Selective Separation of Lead and Mercury Ions from Synthetic Produced Water via a Hollow Fiber Supported Liquid Membrane

S. Suren, U. Pancharoen

Abstract—A double module hollow fiber supported liquid membrane (HFSLM) was applied to selectively separate lead and mercury ions from dilute synthetic produced water. The experiments were investigated on several variables: types of extractants (D2EHPA, Cyanex 471, Aliquat 336, and TOA), concentration of the selected extractant and operating time. The results clearly showed that the double module HFSLM could selectively separate Pb(II) and Hg(II) in feed solution at a very low concentration to less than the regulatory discharge limit of 0.2 and 0.005 mg/L issued by the Ministry of Industry and the Ministry of Natural Resource Environment, Thailand. The highest extractions of lead and mercury ions from synthetic produced water were 96% and 100% using 0.03 M D2EHPA and 0.06 M Aliquat 336 as the extractant for the first and second modules.

Keywords—Hollow fiber, Lead ions, Liquid membrane, Mercury ions, Selective separation

I. INTRODUCTION

IN offshore oil and gas production, produced water contaminated with toxic metals, in particular lead and mercury came along with oil and gas. The amounts of contaminants that expose to the environment increase with the amount of produced water due to high petroleum demand. Lead almost appear in $PbCl_2$ form [1] and mercury in the Hg(II) form [2, 3]. Without an appropriate treatment of produced water, lead and mercury or their compounds may contaminate the ecosystem through surface water, underground water and soil. They can occur both severe acute and chronic poisoning to human health [4, 5]. The Ministry of Industry and the Ministry of Natural Resources and Environment, Thailand, have been issuing the regulatory discharge limits of lead and mercury from industrial wastewaters not higher than 0.2 and 0.005 mg/L [6]. In practice, toxic metal ions in produced water are treated by using precipitation, coagulation, adsorption and ion exchange together and the system was controlled by on-line monitors. However, sometimes the system has been problematic to achieve the desired discharge concentrations of metal ions.

S. Suren, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand (phone: +66 0891257570; e-mail: lic_sira@hotmail.com)

U. Pancharoen, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand (phone: +66 022186891; Fax.: +66 022186877; e-mail: ura.p@chula.ac.th)

It is reported that these conventional methods are always ineffective at a very low concentration of the contaminated metal ions in ppm or ppb level, e.g., lower than 100 mg/L [7].

According to several studies of using hollow fiber supported liquid membrane (HFSLM) to treat metal ions from aqueous solutions or wastewaters, inevitably, HFSLM is an effective method to treat a very low concentration of metal ions [8-10]. The HFSLM system combines separation and striping steps in one single-step operation. This makes the process very compact and reduces energy consumption and capital and operating costs. The separation by HFSLM prefers highly selective separation [11, 12]. High surface area of hollow fiber module gives the sufficient separation rates for industrial purposes. The hollow fiber modules can be connected consecutively in series or parallel for a large capacity [13]. Thus, the HFSLM was investigated to cope with the constraint due to very low-level concentration of metal ions.

Types of extractants and stripping solutions play significant roles on removal of metal ions via the HFSLM. Then, they were reviewed from the following literature. Escobar et al. [14] used hollow-fiber contactor to extract lead(II) from cadmium(II) in chloride media using di-2-ethylhexyl phosphoric acid (D2EHPA) dissolved in n-heptane as the extractant. The result showed that lead(II) was removed about 97% after extraction for 7 h at 0.1 M D2EHPA and 0.1 M chloride media. Fabrega and Mansur [15] studied the extraction of Hg(II) from HCl solution by liquid-liquid extraction using Aliquat 336 dissolved in kerosene as the extractant. Mercury(II) was almost totally extracted within 5 min and it was stripped out satisfactorily by using thiourea as stripping solution. Francis et al. [16] demonstrated that Cyanex 471X could be used as a potential extractant for the extraction of mercury(II) from the brine sludge of the Chlor-Alkali industry. Hg(II) of about 99% was recovered by thiosulfate, ammonium chloride, or sodium chloride. Pancharoen et al. [17] investigated the selective extraction of Hg(II) from produced water at a very low concentration via HFSLM using TOA dissolved in toluene as the extractant and NaOH as the stripping solution. The amount of mercury ions that complied with the regulatory limit was obtained in 6-cycle separation at 2% (v/v) TOA and 0.5 M NaOH.

Recently, we observed that 0.9 M HCl was the best stripping solution for stripping Pb(II) from D2EHPA extractant [18]. This work focuses on the selective separation of lead and mercury ions from dilute synthetic produced water via a HFSLM to comply with the regulatory discharge limits. Types of extractants, concentration of the selected extractant, and operating time were investigated.

II. THEORETICAL BACKGROUND

PbCl$_2$, HgCl$_2$, and NaCl were used for preparing feed solution. PbCl$_2$ presents in the form of Pb^{2+} and HgCl$_2$ in the presence of chloride ions dissociates to HgCl$_4^{2-}$ [19]. In the HFSLM operation, feed and stripping solutions are separated by the supported liquid membrane embedded with an organic extractant. Figs. 1 and 2 show schematic mass transports of Pb(II) and Hg(II). The target ions Pb(II) and Hg(II) in feed solution react with the organic extractant at the feed-membrane interface to form complex species. Subsequently, the complex species diffuse across the liquid membrane to the membrane-striping interface to react with the stripping solution. Then, the metal ions are released to the stripping phase.
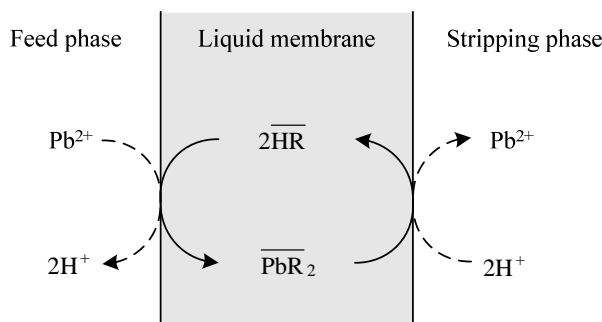

Fig. 1 Schematic mechanisms of the extraction and stripping of Pb(II) using D2EHPA as the extractant and HCl as the stripping solution
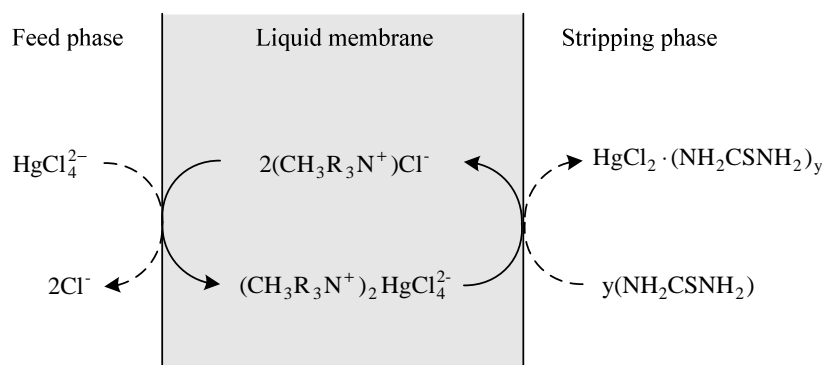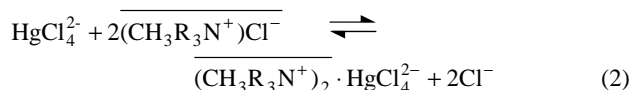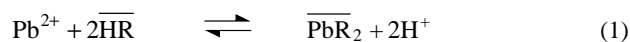

Fig. 2 Schematic mechanisms of the extraction and stripping of Hg(II) using Aliquat 336 as the extractant and thiourea as the stripping solution

The extraction of Pb(II) and Hg(II) from feed solution by D2EHPA ($\overline{HR}$) and Aliquat 336 ($\overline{(CH_3R_3N^+)Cl^-}$) as shown in Figs. 1 and 2 can be described as (1) and (2).

$$Pb^{2+} + 2\overline{HR} \quad \rightleftharpoons \quad \overline{PbR_2} + 2H^+ \tag{1}$$

$$HgCl_4^{2-} + 2\overline{(CH_3R_3N^+)Cl^-} \quad \rightleftharpoons$$
$$\overline{(CH_3R_3N^+)_2 \cdot HgCl_4^{2-}} + 2Cl^- \tag{2}$$

The overbar denotes the species in the organic phase (liquid membrane phase).

The complex species of $\overline{PbR_2}$ react continuously with hydrogen ion at the membrane-stripping interface to strip Pb(II) to the stripping phase as follows:

$$\overline{PbR_2} + 2H^+ \quad \rightleftharpoons \quad Pb^{2+} + 2\overline{HR} \tag{3}$$
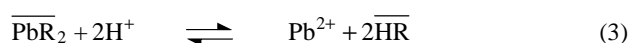
In the case of $\overline{(CH_3R_3N^+)_2 \cdot HgCl_4^{2-}}$ species, it react continuously with NH$_2$CSNH$_2$ at the membrane-stripping interface to strip Hg(II) to the stripping phase as follows:

$$\overline{(CH_3R_3N^+)_2 \cdot HgCl_4^{2-}} + y(NH_2CSNH_2) \quad \rightleftharpoons$$
$$2\overline{(CH_3R_3N^+)Cl^-} + HgCl_2(NH_2CSNH_2)_y \tag{4}$$
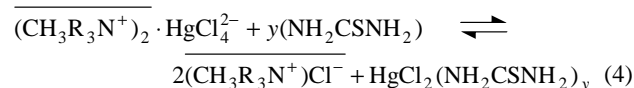
III. EXPERIMENTAL

A. Reagents and Solutions

Extractants were D2EHPA (di-(2-ethylhexyl)phosphoric acid) from Merck Ltd., Cyanex 471 (tri-isobutylphosphine sulfide) from Cytec Canada Inc., Aliquat 336 (tri-octyl methyl ammonium chloride) from Cognis Ltd., and TOA (tri-n-octylamine) from Sigma-Aldrich. Toluene for using as diluent

was obtained from Merck Ltd. $PbCl_2$, $HgCl_2$, and NaCl for preparing feed solution were obtained from Sigma-Aldrich Co.LLC, Ajax Finechem Pty Ltd., and LobaChemie, respectively. AR grades of hydrochloric acid and thiourea (NH_2CSNH_2) as stripping solution were obtained from Merck Ltd. and RFLC (New Zealand). Hydrochloric acid and thiourea were selected as stripping solutions to strip lead and mercury, respectively, because from previous works they showed high lead and mercury recovery [18, 20].

B. Apparatus

The single and double module HFSLM systems were shown in Fig. 3. Each system was composed of a hollow fiber module, two gear pumps, two rotameters with variable flow rate controllers, and four pressure gauges. The hollow fiber module is Celgard® microporous polypropylene fibers woven into fabric and wrapped around a central-tube feeder to supply the shell side fluid. The propertics of the hollow fiber module are listed in Table I. The magnetic stirrer (model CMT-V1) from Protronics Intertrade Co., Ltd. was used to agitate feed and stripping solutions. The inductively coupled plasma optical emission spectrometer (ICP-OES) from JY 2000, JY JOBIN YVON was used to determine the concentration of metals ions.
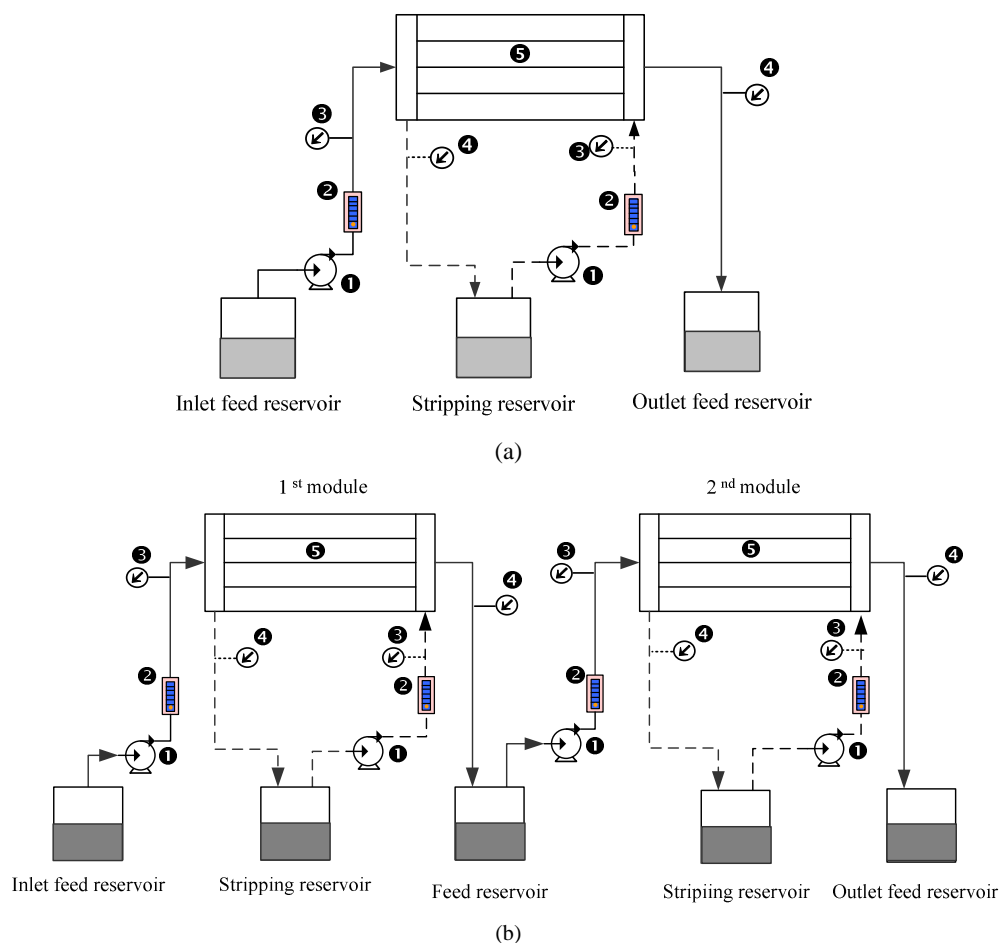

(a)

(b)

Fig. 3 Schematic counter-current flow diagram for separation via HFSLM by continuous flow of feed and circulating flow of striping solution. 1. gear pumps; 2. flow meters; 3. inlet pressure gauges; 4. outlet pressure gauges; 5 hollow fiber modules: (a) Single module HFSLM operation. (b) Double module HFSLM operation

C. Procedures

Double module HFSLM system were applied to selectively separate lead and mercury ions, one module for selective separation of lead ions and another module for mercury ions. Types of extractants (D2EHPA, Cyanex 471, Aliquat 336 and TOA), concentration of the selected extractant, and operating time were investigated. The suitable types of extractants and their concentration of the highest selective separation of lead and mercury were studied by using single module HFSLM. Finally, the double module HFSLM system was applied to study the operating time on the selective separation of lead and mercury ions.

The single module and double module HFSLM operation were shown in Fig. 3. The extractant dissolving in toluene as liquid membrane was circulated simultaneously in shell and tube sides of the hollow fiber module for 25 min. Subsequently, distilled water was fed through the hollow fibers to flush excess liquid membrane. After that, equal flow rates of feed and stripping solutions were simultaneously fed into the tube and shell sides of the HFSLM with continuous flow of feed and circulating flow of striping solution. From previous work [18], these flow patterns of feed and stripping solutions attained a high concentration of Pb(II) in the stripping solution with less-solution consumption. Finally, 10 mL feed and stripping solutions were sampled to determine the concentrations of lead and mercury ions by the ICP. To study the effects of types of extractants and concentration of the selected extractant, 1 L of feed and stripping solutions was used and the solutions were sampled at 10 min. The effect of operating time was studied by using 8 L of feed solution and 1 L of stripping solution. The solutions were sampled at every 10 min up to 80 min. HCl and thiourea were used to strip lead and mercury ions, respectively. The concentrations of HCl and thiourea were 0.9 M and 0.1 M which were the suitable concentrations from previous works [18, 20].

TABLE I
PROPERTIES OF THE HOLLOW FIBER MODULE

Characteristics	Descriptions
Material	Polypropylene
Module diameter	6.3 cm
Module length	20.3 cm
Number of hollow fibers	35,000
Inside diameter of the hollow fiber	240 μm
Outside diameter of the hollow fiber	300 μm
Effective length of the hollow fiber	15 cm
Contact area	1.4 m^2
Area per unit volume	29.3 cm^2/cm^3
Pore size	0.03 mm
Porosity	25%
Tortuosity	2.6

IV. RESULTS AND DISCUSSION

A. Effects of Extractants

The effects of extractants were studied by using single module hollow fiber. The results are shown in Fig. 4. D2EHPA was found to be the best extractant for selective separation of lead ions. High percentage of lead extraction without extraction of mercury by D2EHPA can be explained that lead ions in feed solution are in the Pb^{2+} form that can react well with the acidic extractant D2EHPA while mercury ions are in the HgCl$_4^{2-}$ form that cannot react with the acidic extractant [21]. For the separation of mercury, Cyanex 471 was found to be the best extractant. Howerver, the selective seperation of mercury by Aliquat 336 and TOA was higher than that by the Cyanex 471. This is because the Aliquat 336 and TOA are the basic extractant that can react well with anion of HgCl$_4^{2-}$ and does not react with cation. Basic extractant of Aliquat 336 showed more performance in mercury extraction than basic extractant of TOA because Aliquat 336 (a quaternary amine) is more basicity than TOA (a tertiary amine) [22].

To selectively separate lead and mercecury ions, D2EHPA and Aliquat 336 were selected for further studies on other relevant variables.
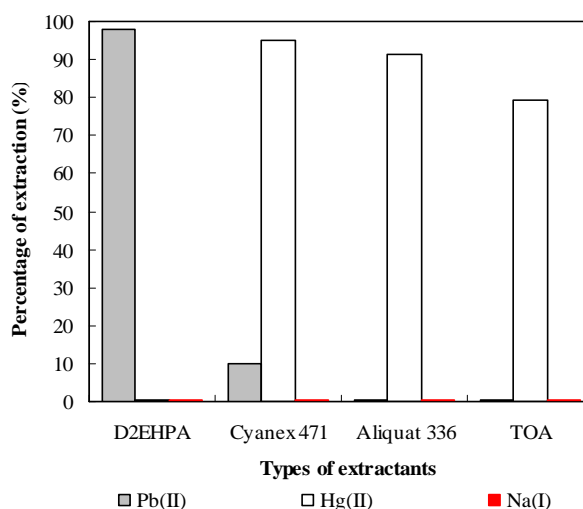
Fig. 4 Percentage of metal ions extraction against types of extractants (0.03 M each) using single module hollow fiber by 0.9 M HCl as striping solution with continuous flow of feed and circulating flow of striping solution at equal flow rates of 100 mL/min

B. Effect of D2EHPA Concentration on the Selective Separation of Lead Ions

D2EHPA was used to study the selective separation of lead ions from feed solution containing Pb(II), Hg(II) and Na(I). As shown in Fig. 5, the percentage of Pb(II) extraction abruptly increased with the concentration of D2EHPA. This corresponded to Le Chatelier's principle that if any reactant is added to the system, the system reacts in a way to use it up. When the concentration of D2EHPA increased to 0.03 M, Pb(II) was almost totally extracted. The highest percentage of Pb(II) extraction was 96%. Hence, 0.03 M D2EHPA was recommended.
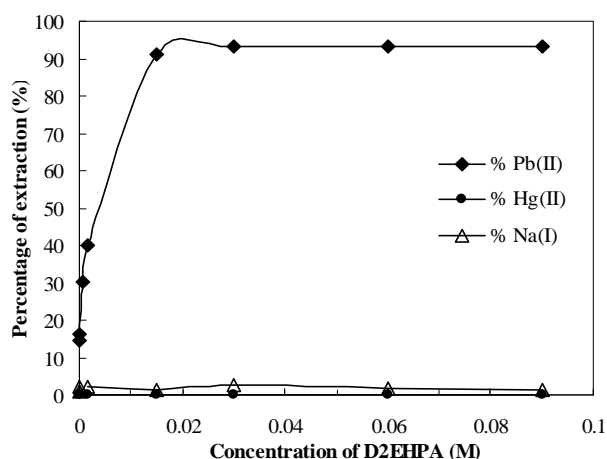
Fig. 5 Percentage of metal ions extraction against concentration of D2EHPA using single module hollow fiber by 0.9 M HCl as striping solution with continuous flow of feed and circulating flow of striping solution at equal flow rates of 100 mL/min

C. Effect of Aliquat 336 Concentration on the Selective Separation of Mercury Ions

To selectively separate mercury ions from feed solution containing Pb(II), Hg(II) and Na(I), Aliquat 336 was selected as the extractant and 0.1 M thiourea which is suitable stripping solution from previous work [20] was used as the stripping solution. The results were shown in Fig. 6. It was shown that the percentage of mercury extraction increased with the concentration of Aliquat 336. This corresponded to Le Chatelier's principles. The maximum percentage of Hg(II) extraction of 100% was attained at 0.06 M Aliquat 336. Therefore, 0.06 M Aliquat 336 was recommended.
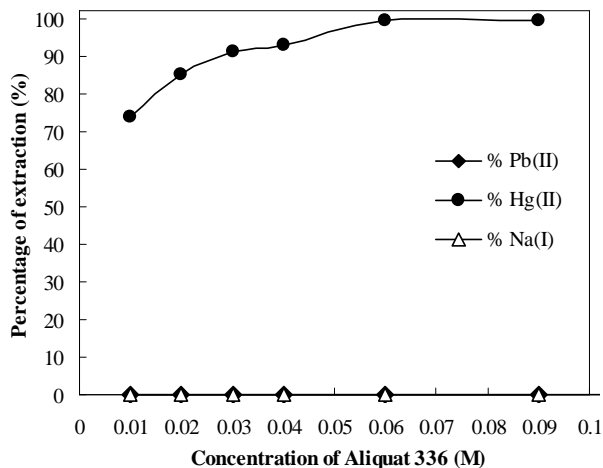
Fig. 6 Percentage of metal ions extraction against concentration of Aliquat 336 using single module hollow fiber by 0.1 M thiourea as striping solution with continuous flow of feed and circulating flow of striping solution at equal flow rates of 100 mL/min

D. The Effect of Operating Time

Fig. 7 shows the concentrations of metal ions in feed and stripping solutions of the first and second modules against operating time. The experiment was studied by using 0.03 M D2EHPA and 0.9 M HCl as the extractant and stripping solution for the first module. For the second module, 0.06 M Aliquat 336 and 0.1 M thiourea were used as the extractant and stripping solution. As shown in Fig. 7(a), lead ions were immediately extracted without extraction of mercury ions. The amount of lead ions in stripping solution continuously increased with operating time due to the continuing Pb(II) accumulation from the circulating of stripping solution. The concentration of Pb(II) in striping solution was attained higher than that in feed solution after 20 min. This attributed to Pb(II) in excess HCl is converted to $PbCl_4^{2-}$ which cannot recombine with the D2EHPA extractant. For the second module, mercury ions were immediately extracted and were continuously recovered by 0.1 M thiourea as shown in Fig. 7(b). Its concentration in stripping solution was kept higher than that in feed solution after 60 min.
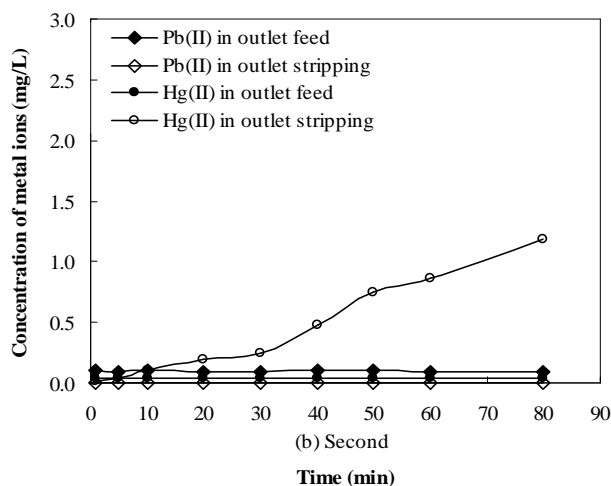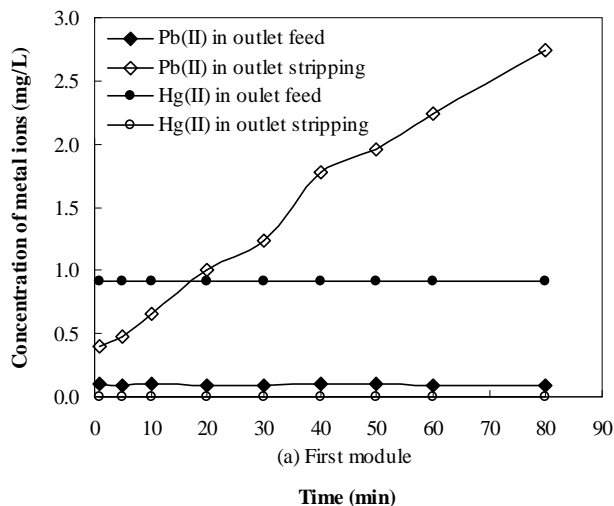
(a) First module

(b) Second

Fig. 7 Percentage of metal ions extraction against operating time with continuous flow of feed and circulating flow of striping solution at equal flow rates of 100 mL/min using 0.03 M D2EHPA and 0.9 M HCl as the extractant and stripping solution for the first module by 0.06 M Aliquat 336 and 0.1 M thiourea as the extractant and stripping solution for the second module

V. Conclusion

This work focuses on the selective separation of lead and mercury ions from dilute synthetic produced water via a HFSLM to comply with the regulatory discharge limits. The separation was studied on several variables: types of extractants, concentration of the selected extractant, and operating time. The results showed that double module hollow fiber supported liquid membrane attained high selective separation of lead and mercury ions.

REFERENCES

[1] D.R. Turner, "Speciation and cycling of arsenic, cadmium, lead and mercury in natural waters, in: T.C. Hutchinson, K.M. Meema (Eds.), Lead, Mercury, Cadmium and Arsenic in the Environment," John Wiley & Sons Ltd., England, pp. 175-186, 1987.

[2] G. Corvini, J. Stiltner, and K. Clark, "Mercury removal from natural gas and liquid streams," UOP LLC, pp. 3, 2007.

[3] D.L. Gallup, and J.B. Strong, "Removal of mercury and arsenic from produced water," Chevron Corporation, pp. 1-9, 2007.

[4] M. Z. Barciszewska, M. Szymanski, E. Wyszko, J. Pas, L. Rychlewski, and J. Barciszewski, "Lead toxicity through the leadzyme," Mutat. Res., Rev. Mutat. Res., vol. 589, pp. 103-110, 2005.

[5] F. Zahir, S. J. Rizwi, S. K. Haq, and R. H. Khan, "Low dose mercury toxicity and human health," Environ. Toxicol. Pharmacol., vol. 20, pp. 351-360, 2005.

[6] Thailand regulatory discharge standards, Ministry of Industry, Thailand, 1996.

[7] B. S. Inbaraj, J. S. Wang, J. F. Lu, F. Y. Siao, and B. H. Chen, "Adsorption of toxic mercury(II) by an extracellular biopolymer poly([gamma]-glutamic acid)," Bioresour. Technol., vol. 100, pp. 200-207, 2009.

[8] R. Guell, E. Antico, V. Salvado, and C. Fontas, "Efficient hollow fiber supported liquid membrane system for the removal and preconcentration of Cr(VI) at trace levels," Sep. Purif. Technol., vol. 62, pp. 389-393, 2008.

[9] U. Pancharoen, W. Poonkum, and A. W. Lothongkum, "Treatment of arsenic ions from produced water through hollow fiber supported liquid membrane," J. Alloys Compd., vol. 482, pp. 328-334, 2009.

[10] P. Kandwal, S. A. Ansari, and P. K. Mohapatra, "Transport of cesium using hollow fiber supported liquid membrane containing calix[4]arene-bis(2,3-naphtho)crown-6 as the carrier extractant: Part II. Recovery from simulated high level waste and mass transfer modeling," J. Membr. Sci., vol. 384, pp. 37-43, 2011.

[11] M. F. San Roman, E. Bringas, R. Ibanez, and I. Ortiz, "Liquid membrane technology: fundamentals and review of its applications," J. Chem. Technol. Biotechnol., vol. 85, pp. 2-10, 2010.

[12] I. M. Coelhoso, M. M. Cardoso, R. M. C. Viegas, and J. P. S. G. Crespo, "Transport mechanisms and modelling in liquid membrane contactors," Sep. Purif. Technol., vol. 19, pp. 183-197, 2000.

[13] U. Pancharoen, A.W. Lothongkum, and S. Chaturabul, "Mass transfer in hollow fiber supported liquid membrane for As and Hg removal from produced water in upstream petroleum operation in the gulf of Thailand, in: M. El-Amin (Ed.), Mass Transfer in Multiphase Systems and Its Applications," InTech, India, pp. 499-524, 2011.

[14] A. Escobar, K. A. Schimmel, J. de Gyves, and E. R. de San Miguel, "Hollow-fiber dispersion-free extraction and stripping of Pb(II) in the presence of Cd(II) using D2EHPA under recirculating operation mode," J. Chem. Technol. Biotechnol., vol. 79, pp. 961-973, 2004.

[15] F. d. M. Fabrega and M. B. Mansur, "Liquid-liquid extraction of mercury (II) from hydrochloric acid solutions by Aliquat 336," Hydrometallurgy., vol. 87, pp. 83-90, 2007.

[16] T. Francis, T. Prasada Rao, and M. L. P. Reddy, "Cyanex 471X as extractant for the recovery of Hg(II) from industrial wastes," Hydrometallurgy., vol. 57, pp. 263-268, 2000.

[17] U. Pancharoen, S. Somboonpanya, S. Chaturabul, and A. W. Lothongkum, "Selective removal of mercury as $HgCl_4^{2-}$ from natural gas well produced water by TOA via HFSLM," J. Alloys Compd., vol. 489, pp. 72-79, 2010.

[18] S. Suren, T. Wongsawa, U. Pancharoen, T. Prapasawat, and A. W. Lothongkum, "Uphill transport and mathematical model of Pb(II) from dilute synthetic lead-containing solutions across hollow fiber supported liquid membrane," Chem. Eng. J., vol. 191, pp. 503-511, 2012.

[19] Y. Kawamura, M. Mitsuhashi, H. Tanibe, and H. Yoshida, "Adsorption of metal ions on polyaminated highly porous chitosan chelating resin," Ind. Eng. Chem. Res., vol. 32, pp. 386-391, 1993.

[20] A. W. Lothongkum, S. Suren, S. Chaturabul, N. Thamphiphit, and U. Pancharoen, "Simultaneous removal of arsenic and mercury from natural-gas-co-produced water from the Gulf of Thailand using synergistic extractant via HFSLM," J. Membr. Sci., vol. 369, pp. 350-358, 2011.

[21] L. Iberhan and M. Wisniewski, "Extraction of arsenic(III) and arsenic(V) with Cyanex 925, Cyanex 301 and their mixtures," Hydrometallurgy., vol. 63, pp. 23-30, 2002.

[22] B. Wassink, D. Dreisinger, and J. Howard, "Solvent extraction separation of zinc and cadmium from nickel and cobalt using Aliquat 336, a strong base anion exchanger, in the chloride and thiocyanate forms," Hydrometallurgy., vol. 57, pp. 235-252, 2000