A study of zinc borne waste water treatment with dispersion supported liquid membrane

Shibao Lu a,*, Liang Pei b

a School of Public Administration, Zhejiang University of Finance and Economics, Hang Zhou 310018, China
b Key Laboratory of Water Cycle and Related Land Surface Processes, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China

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A B S T R A C T

This paper based on a theoretical study of the supported liquid membrane separation technology, explores the appropriate liquid membrane separation system, makes a study on the Pb (II) transmission behavior in the PC-88A-kerosene-HCl dispersion supported liquid membrane system and reviews influence of the feed liquid pH value, volume ratio between the membrane liquid and analytic agent, HCl concentration during analytic phase and initial Pb (II) transmission concentration. The results show that the migration of Pb (II) is well completed for 190 min with the migration rate being up to 95% on the premise that the feed liquid pH is equal to 6.0, Pb (II) initial concentration of 3.0 \( \times \) \( 10^{-3} \) mol/L, HCl concentration during the stripped and dispersed phase is 4.0 mol/L, volume ratio between the stripped liquid and organic phase is 40:160 and that of the conventional supported liquid membrane is only 72.4%. The dispersion supported liquid membrane is characterized by higher transmission efficiency, stable membrane system and long membrane service life. The procedure has provided accurate results with zinc borne waste water treatment.

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I N T R O D U C T I O N

Waste water in industry, daily life waste water and various waste waters in mining contain numerous heavy metals which should lead to food chain biological enrichment and cause serious threats to creatures and human health [1–3]. A heavy metal is a trace element which is indispensable to the human body health with its high content should bring serious consequences and the lead contamination is primarily due to waste water and garbage from mining, smelting, rubber production, dyestuff, printing, ceramics, lead glass, soldering, cables and lead pipes [4–6]. Lead shall be released to environment in production and operation process, and enter into the human body in a direct or indirect way, thus resulting in serious health problems such as stomachache, headache, tremor and neuro-dysphoria [7]. Given a low concentration, the chronic lead poisoning shall primarily affect the brain and nervous system. The lead borne waste water treatment method includes methods such as chemical precipitation, ion exchange, liquid-membrane, biological adsorption, electrolytic and so forth.

In order to minimize the heavy metals’ serious influence on the ecological system, people have been in pursuit of new technology for the treatment of waste water contaminated by such metals. Pei and Yao [8] analyzes the zinc ion
transmission model in the PC-88A-kerosene supported liquid membrane system. Given different experimental conditions, more experiments have been carried out to predict the zinc transmission extent in a supported liquid membrane system. Bhattacharyya and Mohapatra [9] reports the trivalent chrome transmission in the liquid membrane system taking the di-phosphoric acid (2-ethyl hexyl) as carrier. Zhao and Shen [10] analyzes the bivalent and trivalent metal ion transmission behavior in the optional migration carried out in a supported liquid membrane, thereby taking a new type of organic phosphoric acid as carrier; the analysis results show that various adopted extraction agents will properly separate the mixed ions Cu (I), Co (II), Ni (II), Pb (II), Fe (III) and Cd (II). Pei and Yao [11] analyzes the silver and mercury transmission and separation in a generally improved and supported liquid membrane system with two-membrane and three-chamber system established to achieve a rapid silver and mercury ions separation. Artur and Marcelo [12] analyzes the cobalt ion solvent extraction adopting Cyanex272 as extraction agent and its migration by the supported liquid membrane focusing on discussion about the transmission flux in the liquid and the equilibrium constant in solvent extraction to obtain optimum experimental condition based on the liquid phase pH, carrier Cyanex272 concentration, Co (II) concentration in liquid phase and the stripping agent acidity influence analysis. Hamed and Amirmostafa [13] analyzes zinc ion transmission model in the PC-88A-kerosene supported liquid membrane system with more experiments made to predict the zinc transmission extent in the supported liquid membrane system given experimental conditions together with the stirring rate, carrier concentration and temperature influence on the surveyed metal ion transmission.

The Supported Liquid Membrane (SLM) separation technology requires much attention due to its advantages comprising less energy consumption, low cost, favorable selectivity and banned secondary pollution. However, SLM separation technology has not been applied to industrialization, the reason for which is that transmission process shall make membrane phase diminish to nothing and bring about a declined separation performance and a reduced service life. The dispersion supported liquid membrane technology avoids the membrane phase disadvantage, thereby being liable to diminish to nothing in the supported liquid membrane. It is especially applicable to metal ion’s low concentration enrichment and separation. The 2-ethylhexyl phosphoric acid – mono-2-ethylhexyl (P507) is the metal ion extraction agent which is characterized by an excellent extraction property, small water solubility and has no poison. This paper takes P507 as a flow carrier for the liquid membrane and selects PVDF as a support, kerosene as a membrane solvent to analyze the Pb (II) transmission process in the dispersion supported liquid membrane system composed of organic phosphoric acid-kerosene-HCl to discuss various factors and mechanisms which influence on its transmission so as to provide a theoretic foundation for effective Pb (II) borne waste water control.

**Experimental part**

**Instruments and reagents**

- UV-1200 type spectrophotometer (Shanghai Huipuda Instrument Plant);
- JJ-1 type precision and timing motor stirrer (Danyangmen Quartz Glass Plant in Jintan);
- P507: product name PC-88A, from Oba Chemical Industry Company in Japan;
- PbSO4, NH3.H2O, NH4Cl, HAc and NaAc are analytically pure; water for experiment is deionized.

The self-made dispersion supported liquid membrane migration pool comprises liquid, analytical pools and a support. The liquid and analytical pools are 200 mL in volume respectively, equipped with adjustable speed motor stirrer; the support is PVDF, and with 18 cm² effective area.

**Experimental method**

The experiment process is performed as follows:

- PVDF is immersed in the membrane solution for a given time for adsorption;
- Take it out to volatilize the membrane solvent;
- Fix it to the migration pool;
- Add the prepared sample feed liquid and the membrane solution to feed liquid and analytical pools respectively;
- Start the stirrers in the fed liquid and analytical pools;
- Add appropriate HCl to the analytical pool and start timing to sample for analysis at different appropriate intervals.

Pb (II) concentration shall be determined by the spectrophotometric method.

**Experiment principle**

The metal ion reaction and migration processes in dispersion supported liquid membrane system are approximately composed of the following steps:

1. Metal ion in feed liquid phase must pass through water dispersion layer between the feed liquid and membrane phases.
2. The (Pb²⁺) metal ion and carrier (HR), at interface between water-membrane phases, must have the following coordination reactions:
\[ M^{2+} \frac{m + n}{2} (HR)_{2\text{org}} \frac{K_{1}}{K_{2}} \frac{V_{f}}{V_{s}} \cdot mHR_{\text{org}} + nH^{+} \]  \hspace{1cm} (1)

where the subscripts: “t” indicates the water phase and “org” the membrane phase respectively. \( M^{2+} \) is the divalent metal ion and \((HR)_{2}\) the extraction agent which exists in the form of a dimer in non-polar oil.

(3) The metal ion and carrier complex generated in the previous step is diffused in the membrane phase.

(4) The metal ion and carrier complex also diffuses into analytical phase and react with the stripping agent:

\[ MR_{n} \cdot mHR_{\text{org}} + nH^{+} \frac{K_{1}}{K_{2}} \frac{V_{f}}{V_{s}} M^{2+} + \frac{m + n}{2} (HR)_{2\text{org}} \]  \hspace{1cm} (2)

where the right subscript S stands for the stripping dispersion phase.

(5) The carrier shall return to the interface between the feed liquid and membrane phases.

Suppose that the above reactions are of first order, adopt \( K_{1}, K_{2}, K_{3}, \) and \( K_{4} \) to represent the rate constant for forward and backward reactions in the extraction and stripping reactions respectively. The same supposition given in document [16–18] is referred to; which means that you have to use a linear concentration gradient, the concentration of charged species into the supported liquid membrane with low dielectric constant is to be ignored, and the permeated metallic substance concentration is lower. Therefore, proceed with the chemical reaction and stable state on continuous interface so as to derive new equation to describe the metal ion’s permeability coefficient in the dispersion supported liquid membrane [19,20].

\[ P_{t} = \frac{K_{t}}{D_{f} D_{s}^{-1} + D_{0}^{-1} + \frac{V_{0}}{V_{s}}} \]  \hspace{1cm} (3)

where \( K_{t} \) indicates the feed liquid phase metal ion distribution ratio, \( D_{f} \) the metal ion dispersion coefficient, \( D_{0} \) the membrane phase thickness, \( V_{0} \) the membrane phase volume and \( V_{s} \) the stripping phase volume.

It is obtained from the definition of rate constant and Equations (2)-(1) that

\[ K_{1} = \frac{(HR)_{2}}{[M^{2+}] [MR_{n} \cdot mHR]} = \frac{K_{d} [H^{+}]^{n}}{[M^{2+}] [HR]_{2}^{\frac{n}{2}}} \]  \hspace{1cm} (4)

and from Simultaneous Equations (2)-(3) and (2)-(4), it is obtained that

\[ \frac{1}{P_{t}} = D_{f}^{-1} + \left( D_{0}^{-1} + \frac{V_{0}}{V_{s} K_{2} K_{1}} \right) \frac{[H^{+}]^{n}}{[M^{2+}] [HR]_{2}^{\frac{n}{2}}} \]  \hspace{1cm} (5)

It is obvious that given a carrier concentration condition, \( 1/P_{t} \) has a linear relationship with \([H^{+}]^{n}\) and the analytic reaction’s dispersion coefficient and rate constant are obtained by using the straight slope analysis method [21,22] Fig. 1.

By next, the metal ion mass transfer flux is obtained through the determination of the metal ion’s time dependent concentration change rate \( dc_{f}/dt \) in the feed liquid phase. It is given by the following relation:

\[ J = \frac{V_{f} (dc_{f}/dt)}{A} = P_{t} c_{f} \]  \hspace{1cm} (6)

where \( V_{f} \) denotes the feed liquid phase volume, \( A \) is the membrane’s effective area, and \( c_{f} \) is the substance migrates concentration in feed liquid phase.

Integrating the Equation (6) you find:

\[ \ln \left( \frac{c_{f}(t)}{c_{f}(0)} \right) = \frac{A}{V_{f}} P_{t} c_{f} t \]  \hspace{1cm} (7)

where \( c_{f}(0) \) and \( c_{f}(0) \) are the metal ion concentrations in initial feed liquid phase at the time \( t \) respectively. The metal ion in different conditions shall be determined to make a diagram 1 based on \( \ln (c_{f}/c_{0}) \) to \( t \) and analyze the extent of various factors’ influence on the migration rate according to straight slope.

Results and discussion

Volume ratio influence between the membrane solution and HCl on Pb (II) transmission

The feed liquid phase pH is 6.0, Pb (II) initial concentration of \( 3.0 \times 10^{-4} \) mol/L, and HCl concentration of 3.0 mol/L are selected for the experiment. The volume ratio influence between the stripping liquid and membrane solvent is represented by 20:180, 30:170, 40:160, 50:150, 60:140 on the Pb (II) migration. The experiment results are as shown in Fig. 2.

The experiment results show that when volume ratio exists between the stripping agent and membrane solvent, Pb (II) migration is favorable. This is the reason for which when the stripping agent HCl in the dispersion supported liquid membrane system is uniformly dispersed into membrane solution, the volume ratio between the membrane solution and HCl will have an immediate influence on the Pb (II) migration and
stripping rate. The higher the HCl proportion in dispersion phase, the less stable the generated emulsion, a situation which should adverse to Pb (II) migration. The smaller proportion shall result in smaller additional stripping area and Pb (II) migration rate will be reduced accordingly. The volume ratio between the membrane solution and HCl is one of key factors having influence on Pb (II) migration rate.

HCl concentration influence on Pb (II) transmission

The feed liquid phase pH of 6.0 and initial Pb (II) concentration of $3.0 \times 10^{-4}$ mol/L are selected for the experiment. The volume ratio between the membrane solution and HCl in the stripping phase is 160/40 with the HCl concentration influence accounts for 1.0, 2.0, 3.0, 4.0 and 5.0 mol/L on the Pb (II) migration. The experiment results are as shown in the following figure (Fig. 3).

The experiment results show that there is a proper linear relation between $\ln \left( \frac{c_t}{c_0} \right)$ and t, and its straight slope varies with the change of HCl concentration accordingly. When the hydrochloric acid concentration is 4.0 mol/L in the stripping phase (HCl), its straight slope shall increase with the increase in HCl concentration. If the HCl concentration keeps increasing, its straight slope shall decrease; the reason for which the higher HCl concentration in the analytical phase shall results in unstable dispersion liquid. Therefore stripping process cannot keep an effective operation, thus being adverse to the Pb (II) transmission. When the HCl concentration is 6.0 mol/L in the analytical phase, the Pb (II) transmission will be favorable.

Feed liquid phase pH influence on the Pb (II) transmission

The Pb (II) initial concentration of $3.0 \times 10^{-4}$ mol/L in the feed liquid phase is selected for the experiment, the volume ratio is 160/40 between the membrane solution and HCl in stripping phase. HCl concentration is 4.0 mol/L in the stripping phase, the volume ratio between the membrane solution and HCl is 160/40 with the Pb (II) migration surveyed in case the feed liquid phase pH accounts for 4.5, 5.0, 5.5, 6.0 and 6.5 respectively.

The experiment results show that when the feed liquid phase pH is 6.0, the Pb (II) migration will be favorable, the reason for which the difference between H$^+$ concentration in the feed liquid phase and stripping phase is the Pb (II) mass transfer power in the dispersion supported liquid membrane system, hence lower acidity in the feed liquid phase shall be more favorable to the Pb (II) migration. However, since the stripping agent adopted in the stripping phase is a strong acid, when pH is higher in this phase, the difference between H$^+$ concentration into two phases accelerates the H$^+$ permeation into membrane phase, which not only strongly impacts on the liquid membrane stability, but also influences Pb (II) migration rate in the hybrid liquid membrane. Accordingly, the difference in acidity between the feed liquid and stripping dispersion phases is one of the key factors having impact on the Pb (II) mass transfer rate [23] Fig. 4.

Initial Pb (II) concentration influence on the Pb (II) transmission

The feed liquid phase pH of 6.0 is selected for experiment, HCl concentration is 4.0 mol/L during the stripping phase, and the
volume ratio between the membrane solution and HCl is 160/40. When the initial Pb (II) concentration is $1.0 \times 10^{-4}$ mol/L, $2.0 \times 10^{-4}$ mol/L, $2.5 \times 10^{-4}$ mol/L, $3.0 \times 10^{-4}$ mol/L, $4.0 \times 10^{-4}$ mol/L, the experimental Pb(II) migration is as shown in Fig. 5.

Experiment results show that when the initial Pb (II) concentration is $3.0 \times 10^{-4}$ mol/L in the feed liquid phase, its migration will have a best effect; the reason for which it is observed from Equations (2)–(1) that there is a complex as a result of the chemical reaction between Pb (II) and P507 at the interface between the feed liquid and membrane phases. When the Pb (II) concentration is smaller, the equilibrium will move leftward, leading to the reduction in Pb (II) migration rate. With the increase in Pb (II) concentration, the equilibrium moves rightward, gradually increasing the Pb (II) migration rate. But the Pb (II) migration rate shall also be subject to the carrier concentration and membrane area influence. When the carrier concentration and membrane area are given, the number of Pb (II) migrating in a unit time will also be definite. Pb (II) migration rate shall not unboundedly increase with the increase in initial Pb (II) concentration accordingly. Therefore, initial Pb (II) concentration shall also be one of the key factors having impact on the Pb (II) migration rate.

It is obvious that there is a proper linear relation between $-\ln (c_i/c_0)$ and the transmission time. Its slope will gradually increase with the increase in initial Pb (II) concentration [24]. The results show that when Pb (II) concentration is higher than $3.0 \times 10^{-4}$ mol/L, the curve slope will fall and the migration rate will decrease. Therefore, the suitable initial Pb (II) concentration shall be of about $3.0 \times 10^{-4}$ mol/L.

**Dynamic analysis**

In the dispersion supported liquid membrane separation system, the feed liquid and dispersion phases are connected by an organic membrane which cannot dissolve in water to make up a three phase system with phases which could not dissolve in each or each other [25–27]. These three phases form one body by a chemical reaction at the interfaces to compose a liquid membrane transmission system. It is observed from the above discussion that in addition to the carrier concentration, the feed liquid phase acidity shall be a primary factor having impact on the metal ion given a temperature Fig. 6.

In order to further describe the metal ion migration process in DSLM, experiments have been made under different pH values on it. The relation between Pb (II) $P_c$ and $[H^+]^2$ is as shown in Fig. 5. The relation between Pb (II) permeability coefficient and $[H^+]^2$ concentration under different feed liquids acidity conditions has been experimented according to the Equation (5). The relation curve between $l/P_c$ and $[H^+]^2$ has been plotted according to Equation (6), and the result shows that there is a proper linear relation ($r = 0.9985$) between $1/P_c$ and $[H^+]^2$ with its slope and intercept being $0.1128 \times 10^{12}$ and $3.6815 \times 10^4$ respectively. Suppose that metal ion migration is primarily in the diffusion form. According to the diffusion coefficient $K = 6.94 \times 10^{-10}$ m$^2$s$^{-1}$ Pb (II) extraction complexes in water solution, the diffused layer thickness of Pb(II) in water phase is $4.23 \times 10^{-5}$ by calculation. According to membrane thickness, the Pb (II) diffusion coefficient in the membrane phase is $2.24 \times 10^{-13}$m$^2$s$^{-1}$ by calculation. The obtained parameters will be substituted in Equation (7) to obtain the Pb (II) mass transfer dynamic equation in DSLM system as follows:

$$P_c = \frac{1}{3.6815 \times 10^4 + 0.1128 \times 10^{12}[H^+]^2}$$

The theoretical curve obtained according to the equation is as shown in Fig. 5 and this is obvious that the established equation properly tallies with experimental results.

**Conclusion**

PC-88A-kerosene–HCl dispersion supported liquid membrane system effects on the Pb (II) transmission [28,29]. In the system, the feed liquid phase pH value, initial Pb (II) concentration, volume ratio between the membrane solution, and
analytical agent and HCl concentration in analytical phase shall have an impact on the Pb (II) transmission.

(1) Experiment shows that P507/kerosene-HCl dispersion supported liquid membrane system has an effect on the Pb (II) migration. In the system, the feed liquid phase pH value, initial Pb (II) concentration, HCl concentration in the stripping phase, and the volume ratio between membrane solution and HCl shall have an impact on the Pb (II) transmission as well.

(2) The results also show that when the feed liquid pH is 6.0 and initial Pb (II) concentration is $3.0 \times 10^{-3}$ mol/L, HCl concentration is 4.0 mol/L in the stripping dispersion phase, the volume ratio between the stripping agent and organic phase is 40:160. Therefore, Pb (II) migration is favorable with 190 min accounted migration time and the migration rate of up to 95%.

(3) For the dispersion supported liquid membrane system taking P507 as the flow carrier, since a great amount of membrane solution is adopted in the stripping phase, the problem of the flow carrier diminishing to nothing in the supported liquid membrane shall be solved and the Pb (II) migration rate improved, leading to an enhanced membrane stability and a prolonged membrane service life.

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