Transport Behavior of Divalent Lead Ions through Disphase Supplying Supported Liquid Membrane with PC-88A as Mobile Carrier

Liang Pei[*]   Li-ming Wang[†]

[*]Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beiing, pellys_0311@163.com

[†]Xi'an University of Technology, Xi'an, pellys38994327@qq.com

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Liang Pei and Li-ming Wang

Abstract

The transport behavior of Pb(II) through a novel disphase supplying supported liquid membrane (DSSLM) with 2-ethyl hexyl phosphonic acid-mono-2-ethyl hexyl ester (PC-88A) as the carrier in kerosene, polyvinylidene fluoride membrane(PVDF) as the support and HCl as the stripping agent, has been studied. The effects of organic-to-feed volume ratio (O:F), pH, initial concentration of Pb(II) and ionic strength in the feed solution, organic-to-strip volume ratio (O:S), concentration of HCl solution and PC-88A concentration in the supplying strip phase on transport of Pb(II) have also been investigated. The advantages of DSSLM campared to the traditional SLM were investigated. The system stability, the reuse of membrane solution and the retention of membrane phase were also studied. When initial Pb(II) concentration was 2.00×10^{-4} mol/L, the transport percentage of Pb(II) was up to 92.9% under the optimun conditions in 175 min. The kinetic equation was developed in terms of the law of mass diffusion and the theory of interface chemistry. The results were in good agreement with experimental results.

KEYWORDS: disphase supplying supported liquid membrane, organophosphates, supplying feed phase, supplying strip phase, lead ion

INTRODUCTION

The removal and recovery of toxic heavy metals such as lead, cadmium, nickel, copper, platinum, chromium, mercury and zinc from aqueous environment have received considerable attention in recent years due to their carcinogenicity and toxicity which may cause damage to various systems of the human body. They also can be readily adsorbed by marine animals and directly enter the human food chains, thus presenting a high health risk to consumers (Kandah *et al*., 2007). Lead ions are non-biodegradable toxic heavy metals and may cause high blood pressure, kidney disease and so on (Chmielewski *et al*., 1997; He *et al*., 2006). According to the World Health Organization, concentration of lead in effluents in the US from the electroplating process wastewater is 3.6 *mg/L*, while that in drinking water should be less than 0.015 *mg/L* (Meng *et al*., 2000). The major sources of lead contamination to water come from industrial process such as aerospace, petrochemical, electroplating, batteries manufacturing, mine, metal material and many other industries. It is necessary to remove and recover these highly toxic and nonbiodegradable heavy metals in order to meet increasingly stringent environmental quality standards and promote the recycling and reuse of heavy metal resources (Ren *et al*., 2007). The conventional methods for these purposes include adsorption, filtration, chemical precipitation, reverse osmosis, sorbents(typically ion-exchange), solvent extraction processes, liquid membrane, biological systems, evaporation etc. Amongst these methods, precipitation is usually frowned upon because it produces a sludge which must be land filled , the metal of interest is not recovered , there is a high chemical cost, and it is a semi-continuous process. Biological systems are typically unstable and have slow kinetics. Sorbents can have high selectivity, capacity and adsorption rate but can only work in semi-continuous operations in which the sorbent must be periodically regenerated (Özer *et al*., 2007; Darvishi *et al*., 2007; Ghaedi *et al*., 2007). Evaporation, reverse osmosis and eletrodialysis exhibit no selectivity whereas precipitation, solvent extraction and ion exchange are allow the recovery of metal ions, but are rarely used because of high capital and operating costs when compared to the value of materials recovered (Trtic-Petrovic *et al*., 2002). So it is necessary to develop more efficient and cost-effective removal and recovery methods, which are needed to overcome these problem.

Recently, many scientists have paid more attention to liquid membrane(LM) techniques due to the specific characteristics. The potential advantage of LM techniques, over traditional transport techniques and solid membrane techniques, are low capital and operating costs, low energy and extractant consumption, high concentration factors and high transport percentagees (Trtic-Petrovic *et al*., 2002; Pei *et al*., 2009). LMs can carry out simultaneous extraction and stripping processes in the same stage, and it has

benefits of nonequilibrium mass transfer and up-hill effect, where solute can move from low-to-high concentration solution. The main type of liquid membrane systems include emulsion liquid membrane(ELM) and supported liquid membrane(SLM). However, LM techniques have not been adopted for large-scale industrial process. One disadvantage of ELM is that the emulsion swells upon prolonged contact with the feed stream. This swelling causes a reduction of the stripping reagent concentration in the aqueous droplets, which reduces stripping efficiency. A second disadvantage is membrane rupture, resulting in leakage of the contents of the aqueous droplets into the feed stream and a concomitant reduction of transport efficiency. SLM is not used on a large scale in industry. The major reason for this is stability or lifetime of membrane, which is due to the loss of carrier or membrane solvent from the membrane phasethat has an influence on both percentage and selectivity of the membrane (Pei *et al*., 2009).

In order to overcome these difficulties, more new liquid membrane configurations were studied, such as supported emulsion liquid membrane(SELM) and hollow fiber liquid membrane(HFRLM) (Ren *et al*., 2007; Zeng *et al*., 2010; Rosell *et al*., 1998) etc. In our previous work, one phase supplying supported liquid mambrane named dispersion supported liquid mambrane(DSLM) has been studied for transport of rare earths and the transport results compared with the traditional SLM were very obvious (Zeng et al. 2010; Rosell *et al*., 1998; Pei *et al*., 2010; Danesi *et al*., 1984). In this paper, a new liquid membrane technique, named disphase supplying supported liquid membrane(DSSLM), was investigated for the removal and recovery of target species from a feed solution. This is a new liquid membrane process, which has some advantages compared with DSLM in our previous work and traditional SLM: increased transport percentage and more stable membrane phase. The influence of various experimental parameters on the transport of Pb(II) from wastewater was investigated. As a model system, we have studies single Pb(II) transport by DSSLM with PC-88A as mobile carrier, which has little research reported at present.
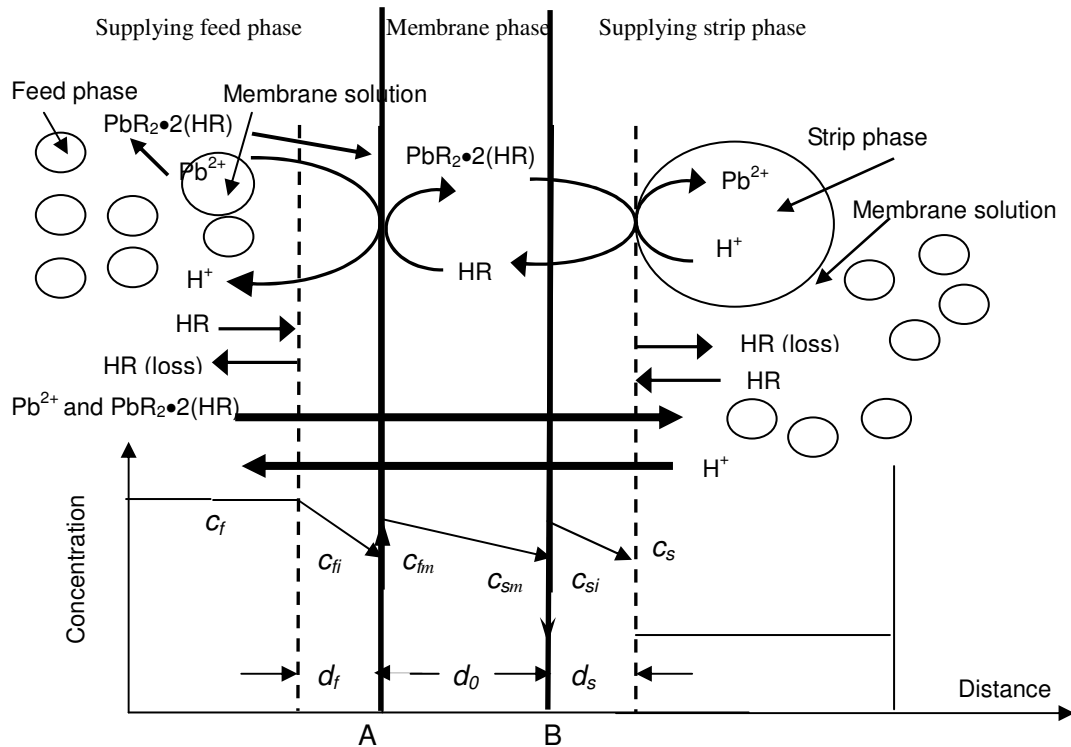
Supplying feed phase   Membrane phase   Supplying strip phase

Feed phase

Membrane solution

$PbR_2 \bullet 2(HR)$

Pb^{2+}

$PbR_2 \bullet 2(HR)$

Strip phase

Pb^{2+}

Membrane solution

H^+

HR

H^+

HR

HR (loss)

HR (loss)

HR

Pb^{2+} and $PbR_2 \bullet 2(HR)$

H^+

Concentration

c_f

c_{fi}

c_{fm}

c_{Sm}

c_{si}

c_s

d_f d_0 d_s

Distance

A   B

Figure 1. Diagram of Pb(II) transport through disphase supplying supported liquid membrane.
HR stands for the carrier within the membrane, which is PC-88A in this case. $PbR_2 \bullet 2(HR)$ stands for the organometallic compound, H^+ is the hydrogen ion and Pb(II) is the uncomplexed Pb(II) (A and B are the boundaries of the membrane phase)

THEORETICAL

Figure. 1 is the principle of DSSLM process, in which concentration changes and transport processes are depicted.

The DSSLM system consists of three phases: (1) the supplying feed phase containing metals ions and membrane solution, (2) the membrane phase, which is supported by PVDF, impregnated with an organic solution containing carrier and solvent, and membrane serves as uniform barrier between two phases, (3) supplying strip phase containing membrane solution and stripping solvent in which the metal ion is uncomplexed from membrane phase.

The co-transport involves various equilibrium reactions, which are described as follows:

(1) The diffusion of divalent metal ions from the supplying feed phase to the interface of feed-membrane phase.

(2) On the feed side interface of the SLM, extraction of the divalent metal ions from feed solutions with carriers can be expressed as the following Eq. 1.

$$M_f^{2+} + \frac{m+n}{2}(HR)_{2,org} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} MR_n \cdot mHR_{(org)} + nH_f^+ \tag{1}$$
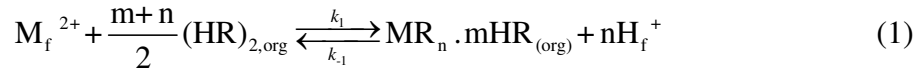
Where f, M_f^{2+} and *org* stand for supplying feed phase, divalent metal ions, and organic phase, $(HR)_2$ denotes the dimeric form of active carriers such as PC-88A.

(3) The metal-complex diffuses through the membrane A-B.

(4) At the other side interface of the membrane, the metal-complex is dissolved membrane solution and the metal ions is stripped by stripping solvent. The chemical reaction can be written as the following Eq. 2.

$$MR_n \cdot mHR_{(org)} + nH_s^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} M_s^{2+} + \frac{m+n}{2}(HR)_{2,org} \tag{2}$$
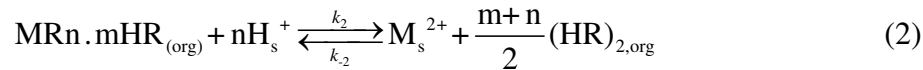
Where s stands for supplying strip phase. k_1、k_{-1}、k_2、k_{-2} are the pseudo-first-order rate constants of the forward and backward reactions of two interfaces.

(5) Carrier PC-88A returns from B to A (Pei *et al*., 2010; Danesi *et al*., 1984; Danesi *et al*., 1982; Elhassadi *et al*., 1999).

In this mechanism the transport of Pb(II) across DSSLM is described by considering only diffusional parameters, because the complex reaction between the Pb(II) and PC-88A at the interfaces is faster compared to the diffusion in the aqueous and membrane phase (Ho *et al*., 2001; Juang *et al*., 2003). Then in this model, the transport of Pb(II) in the DSSLM process can be considered as four sequential steps. If the diffusion process is described by the Fick´ law, the transport flux of each step can be writen as follows:

$$J_f = \frac{D_f}{d_f}(c_f - c_{fi}) \tag{3}$$

Where D_f, d_f, c_f and c_{fi} stand for diffusional parameters and the thickness of aqueous and membrane interface, the concentration of Pb(II) in supplying feed phase, and the concentration of Pb(II) in aqueous and membrane interface.

$$J_{i0} = k_1 c_{fi} - k_{-1}\overline{c_f} \tag{4}$$

Where $\overline{c_f}$ indicates that the concentration of Pb(II) in the membrane phase.

$$J_0 = \frac{D_0}{d_0}(\overline{c_f} - \overline{c_s}) \tag{5}$$

Where $\overline{c_s}$, D_0 and d_0 stand for the concentration of Pb(II), diffusional parameters and thickness in membrane phase.

$$J_{os} = k_2 \overline{c_s} \frac{V_0}{V_s} \tag{6}$$

Where V_s and V_0 stand for volume of strip phase in supplying strip phase and membrane phase, respectively.

Then, at steady state, all of these individual transfer transport percentagees are equal (Meng *et al*., 2000; Darvishi *et al*., 2007; Danesi *et al*., 1981; Ren *et al*., 2007; Cooper *et al*., 2004; Voorde *et al*., 2004; Swain *et al*., 2007). Respectively, by combining Eqs.1 to 6,

$$J = \frac{k_d . c_f}{k_d \dfrac{d_f}{D_f} + d_0 \dfrac{1}{D_0} + \dfrac{1}{k_2}\dfrac{V_s}{V_0}} \tag{7}$$

Where can be defined as $k_d = k_1/k_{-1}$.

Eq.7 can also be written as:

$$J = P_c . c_f \tag{8}$$

Where c_f stands for the concentration of supplying feed phase, P_c stands for the permeability coefficient, which is obtained as:

$$P_c = \frac{k_d}{k_d \dfrac{d_f}{D_f} + d_0 \dfrac{1}{D_0} + \dfrac{1}{k_2}\dfrac{V_s}{V_0}} \tag{9}$$

Eq.10 is attainable by rate constant and Eq.1.

$$k_1 = \frac{[\text{H}^+]^n [\text{MR}_n . m\,\text{HR}]}{[\text{M}^{2+}][(\text{HR})_2]^{\frac{m+n}{2}}} = \frac{k_d . [\text{H}^+]^n}{[(\text{HR})_2]^{\frac{m+n}{2}}} \tag{10}$$

By combining Eqs.10,

$$\frac{1}{P_c} = \frac{d_f}{D_f} + (\frac{d_0}{D_0} + \frac{V_s}{k_2 V_0}) \frac{1}{k_1} \frac{[\text{H}^+]^n}{[(\text{HR})_2]^{\frac{m+n}{2}}} \tag{11}$$

The rate of strip is very fast in the DSSLM, so $1/k_2$ can be ignored. Equation 11 can be simplified as:

$$\frac{1}{P_c} = \Delta_f + \Delta_0 \frac{1}{k_1} \frac{[\text{H}^+]^n}{[(\text{HR})_2]^{\frac{m+n}{2}}} \tag{12}$$

We can define $\varDelta_f$ and $\varDelta_o$ as:

$$\varDelta_f = \frac{d_f}{D_f}, \tag{13}$$

$$\varDelta_0 = \frac{d_0}{D_0} \tag{14}$$

The relationship between $1/P_C$ and $[\text{H}^+]^n$ are examined to be linear at the same carriers concentration. So the diffusion coefficient of Pb(II) in the membrane and the thickness of diffusion layer between the supplying feed phase and membrane phase can be obtained with the linear slope method. In the same way, the relationship between $1/P_C$ and $[(\text{HR})_2]^{-2}$ were examined to be linear at the same H^+ concentration in the supplying feed phase.

Based on the definition of permeability coefficient, transport flux of membrane can also be written as:

$$J = -\frac{V_f}{A}(\frac{dc_f}{d_t}) = P_c . c_f \tag{15}$$

Where V_f stands for the volume of supplying feed phase and A stands for effect area of membrane.

Considering and integrating Eq.15, we obtain the fowllowing equation:

$$\ln \frac{c_{f(t)}}{c_{f(0)}} = -\frac{A}{V_f} P_c.t \tag{16}$$

Where $c_{f(0)}$ and $c_{f(t)}$ stand for the concentrations of Pb(II) in the supplying feed phase at $t = 0$ and $t = t$ time, respectively. Eq.16 demonstrates the value of P_C is the slope of linear in figure, which is obtained in different operation conditions.

To formulate the model, the following assumptions were also made:

(1) The Pb(II) diffuses in the organic medium only as the PbR$_2$•2(HR) complex.

(2) There is no net flow due to convection within the liquid membrane.

(3) The metal ions react only with PC-88A at the membrane interfaces.

(4) The PC-88A monomer and dimer are in equilibrium at all times through the organic phase.

(5) The solubility of PC-88A in the aqueous acid solution has been found to be negligible and, therefore, its concentration in the DSSLM is assumed to remain constant (Juang *et al.*, 2003; Parhi *et al.*, 2008).

Metal-complex(PbR$_2$•2(HR)) diffusion through the membrane may be described by Fick's second law:

$$\frac{\partial C_{PbR}}{\partial t} = D_{PbR} \frac{\partial^2 C_{PbR}}{\partial x^2} \tag{17}$$

where C_{PbR} stands for concentration of the PbR$_2$•2(HR) complex in the organic solution; D_{PbR} stands for diffusivity of the PbR$_2$•2(HR) complex; x stands for distance in the liquid membrane. The boundary conditions at each of the DSSLM–aqueous solution interfaces represent the equality of the free Pb(II) mass transfer to or from the interfaces in the aqueous phase with the diffusion of the organometallic Pb(II) complex into or out of the organic phase at each boundary:

$$D_{PbR} \left. \frac{\partial C_{PbR}}{\partial x} \right|_A = k(C_{PbR}^0 - C_{PbR}^A) \tag{18}$$

$$D_{PbR} \left. \frac{\partial C_{PbR}}{\partial x} \right|_A = k(C_{PbR}^B - C_{PbR}^0) \tag{19}$$

where k stands for mass transfer coefficient in the aqueous phase at boundary A or B; C_{PbR}^0 stands for equivalent PbR$_2$•2(HR) concentration corresponding to the bulk aqueous phase Pb(III) concentration; C_{PbR}^A stands for interfacial PbR$_2$•2(HR) concentration at interface A; C_{PbR}^B stands for interfacial PbR$_2$•2(HR) concentration at interface B; A, B stands for extraction and stripping boundaries,

respectively. Given that the PbR$_2$•2(HR) complex does not exist in the aqueous phase, the mass transfer driving force of Pb(II), as Pb^{2+}, must be estimated by transforming the aqueous phase concentrations to equivalent organic phase concentrations $C_{PbR}{}^0$, using the extraction equilibrium constant. Therefore, it is possible to calculate the equivalent PbR$_2$•2(HR) concentration for the bulk aqueous free Pb^{2+} in the following manner:

From Eq.10, we obtain:

$$C^0_{PbR} = [\text{PbR}_2 \bullet 2(\text{HR})]_{bulk} = k_I \frac{[\text{Pb}^{2+}]_{bulk}[(\text{HR})_2]^3}{[\text{H}^+]^2} \tag{20}$$

where $[\text{Pb}^{2+}]_{bulk}$ stands for uncomplexed Pb(II) in the bulk aqueous solution; $[\text{PbR}_2 \bullet 2(\text{HR})]_{bulk}$ stands for PbR$_2$•2(HR) concentration in the organic phase in equilibrium with the bulk aqueous phase Pb(II) concentration; $[(\text{HR})_2]$ stands for PC-88A dimer concentration in the organic phase. On the other hand, in order to describe the PC-88A diffusion through the DSSLM, the different compounds which contain the extractant are in equilibrium and must be grouped together. Since the PC-88A dimer and the Pb(II) complex contain 2 and 6 PC-88A molecules, respectively, the total PC-88A transport percentage may be expressed as:

$$\frac{\partial C_{(HR,DR,PbR)}}{\partial t} = D_{HR}\frac{\partial^2 C_{HR}}{\partial x^2} + 2D_{DR}\frac{\partial^2 C_{DR}}{\partial x^2} + 6D_{PbR}\frac{\partial^2 C_{PbR}}{\partial x^2} \tag{21}$$

where $C_{(HR, DR, PbR)}$ stands for PC-88A total $= C_{HR} + C_{DR} + 6C_{PbR}$; C_{HR} stands for concentration of the PC-88A monomer; C_{DR} stands for concentration of the PC-88A dimer. Since no PC-88A enters the aqueous phases, in any form, its diffusion at both interfaces is considered to be negligible and the boundary conditions at A and B may be expressed as follows:

$$D_{HR}\frac{\partial C_{HR}}{\partial x} + 2D_{DR}\frac{\partial C_{DR}}{\partial x} + 6D_{PbR}\frac{\partial C_{PbR}}{\partial x}\bigg|_{A,B} = 0 \tag{22}$$

The initial conditions reflect the uniformity of the PC-88A monomer and dimmer concentrations, as well as the absence of Pb(II), throughout the DSSLM:

Then for all x,

$$C_{PbR} = 0 \qquad (23)$$

$$C_{HR,DR} = [PC\text{-}88A]^0 \qquad (24)$$

where $[PC\text{-}88A]^0$ stands for initial concentration of PC-88A.

To solve the model, aqueous solution mass balances and species distributions must be determined before solution of the diffusion equations is carried out. Since the extraction and stripping solutions contain an appreciable amount of sulfate, hydrogen and hydroxide ions, much of the Pb(II) is present as complexes with these ions. At each time, the free (uncomplexed) Pb(II) concentration must be calculated in order to evaluate the boundary conditions with Eq.(20). After this, the diffusion equations for Pb(II) and total PC-88A are discretized using the finite difference technique as proposed by Hoffman (Hoffman *et al*., 1988). The set of non-linear algebraic equations formed by the diffusion equations and the boundary conditions are solved by a Newton–Raphson type method. Finally, Pb(II) removal from the extraction phase and addition to the stripping phase are calculated using differential mass balances.

$$D_{PbR} \left. \frac{\partial C_{PbR}}{\partial x} \right|_{A,B} = \frac{V}{A} \frac{dC_{Pb}}{dt} \qquad (25)$$

where A stands for area of the aqueous–organic interface; V stands for volume of the aqueous phase; C_{Pb} stands for total Pb(II) concentration in the aqueous phase.

The flow of the hydrogen ion from the unreacted PC-88A takes place in the opposite direction and balances the charge of the Pb(II) lost or gained in each aqueous phase.

$$\left. \frac{dC_H}{dt} \right|_{A,B} = -2 \left. \frac{dC_{Pb}}{dt} \right|_{A,B} \qquad (26)$$

where C_H stands for total hydrogen ion transferred into or out of the aqueous phase. The entire procedure is repeated subsequently.

The model presented may easily be applied for a continuous process by eliminating the time dependency of Eq.(17). and Eq.(21), and converting the aqueous phase mass balances, Eq.(25)., to a flow scenario.

$$D_{PbR} \left. \frac{\partial C_{PbR}}{\partial x} \right|_{A,B} = \frac{V_A}{A_A} \frac{dC_{Pb}}{dz} \qquad (27)$$

where V_A stands for volumetric flow of aqueous solution, A or B; A_A stands for area of the aqueous–organic interface per distance of tangential flow; z stands for distance in the direction of flow. Despite these changes, the extraction velocity will still be controlled by the diffusion through the DSSLM and therefore subject to the same limitations as found in the nonsteady-state case.

EXPERIMENTAL

Reagents and Instruments

All the reagents such as Pb(II) nitrate (Pb(NO$_3$)$_2$•4H$_2$O), acetic acid glacial and sodium acetate anhydrous(HAc-NaAc) and 4-(2-pyridyla20) resoroin(PAR) used in the present work were of analytical grade. All chemical reagents are dissolved by deionized water. The 2-ethyl hexyl phosphonic acid-mono-2-ethyl hexyl ester (PC-88A) is a commercial extractant (purity > 95%) and used without any further purification. Kerosene was washed with concentrated sulfuric acid and distilled at 185–225$^o C$.

      All the experiments are conducted using 110 *ml*. The volume of supplying feed phase or supplying strip phase is 90 *ml*. Two cells are separated by the PVDF film as support, which has a porosity of 75%, thickness of 65 *μm*, pore size of 0.30 *μm* and refractive index of 1.67. The effect area is 10.5 *cm*^{2}. The JJ-1 accurate strengthen electronic stirrer was made in Jiangsu province of China. The UV-1200 spectrophotameter was made in Shanghai city of China. The water purification systems was made in Jiangsu province of China.
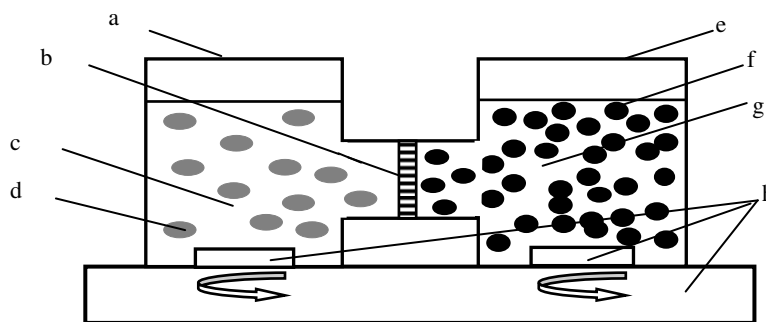
a—Supplying feed pool b—PVDF membrane c—Supplying feed phase d—Membrane solution in supplying feed phase e—Supplying strip pool f—Membrane solution in supplying strip phase g—Strip phase c+d—Supplying feed phase f+g—Supplying strip phase g—Magnetic stirrers
Figure 2. Experimental installation of DSSLM process

Experimental procedure

The supplying feed phase contained Pb(II) solution and membrane solution. The metal solution was prepared by dissolving the required amount of $Pb(NO_3)_2.4H_2O$. The supplying strip phase was the mixture of aqueous solution containing HCl solution and membrane solution. The membrane solution was prepared by dissolving of PC-88A in kerosene. The PVDF support was pre-wetted with the required amount of membrane solution more than 5.0 *h* in order to make the pores filled with carriers. The experiments were performed in the pH range of 3.0-5.6 to investigate the effect of pH in supplying feed phase on transport, the hydrogen ion concentration in supplying strip phase, the volume ratio of membrane solution and HCl solution and concentration of Pb(II) in supplying feed phase. The pH in supplying feed phase at each section of experiment was kept constant using buffer solutions.

We took a sample of Pb(II) soluton with sampling tubes after separation of organic phase and inorganic phase into layers within a given period. The Pb(II) concentration was analylyzed by spectrophotometric method(524 *nm*) with PAR as the chromogenic agent. And a digital precision ionometer model PHS-3C with a combined glass electrode was used for pH measurements (+0.01 pH).

RESULTS AND DISCUSSION

Stability of DSSLM

In order to define stability of DSSLM compared with traditional SLM, the tendency of Pb(II) concentration changes in supplying feed phase and supplying strip phase with time were studied under the fixed operating condition for a long time.
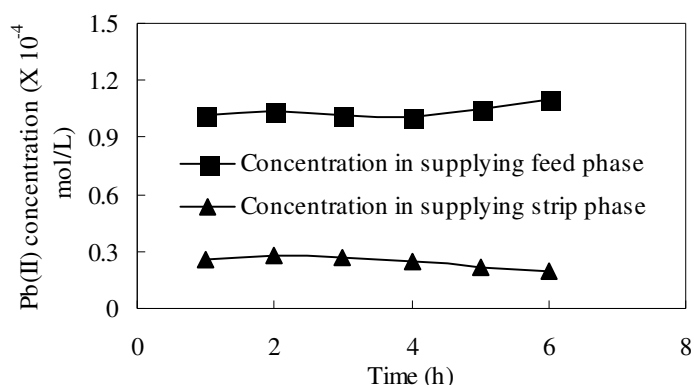

Figure 3. The stability of traditional SLM.

The assumed experimental conditions were chosen in the certain pH in the supplying feed phase, which was adjusted to 4.80. Initial concentration of Pb(II) was 1.30×10^{-4} *mol/L*, organic-to-feed volume ratio (O:F) was 1:10 in the supplying feed phase, organic-to-strip volume ratio (O:S) was 1:1, the HCl concentration was 3.00 *mol/L* and the PC-88A concentration was 0.150 *mol/L* in supplying strip phase. The results are shown in the Fig. 3. After 60 *min*, the tendency of Pb(II) concentration changes was stable, so we took a sample in 30 min in each transport experiment. We can find that after 6.0 *h*, the Pb(II) concentration and stablity of supplying strip phase decreased gradually under using traditional SLM and the Pb(II) concentration in both supplying feed phase and supplying strip phase remain stable under using DSSLM. This is because the carrier in traditional SLM loses gradually and DSSLM with supplying phase can supply carrier to the membrane system. So we can draw the conclusion that stability of DSSLM is better than traditional SLM.
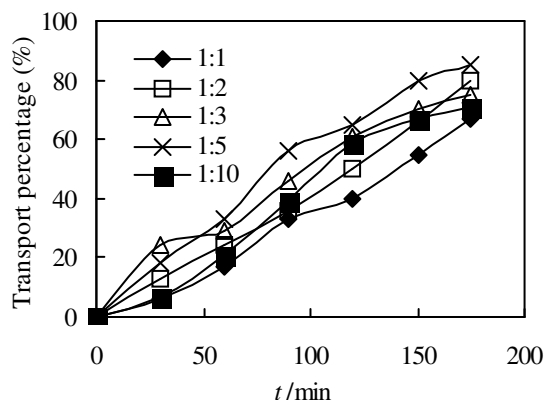
**Figure 4. Effect of organic-to-feed
volume ratio on transport of Pb(II)**

Effect of the organic-to-feed volume ratio (O:F)

The effect of organic-to-feed volume ratio(O:F) in supplying feed phase was studied. All other parameters such as pH, concentration of Pb(II) in supplying feed phase, concentration of carrier, concentration of HCl solution and the organic-to-strip volume ratio (O:S) in supplying strip phase were ajusted to 4.5, 2.0×10^{-4} *mol/L*, 0.15 *mol/L*, 4 *mol/L* and 3:1. The effect of organic-to-feed volume ratio (O:F) in the supplying feed phase on transport of Pb(II) is shown in Fig. 4. It indicates that the transport percentage of Pb(II) decreased with increasing of the volume ratio from O:F 1:1 to 1:10. When volume ratio of O:F was 1:5, the transport percentage of Pb(II) was 84.1%, it is the most effective volume ratio. Considering saving chemical agents as well as increasing transport percentage, we chose 1:5 mol/L as the optimum organic-to-feed volume ratio for the following experiments.
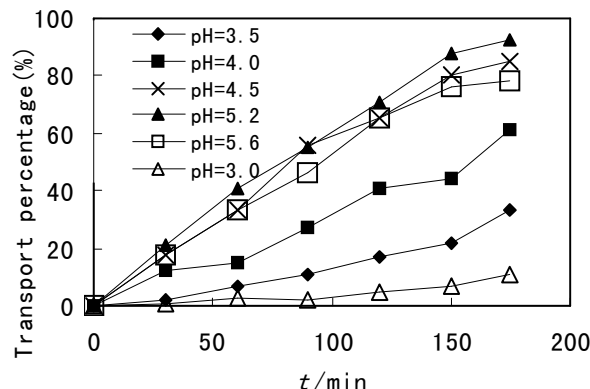
**Figure 5. Effect of pH in the supplying
feed phase on transport of Pb(II)**

Effect of pH in the supplying feed phase

The effect of pH in the supplying feed phase on permeation and transport of Pb(II) was studied in the pH range from 3.0 to 5.6, which was adjusted with an acetic acid/acetate sodium buffer solution. The O:F was adjusted to 1:5. The concentration of Pb(II) in the supplying feed phase was adjusted to 2.0×10^{-4} *mol/L.* The O:S, concentration of carrier and concentration of HCl solution in supplying strip phase were adjusted to 3:1, 0.15 *mol/L* and 4.0 *mol/L*. The results are shown in the Fig. 5. The transport percentage of Pb(II) increased, when pH of supplying feed solution increased from 3.0 to 5.2, and a maximum transport percentage observed at pH of 5.2 was 88.3% during 175 min.. Above pH of 5.2 in the feed solution, the transport percentage of Pb(II) decreased. This is similar to the influence of pH on distribution coefficient of extraction process (Ren *et al*., 2007). Contrast to the previous cases, the literature (Pei *et al*., 2009) suggested the influence of pH on distribution coefficient of extraction process. It is large because the transport process is mainly governed by the mass transfer driving force caused by the distribution equilibrium, when the renewal effect of the liquid membrane and the diffusional mobility of Pb(II) ions are definite under specific experimental conditions (Kandah *et al*., 2007). The concentration difference between supplying feed phase and supplying strip phase is the driving power of mass transfer process. In the supplying feed phase the lower the H$^+$ concentration is, the stronger the driving power of mass transfer process is. Stronger power promotes the transport efficiency of Pb(II). Equally, the greater the pH value in the supplying feed phase is, the higher the transport efficiency of Pb(II) is.

Effect of initial concentration of Pb(II) in the supplying strip phase

Table 1 Effect of initial concentrations of Pb(II) on transport of Pb(II)

Time , min	Transport percentage (%)				
	1.00×10^{-4} mol/L	1.50×10^{-4} mol/L	2.00×10^{-4} mol/L	3.00×10^{-4} mol/L	4.00×10^{-4} mol/L
0	0	0	0	0	0
30	27.8	24.0	12.3	5.9	2.4
60	60.1	52.2	30.1	21.2	13.8
90	77.7	66.1	41.9	40.7	26.1
120	91.9	80.6	57.2	60.5	31.8
150	100	98.1	79.3	63.3	38.0
175			88.1	73.7	59.3

Initial concentration of Pb(II) on transport of Pb(II) was studied in the range of 1.0×10^{-4} *mol/L* to 4.0×10^{-4} *mol/L*. The pH of supplying feed phase was adjusted to 5.2. The O:F was adjusted to 1:5. The concentration of carrier was adjusted to 0.15mol/L, O:S was adjusted to 3:1 and HCl was also adjusted at 4.0 *mol/L* in the supplying strip phase. The results obtained are presented in Tab. 1. With the increasing of Pb(II) concentration in the supplying feed phase from 1.0×10^{-4} *mol/L* to 4.0×10^{-4} *mol/L*, the transport percentage of Pb(II) decreased in the supplying feed phase. This is because the number of PC-88A is definite through the membrane when the interface between the feed phase and the membrane phase is definite. That is to say, the number of Pb(II) transported is definite in this transport process.

Effect of the organic-to-strip volume ratio (O:S)

The organic-to-strip volume ratio (O:S) in the supplying strip phase on transport of Pb(II) is shown in Fig. 6. It indicates that the transport percentage of Pb(II) increased with an increasing of the volume ratio. When organic-to-strip volume ratio O:S increased, the droplets of the stripping solution dispersed in the membrane phase increased obviously (Meng *et al*., 2000). In this way, the mixing between the membrane phase and supplying strip phase provides an extra stripping surface and promotes renewal rate of liquid membrane, which leads to faster stripping rate for the supplying feed phase from membrane phase and extension of liquid membrane life. Therefore it enhances the transport percentage

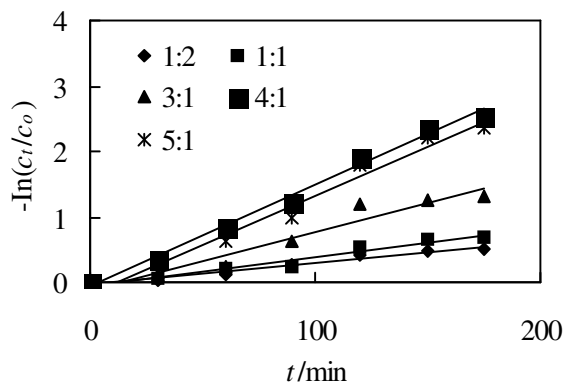of Pb(II). So the 4:1 can be chosen as the optimum organic-to-strip volume ratio in the following experiments.

**Figure 6. Effect of organic-to-strip
volume ratio on transport of Pb(II)**

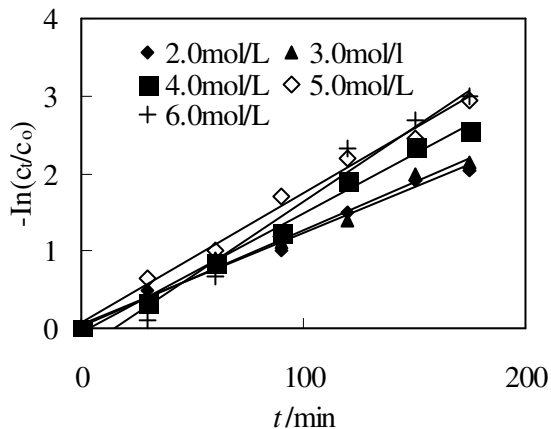*Effect of the concentration of HCl in the supplying strip phase*

**Figure 7. Effect of concentrations of
HCl on transport of Pb(II)**

The stripping reaction at the membrane-strip side plays a vital role in the transport of metal ions from supplying feed phase to supplying strip phase. So the effect of concentration of HCl was studied in this paper. All other parameters such as pH, concentration of Pb(II), O:F in supplying feed phase, the O:S and concentration of

carrier were adjusted to 1:5, 5.2, 2.0×10^{-4} *mol/L*, 4:1 and 0.15 *mol/L*. The Fig. 7 shows effect of transport rate of Pb(II) in different concentration of HCl. It indicates that the transport percentage of Pb(II) increased with the increasing of acid concentration. Further increasing of concentration of HCl from 2.0 *mol/L* to 6.0*mol/L* has no significant effect on the transport percentage of Pb(II), because the number of complex of Pb(II) and PC-88A which transport through the membrane per unit area of the membrane per unit time are determined when the concentration of PC-88A, the concentration of Pb(II) in the supplying feed phase and the effect area of membrane and time are determined. So the concentration of HCl in the supplying strip phase was 5.0 *mol/L* as the optimum condition.

Effect of ionic strengths in the supplying feed phase

Effect of ionic strengths in the supplying feed phase on transport percentage of Pb(II) was studied in this paper. We used the KNO_3 or NaCl to change the ionic strength,the concentrtion of K^+ or Na^+ with Pb(II) can be calculated to stand for the ionic strength. The results are shown in Fig. 8. It indicates that the ionic strengths has not effect on transport of Pb(II), because the HCl is contained by membrane solution, which leads to the ionic strengths of supplying strip phase is ignorable. So when the concentration of ions in the supplying feed phase are low, the ionic strengths of two phase is neglected. The operational condition, comparing to other technologies of liquid membrane, is further simplified.
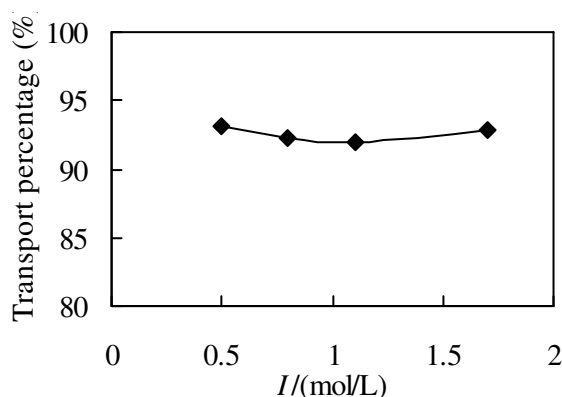

Figure 8. Effect of ionic strengths on transport of Pb(II)

The reuse of membrane solution

The reuse of membrane solutition was studied under the optimal conditions. From the Fig. 9, we can know the membrane solution in DSSLM can be reused many

times before the re-extraction with the strong acid after every experment. Membrane solutition in DSSLM can be reused many times and the tendency of transport percentage changes was stable with DSSLM in 3 experiments. After 3 experiments, the Pb(II) transport percentage decreased gradually.
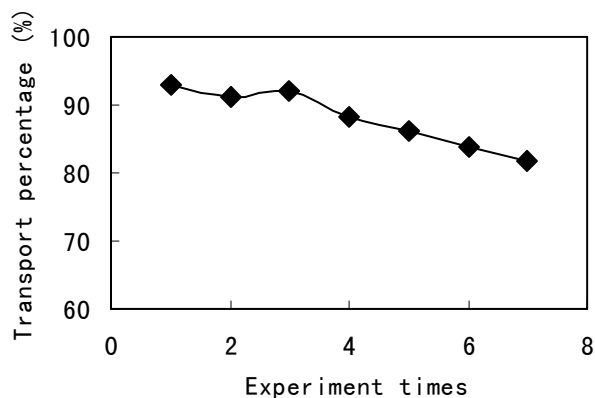

Figure 9. The reuse of membrane solution

The reuse of membrane sheet

The reuse of membrane sheet was studied under the optimal conditions. The membrane solution was reused only 3 experiments and we took new membrane solution or membrane solution after being purged by reversed extraction with the strong acid in the forth experiment. The results are shown in the Fig. 10. Membrane sheet of DSSLM with supplying strip phase can be reused many times and the tendency of transport percentage changes was stable with DSSLM in 8 experiments, but under the condition of membrane sheet of traditional SLM without supplying phase, the tendency of transport percentage changes was unstable and transport percentage decreased gradually after 3 experiments. In this study, we can also draw the conclusion that stability of DSSLM is better than traditional SLM.
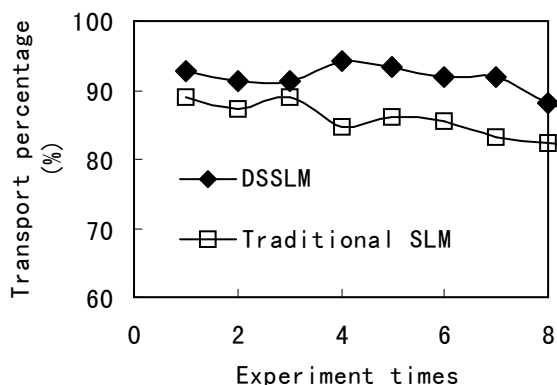
Figure 10. Reuse effect of membrane sheet

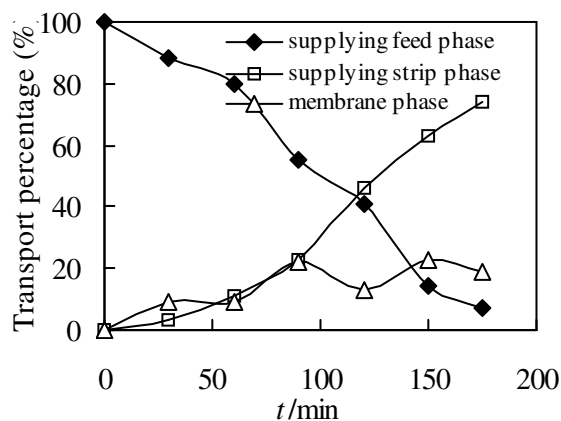*Retention in membrane phase*

Figure 11. Retention in membrane phase

The retention in membrane phase and effect of stripping was studied under the optimal conditions. The pH value was adjusted to 5.20, O:F was adjusted to 1:5, initial concentration of Pb(II) was 2.00×10^{-4} *mol/L* in the supplying feed phase, O:S was adjusted to 4:1, concentration of carrier was adjusted to 0.15 *mol/L* and concentration of HCl solution was also adjusted to 5.00 *mol/L* in the supplying strip phase. According to the concentrations of supplying feed phase and stripping phase, the concentration of Pb(II) in membrane phase can be obtained, then the effect of stripping in supplying strip phase and retention phenomenon of membrane phase can be obtained. The results are shown in the Fig. 11.

KINETIC ANALYSIS

Based on the data of the effect of pH in the supplying feed phase, the relationship between $1/P_C$ and $[H^+]^2$ is developed. When concentration of mobile carrier is determined, P_C is definite, too. The results are shown in Fig. 12.

It indicates that the relationship between $1/P_C$ and $[H^+]^2$ is linear in a certain pH. The value of R^2 is 0.9891, which is a good agreement with the theory from Eq.12. The slope and intercept are 5.39×10^{12} and 5.12×10^4. The thickness of diffusional layer d_f, which is calculated by using diffusional parameters of Pb(II) in the aqueous solution that is $5.99 \times 10^{-10} \, m^2/s$ (Zhao *et al*., 2005), is $4.64 \times 10^{-5} \, m$. The k_1 which can be determined by extraction experiment is 3.9×10^{-8}. Then the diffusion coefficient D_o in the membrane, obtained via Eqs.13 and 14, is $1.33 \times 10^{-8} \, m^2/s$.
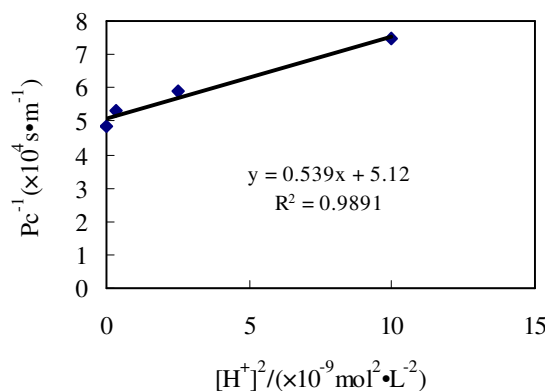

Figure 12. Comparison between experimental and theoretical

The new kinetic equation is determined by d_f and D_o in the DSSLM systerm. It can be written as

$$P_C = \frac{1}{5.12 \times 10^4 + 5.39 \times 10^{12}[H^+]^2} \tag{28}$$

CONCLUSIONS

The transport of Pb(II) through DSSLM system using PC-88A as mobile carrier was studied with the follow conclusions.

The optimum conditions for transport Pb(II) were that the concentration of carrier was 0.15 *mol/L*, concentration of HCl was 5.0 *mol/L* and O:S was 4:1 in the supplying strip phase and initial concentration of Pb(II) was 2.0×10^{-4} *mol/L*, O:F was 1:5 and pH was 5.2 in the supplying feed phase. When transport time was 175 *min*, the transport percentage was 92.9% under optimum conditions.

Through the experiment, a modal was established to describe the reaction and transport of metal ions in the DSSLM. The new kinetic equation was developed. The diffusion coefficient in the membrane phase and thickness of diffusion layer in the supplying feed phase were obtained by linear slope method. They were $1.33 \times 10^{-8} m^2/s$ and $4.64 \times 10^{-5} m$, respectively.

In the DSSLM, owing to the large number of membrane solution is used, this can be renewal the losing carrier in the supported liquid membrane. As a result, the transport percentage of Pb(II) is increased, the stability of membrane is increased, and the life of the membrane is extended.

NOTATIONS

A	effective area of membrane, m^2
c_f	concentration of metal ion in the supplying feed phase, $mol \cdot L^{-1}$
c_{fi}	concentration of metal ion in the diffusion layer in supplying feed phase, $mol \cdot L^{-1}$
c_{mf}^{0}	concentration of metal ion in the membrane near supplying feed phase, $mol \cdot L^{-1}$
c_{ms}^{0}	concentration of metal ion in the membrane near supplying strip phase, $mol \cdot L^{-1}$
$c_{f(0)}$	concentration of metal ion in the supplying feed phase when time=0, $mol \cdot L^{-1}$
$c_{f(t)}$	concentration of metal ion in the supplying feed phase when time=t, $mol \cdot L^{-1}$
d_f	thickness of diffusion layer between the supplying feed phase and membrane phase, m
d_i	inner diameter of fiber, mm
d_m	thickness of the membrane, m
D_f	diffusion coefficient of metal ion in the supplying feed phase, $m^2 \cdot s^{-1}$
D_m^{0}	diffusion coefficient of metal ion in the membrane, $m^2 \cdot s^{-1}$
[HR]	concentration of carrier PC-88A, $mol \cdot L^{-1}$
(HR)$_2$	extractant/carrier PC-88A
[H$^+$]	concentration of H$^+$, $mol \cdot L^{-1}$
J	membrane flux, $mol \cdot m^{-2} \cdot s^{-1}$
k_1	forward reaction percentage constant at the left interface of the membrane

k_{-1} backward reaction percentage constant at the left interface of the membrane

k_2 forward reaction percentage constant at the right interface of the membrane

k_{-2} backward reaction percentage constant at the right interface of the membrane

k_{ex} extraction equilibrium constant

k_d distribution ratio of metal ion

L effective length of module, m

P_c permeability coefficient of metal ion, $m \cdot s^{-1}$

$PbR_2 \bullet 2(HR)$ lead-carrier complex

V_f volume of the supplying feed phase, m^3

Greek letters

ε porosity of the membrane

τ tortuosity of the membrane

η transport efficiency of Pb^{2+}, %

$\triangle_f$ transport resistance due to diffusion by aqueous feed boundry layer, $s \cdot m^{-1}$

$\triangle_m$ transport resistance due to diffusion through the membrane, $s \cdot m^{-1}$

Subscripts

f supplying feed phase

m membrane phase

org organic phase

s supplying strip phase

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