroplating and other industries. In this work, an experimental study regarding transport of cyanide through a dispersion supported liquid membrane was performed. A model was established to describe the reaction and transport of CN(I) in the supported liquid membrane and the mass transfer kinetics equations were deduced. Through mass transfer kinetic equation it was derived that, when the carrier concentration was under certain conditions, there was a linear relationship between the reciprocal of the permeability coefficient of CN(I) (1/Pc) and n-th power of the concentration of H⁺ (cnH⁺), and the parameters Δa(δa/da) and Δo(δo/do) could be obtained from the slope and intercept of the straight line. Then the diffusion coefficient do and the diffusion layer thickness δo of the phase interface between the feed phase and membrane phase could be calculated. Factors affecting migration of CN(I) were analyzed, and the stable removal rate of CN(I) was more than 90% with carrier concentration (%TOA) of 2%, feed phase pH of 4, initial CN(I) concentration of 30 mg/L, stirring time of 1 hour, volume ratio of membrane solution to NaOH solution of 2:1, strip phase concentration of 2 mol/L. The results showed that the overall mass transfer rate increased first and then decreased with an increase of TOA concentration, organic-to-strip volume ratio, and strip concentration. Furthermore, the transport percentage of CN(I) was increased, the stability of membrane was enhanced, and the lifetime of the membrane was extended.

Key words | cyanide wastewater, dispersion supported liquid membrane, trioctylamine

INTRODUCTION
A supported liquid membrane (SLM) is a porous membrane whose pores are filled with liquid, and the solute transport conducts through the liquid phase in the pores. It has advantages such as high separation efficiency, high selectivity, high enrichment ability and low amount of extracting agent. SLM is promising in separation technologies because it combines the processes of extraction and back-extraction. The diffusion in liquid is faster than that in solid, and the amount of solvent in the SLM process is also much lower than that in other solvent extraction processes (Matsumoto et al. 2009; Roman et al. 2010; Lozano et al. 2011; Kamal et al. 2014). SLM separation technology has been widely used in the separation of metal ion extraction (Katrin et al. 2014; Thanaporn et al. 2014), separation of organic compounds (Plaza et al. 2013; Smita & Mousumi 2014), separation of gas (Gabriel et al. 2014), separation of biological products (André et al. 2014), and the enrichment of trace substances.

However, SLM often suffers from the loss of the liquid phase either by evaporation, dissolution in the adjacent phases or by the effect of pressure difference between the two sides of the SLM (Malik et al. 2011; Eduardo et al. 2014). Consequently, the instability of SLMs has limited their commercial application.

The use of dispersion supported liquid membranes (DSLMs) has significantly improved the stability of SLM. DSLM is based on SLM, and the membrane solution containing the carrier is adsorbed in the microporous support body. The feed phase and strip phase are in both sides of the membrane, and extraction and back extraction processes...
occur simultaneously. Owing to membrane stability problems such as the loss of membrane phase, fouling and pore blocking of membrane, the membrane solution is joined in the dispersed pool to supply the loss.

Cyanide wastewater refers to the industrial wastewater containing cyanide, mainly from mineral processing, electroplating, rare and precious metal smelting, agriculture, medicine, and coal gasification industry (Dvořák et al. 2011; Shen et al. 2014). Cyanide is a highly toxic compound, which can cause human or livestock death with very few doses in a short period of time. The developed treatment methods for cyanide wastewater are active carbon adsorption, ferrate oxidation process, photo-catalytic oxidation, membrane method, ion exchange method, solvent extraction, electrolys is and so on. Although these treatment methods for cyanide have a certain effect, they are still insufficient in some aspects. For instance the solvent extraction developed by Tsinghua University has achieved industrial-scale application, but the method is only suitable for wastewater containing high concentration of cyanide (Yang et al. 1997); electrolytic method is also suitable for wastewater containing high concentration of cyanide, but the current efficiency is low, and it is difficult to meet the discharge standard of wastewater (Chen & Li 2005).

In this work, DSLM was investigated for the removal of target species from a feed solution. The new liquid membrane process is featured with supplying the carriers to make up the carrier loss, in addition to high transport percentage and other advantages compared with traditional SLM. As a model system, some experiments were performed to investigate the efficiency of cyanide recovery from wastewater using kerosene as the liquid membrane solvent and trioctylamine (TOA) as a carrier. The experiments studied the influences of carrier concentration, stirring time, volume ratio of membrane solution to NaOH, initial concentration of CN(I), NaOH concentration in strip phase and reuse of membrane.

All the experiments were conducted using 400 mL cells with effective volume of 150 mL for both feed solution and stripping phases. Two cells were separated by the poly(vinylidene fluoride) (PVDF) film (Shanghai Yadong Peucine Co., Shanghai) as support, which had a porosity of 75%, thickness of 65 μm, pore size of 0.22 μm and refractive index of 1.67. The effective area was 10 cm². The membrane was pre-wetted with the organic phase for at least 24 hours in order to make the pores of the membrane fully filled with membrane solution. JJ-1 accurate electronic stirrers (Shanghai Pudong physical and chemical instrument factory) were used to stir the two cells at 350 rev/min. The concentration of cyanide(I) was determined by the silver nitrate titration method.

Migration experiments

The membrane solution was prepared by dissolving the carrier in kerosene. The PVDF membrane was cut according to the size of the reaction tank and put into the prepared solution, and soaked for 12 hours. A certain volume of wastewater was diluted with deionized water to a certain ratio, then regulated to pH 4, and filtrated. The pre-wetted polymer membrane was taken out, and liquid on the membrane surface was blotted with the filter paper, then fixed on the reaction tank. The feed solution and membrane solution were added, respectively, to the feed pool and dispersion pool, and then stirring was started on both sides after NaOH dispersed in the strip pool. Equal stirring speeds were used, and counting started at the same time as the stirring. Figure 1(a) shows the experimental installation of the DSLM process.

Transport studies

With TOA as the mobile carrier and kerosene as a membrane solvent, the dispersion reaction and transfer process of CN(I) in the system can be roughly divided into the following processes (Yang et al. 1994). Figure 1(b) shows the principle of DSLM, in which transport processes and concentration changes are depicted.

1. First, CN(I) of feed phase passes through the aqueous diffusion layer between the feed phase and the membrane phase; CN(I) and TOA undergoes complexation reaction as follows:

$$nH^+ + nCN^- + TOA_{org} \rightarrow [TOA_{m,n}]CN_n$$

(1.1)

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 the membrane phase, then continue to diffuse in the membrane phase, and then reaction with the desorption agent occurs on the phase interface between the membrane phase and dispersion phase:

\[
\text{[TOAH}_n\text{]CN}_n + n\text{Na}^+ + n\text{OH}_s^- \\
= n\text{NaCN}_s + \text{TOA}_{org} + n\text{H}_2\text{O}
\] (1.2)

where ‘s’ is the strip phase. The stirring provides opportunity for full contact between cyanide–carrier generated complexes and desorption agent, which ensures continuation of the process of extraction and back-extraction, and improves the transport rate of the CN(I) and the stability of the membrane.

RESULTS AND DISCUSSION

Mass transfer kinetics equation

According to the characteristics of the coupling process, the migration process of cyanide(I) in the support membrane system is divided roughly into the following five steps, and Figure 1(c) shows the migration model of CN(I).

1. When CN(I) of the feed phase passes from the feed phase to the phase interface between the feed phase and the membrane phase, assuming the change of CN(I) concentration in the phase interface is linear, and its transmission complies with Fick’s first law, its transmission flux \( J_f \) can be expressed as:

\[
J_f = -d_a \frac{\partial [CN^-]}{\partial s}
\] (2.1)

The above formula can be rewritten as:

\[
J_f = \frac{d_s}{\delta_a} (c_f - c_{im})
\] (2.2)

where \( d_a \) is diffusion coefficient of CN(I) in the feed phase, \( \delta_a \) is thickness of phase boundary diffusion layer.
between the feed phase and the membrane phase, $c_t$ is CN(I) concentration in the feed phase and $c_{m}$ is CN(I) concentration on the phase interface between feed phase and membrane phase.

2. In the phase interface between the feed phase and the membrane phase occurs the coordination reaction, and [TOAH$_4$]CN$_n$ are generated. The flux of CN(I) in the membrane phase is:

$$J_p = k_1 c_{m} c_{TOA} - r_{-1} c_{CT} c_H^+$$

(2.3)

where $k_1$ and $k_{-1}$ are the pseudo-first-order rate constant of the positive and inverse interface reaction, $c_{TOA}$ is the concentration of TOA, $c_{CT}$ is concentration of [TOAH$_4$]CN$_n$ on the phase interface. Because the concentration of TOA and the concentration of $H^+$ are much lower than the concentration of [TOAH$_4$]CN$_m$, formula (2.3) is simplified as follows:

$$J_p = k_1 c_{m} - r_{-1} c_{CT}$$

(2.4)

3. [TOAH$_4$]CN$_n$ diffuses from the membrane phase into the back-extraction phase; assuming its diffusion complies with Fick’s first law, the flux can be expressed as:

$$J_m = \frac{d c}{d t} = \frac{d c_{CT} - c_{CS}}{\delta_o}$$

(2.5)

where $d_o$ is the diffusion coefficient of [TOAH$_4$]CN$_n$ in the membrane phase, $\delta_o$ is the thickness of the membrane, $c_{CS}$ is concentration of [TOAH$_4$]CN$_n$ in the phase interface between the membrane phase and dispersion phase.

4. [TOAH$_4$]CN$_n$ undergoes desorption reaction on the phase interface between the membrane phase and dispersion phase. Because of the higher concentration of back-extraction solution, the equilibrium constant is much larger than the extraction equilibrium constant, so the desorption reaction of [TOAH$_4$]CN$_n$ is very fast. Therefore, we can ignore the influence of this step on the whole process. After the desorption reaction the carrier migrates back to the phase interface between the feed phase and the membrane phase. So, the concentration of [TOAH$_4$]CN$_n$ is not the determining rate step of the process. $c_{CS} = 0$. Therefore, formula (2.5) is simplified as follows:

$$J_m = \frac{d c}{d t} c_{CT}$$

(2.6)

5. Similar to step 1, this step is also an aqueous diffusion process. The diffusion speed of CN(I) is very fast, and it can be neglected. Therefore, in steady-state, the transfer flux of CN(I) is:

$$J = J_f = J_p = J_m$$

(2.7)

The flux equation of CN(I) can be derived by formulas (2.2), (2.4), (2.6) and (2.7):

$$J = \frac{k_1}{k_1 \Delta_\alpha + k_{-1} \Delta_0 + 1} c_f$$

(2.8)

where $\Delta_\alpha = \delta_o / d_o$, $\Delta_0 = \delta_0 / d_0$, and $J$ is the transfer flux of the CN(I) through the membrane. According to the diffusion process of CN(I), the relationship between the transfer flux $J$ of CN(I) and change rate of the concentration of CN(I) is:

$$J = - \frac{V_f}{A} \frac{d c}{d t} = P c c_f$$

(2.9)

where $V_f$ is the feed phase volume; $A$ is membrane effective area; and $P_c$ is the permeability coefficient of CN(I).

The mass transfer flux of CN(I) can be determined by the change rate of concentration over time, as follows:

$$\ln \frac{c_t}{c_0} = - \frac{A}{V_f} P c t$$

(2.10)

where $c_t$ and $c_0$ are, respectively, concentration of CN(I) at time $t$ and initial concentration in feed phase, and $t$ stands for the transfer time (s). The reaction of CN(I) in the phase interface is assumed to be a first-order reaction, as follows:

$$k_1 \Delta_\alpha + k_{-1} \Delta_0 + 1 \approx k_1 \Delta_\alpha + k_{-1} \Delta_0$$

(2.11)

$P_c$ can be obtained by formulas (2.8)–(2.10):

$$P_c = \frac{k_1}{k_1 \Delta_\alpha + k_{-1} \Delta_0} = \frac{D}{D \Delta_\alpha + \Delta_0}$$

(2.12)

where $D = k_1 / k_{-1}$ is the distribution ratio. According to the definition of distribution ratio:

$$D = K_{ex} c_{TOA} c_H^n$$

(2.13)

where $K_{ex}$ is the extraction equilibrium constant of CN(I).
Formula (2.12) is put into (2.11):

\[ P_c = \frac{K_{exc}c_{TOA}}{K_{exc}c_{TOA}^2 + \Delta_0 e_{H}^n} \]  

(2.14)

Further derivation:

\[ \frac{1}{P_c} = \frac{\Delta_0 e_{H}^n}{K_{exc}c_{TOA}} + \Delta_0 \]  

(2.15)

Under the condition of \( c_{TOA} \) is in a certain concentration, \( 1/P_c \) and \( e_{H}^n \) have a linear relationship, and parameters \( \Delta_0 \) and \( \Delta_0 \) can be obtained by the intercept and slope of the straight line. The diffusion coefficient \( d_0 \) of CN(I) and phase interface thickness \( \delta_0 \) between feed phase and membrane phase can be calculated.

**Extraction of cyanide by DSLM**

**Effect of the carrier type on transport of CN(I)**

Selecting the appropriate mobile carrier was not only the key to improving the selectivity of membrane, but also the key to liquid membrane system design. The experimental comparison of effect of TOA and TBP on the removal CN(I) was studied. The results are shown in Table 1: when the carrier concentrations was 1 and 2%, cyanide removal effect was much better than the effect of TBP because the chemical structure of TOA was conducive to the formation of complexes with CN(I). PVDF membrane soaked using TBP was observed to be much softer than the one soaked using TOA. The membrane material had suffered chemical and physical erosion by organic solvent for a long time, which led to the occurrence of physical and chemical changes of the polymer support structure, thus losing long-term stability. PVDF tends strongly to crystallize when the carrier is brought into the phase separation boundary in the immersion process (Chang et al. 2014). Thus, TOA should be a suitable mobile carrier for the following experiments.

**Effect of the carrier concentration on transport of CN(I)**

Because the mobile carrier was in the charge of the selective transmission of CN(I), it played an important role in the transport process of CN(I), and it also played a decisive role in the migration selectivity and flux for CN(I). Therefore, the carrier concentration directly affected transport rate of CN(I). Figure 2(a) indicates that, when the carrier concentration increased from 1 to 2%, removal rate of CN(I) increased significantly, but when the carrier concentration increased to a certain extent, removal rate of CN(I) decreased because the migration process of CN(I) was jointly controlled by chemical reaction and diffusion dynamics, which was a dynamic equilibrium process. When the carrier concentration was low, the whole process was controlled by chemical reaction (Du et al. 2004). According to the principle of chemical equilibrium, increasing the concentration of reactants favored the formation of carrier complexes, so removal rate of CN(I) increased rapidly; but when the carrier concentration reached a certain value, interfacial concentration was close to saturation, and the diffusion process would play a decisive role. While continuing to increase the carrier concentration, the viscosity of the dispersion phase would become bigger, and the membrane pore may be blocked up, which would reduce the diffusion coefficient of the complex, so the removal rate of CN(I) decreased (Bhatluri et al. 2014). Therefore, the TOA concentration of 2% achieved greater extraction effect. Thus, 2% should be chosen as the optimum concentration of TOA.

**Effect of volume ratio of membrane solution to NaOH on transport of CN(I)**

Because the disperse phase was uniformly mixed with NaOH solution and membrane solution, the volume ratio of membrane solution to NaOH (O/S) directly affected the reaction rates of the coordination reaction and desorption reaction of CN(I). Figure 2(b) indicates that, when the proportion of NaOH was greater, the emulsion was less stable, so the volume ratio of O/S was lower, which was not conducive to transport of CN(I). When the volume ratio of O/S increased, the droplets of the stripping solution dispersed in the membrane, phase increased obviously (He et al. 2006). In this way, the membrane phase and supplying stripping phase provide an extra stripping surface and promotes the renewal rate of the liquid membrane, which lead to extremely fast transport rate and extension of the liquid membrane.

**Table 1 | Effect of the carrier type on transport of CN(I)**

<table>
<thead>
<tr>
<th>Carrier</th>
<th>TOA</th>
<th>TBP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration /%</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>NaOH /%</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Removal rate /%</td>
<td>68.55</td>
<td>92.52</td>
</tr>
</tbody>
</table>
lifetime (Pei et al. 2012). So All things considered, 2:1 was suitable for the volume ratio of O/S.

**Effect of the concentration of NaOH on transport of CN(I)**

The effect of NaOH concentration in the strip phase on the removal rate of CN(I) is presented in Figure 2(c). 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. As observed, the removal rate increased with increasing NaOH concentration. When the concentration of NaOH was more than 2 M, removal rate decreased. Probably due to the alkalinity being too high, the support membrane carrier was partially soluble in the extraction phase and ran off, resulting in the loss of the system and decreasing of stability. Therefore, the extraction process could not continue effectively, causing the decreasing of the mass transfer effect of CN(I) (Kazemi et al. 2014). So 2 mol/L was a suitable concentration for the NaOH.

**Effect of the initial concentration of CN(I) on transport of CN(I)**

The CN(I) complexed with TOA formed on the interface between the feed phase and the membrane phase across the chemical reaction. Table 2 indicates that, when CN(I) concentration increased, equilibrium shifted right, leading to CN(I) migration rate increasing. But CN(I) migration rate was also influenced by the carrier concentration and the membrane area (Muthuraman & Teng 2009). With increasing of CN(I) concentration from 10 to 30 mol/L, the removal rate of CN(I) increased, then decreased as the initial concentration of increased higher than 30 mol/L. This indicated that the number of moles transported through the
membrane per unit area of the membrane per unit time was 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 CN(I) proportionally (Venkateswaran et al. 2007). When the feed phase contains low concentration of CN(I) (up to 50 mg/L), the initial sharp increasing in removal rate is partly in accordance with the expected trend, since the flux was proportional to the CN(I) concentration (Kazemi et al. 2014). Thus, 30 mol/L was suitable for the initial concentration of CN(I).

### The reuse of membrane

The membrane in DSLM could be reused many times before the re-extraction with the membrane solution after every experiment. Figure 2(d) indicates that the membrane solution in DSLM could be also reused many times and the removal rate of CN(I) was stable in five experiments. With increasing of experimental times, because the membrane pore was wet for a long time and the cyanide underwent a complexation reaction and dissociation reaction with the carrier, surface tension of the interface was gradually reduced. So the aqueous phase entered into the membrane pore, and part of the organic phase was replaced, leading to instability in SLM. Therefore, after five experiments, the removal rate of CN(I) started decreasing gradually (Chen et al. 2011; Kang & Cao 2014). In addition, the membrane body was organic polymer materials, and the structure experienced physical and chemical changes because of contact with the organic solvent, thus losing long-term stability (Kocherginsky et al. 2007).

### CONCLUSION

CN(I) could be effectively extracted by DSLM containing TOA and kerosene as the membrane phase. Various factors affecting the removal rate of CN(I) such as initial CN(I) concentration, carrier concentration, stirring time, volume ratio of O/S and NaOH concentration were investigated in detail. Optimal experimental conditions for transport of CN(I) were obtained: initial CN(I) concentration of 30 mg/L; carrier concentration (%TBP) of 2%; stirring time of 1 hour; volume ratio of O/S of 2:1 and NaOH concentration of 2 mol/L, and the stable removal rate of CN(I) was more than 90%. The results showed that DSLM can lead to high mass transfer rate and could be good approach for recovery of CN(I) from wastewater. In the DSLM, owing to the large volume of membrane solution used, it makes up for the loss of carrier in the SLM. As a result, the transport percentage of CN(I) was increased, the stability of membrane was enhanced, and the lifetime of the membrane was extended.

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