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Selective removal of mercury as $HgCl_4^{2-}$ from natural gas well produced water by TOA via HFSLM

Ura Pancharoen[a], Sawatpop Somboonpanya[a], Srestha Chaturabul[a], Anchaleeporn Waritswat Lothongkum[b,*]

[a] Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Patumwun, Bangkok 10330, Thailand
[b] Department of Chemical Engineering, Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang, Ladkrabang, Bangkok 10520, Thailand

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ABSTRACT

Handling produced waters from oil and gas production is an important aspect of making future oil and gas operations more environmentally acceptable since produced waters generally contain trace heavy and toxic metals, radioactive elements and chemicals. This research shows the selective removal of mercury ions (Hg(II)) as $HgCl_4^{2-}$ from produced water of natural gas well in the Gulf of Thailand, in which the concentrations of arsenic and mercury are high, by using a lab-scale hollow fiber supported liquid membrane (HFSLM). Emulsion liquid membrane (ELM) with different types of extractants and solvents was initially used to select the extractant of high mercury ions selectivity and extractability for the HFSLM system. Tri-*n*-octylamine (TOA) in toluene was found to be the most suitable extractant. The study parameters were pH of feed solution or produced water, concentration of extractant in liquid membrane, concentration of stripping or recovery solution (sodium hydroxide), volumetric flow rates of feed and stripping solutions, numbers of separation cycles, and stability of HFSLM. The increase in numbers of separation cycles, significantly increased the extraction and stripping of mercury ions. For 300 min at 6-cycle operation, the highest percentages of extraction and stripping of 99.8% and 62%, respectively, were achieved at the pH of feed solution of 2.5, 2% (v/v) TOA, 0.5 M NaOH and 50 ml/min of feed and stripping solutions. Furthermore, the mass transfer coefficients of aqueous phase (k_i) and organic phase (k_m) were 0.011 and 0.413 cm/s, respectively. Because the mass transfer coefficient of the organic phase was much higher than that of the aqueous phase implying that the rate controlling step was the diffusion of mercury ions through the film layer between feed solution and liquid membrane.

1. Introduction

Mercury is one of the most hazardous metals because of its ability to evaporate in soil or water. It is extremely dangerous. Short-term exposure to mercury in water can result in kidney damage, while a lifetime of exposure can lead to impairments in neurological functioning. Though the most common source of mercury in water is natural erosion of soil and ore deposits, runoff from factories and refineries can leak mercury into surface water sources [1]. Some activities of offshore oil and gas operations can potentially impact on the environment. In general, oil and gas reservoirs have natural water layer so-called formation water that, being denser, lies under the hydrocarbons. To achieve the maximum recovery oil and gas, additional water and chemicals are usually injected into the reservoirs. Therefore, both formation water and injected water are eventually produced along with the hydrocarbons, and the volumes and the difficulties of their treatment tend to increase extensively over time. In particular, offshore oilfield and gas field productions have increased dramatically and are expanding to shallow coastal and deep slope waters. An ongoing concern has been the potential environmental impacts associated with the produced waters and large quantities of contaminated water produced from almost all offshore oil and gas operations. Produced waters can have significant environmental impacts if they are not handled suitably because they contains trace heavy and toxic metals, radioactive elements and chemicals that are used during oil and gas drillings. Heavy elements and compounds of arsenic, chromium, mercury, lead, nickel, copper, cadmium, zinc, and others are found [2,3]. Produced water discharges lead to acute and chronic toxicity. Studies by Jacobs et al. indicate that the produced waters discharged from gas/condensate platforms are about 10 times more toxic than the produced waters discharged from oil platforms [4]. The driving forces by the government and community demand make the chemists and engineers putting efforts on preventing the pollution both risk to human health and the environment. Six water treatment technologies, i.e., carbon adsorption, air stripping, filtration

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[*] Corresponding author. Tel.: +66 023264424; fax: +66 023264424.
E-mail address: kwanchal@kmitl.ac.th (A.W. Lothongkum).

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Nomenclature

$C_{\mathrm{f,in}}$	concentration of inlet feed solution (ppm)
$C_{\mathrm{f,out}}$	concentration of outlet feed solution (ppm)
$C_{\mathrm{s,in}}$	concentration of inlet stripping solution (ppm)
$C_{\mathrm{s,out}}$	concentration of outlet stripping solution (ppm)
HR	acidic extractant
R_3N	basic extractant
S	selectivity (%)

using very fine membrane, UV light, chemical oxidation, and biological treatment, already proven onshore, were evaluated and costed for offshore use. The technologies available for mercury and arsenic removal, such as precipitation, coagulation/co-precipitation, activated carbon adsorption, ion exchange are not sufficiently effective for mercury and arsenic removal [5], especially with environmental discharge limits becoming more stringent. In principle, the primary alternatives to manage produced waters being used today are minimizing the production of water, and depending on the quality of produced waters by underground injection or discharging into the sea after cleaning up or beneficial reuse, although some other options are used at selected locations [6]. Chevron Thailand applied a chemical treatment process to remove arsenic and mercury from the produced water prior to overboard discharge. The continuous on-line As and Hg monitors to determine the concentrations have been problematic and are needed to allow adjustment of chemical treatment rates to achieve the desired metal discharge concentrations [7]. A multidisciplinary research and technology have been increasingly working out to reduce and control the environmental effects of drilling waste discharges, particularly produced water. It is noted that the combination of different technologies is possible to reduce and regulate the undesired components in produced water to almost undetectable levels and comply with the legislation discharge [2].

Membranes have being used to a widely practiced technology in industry and gained a broad range of applications, for example, packaging applications, drug delivery applications and separation applications. In separation, membranes allow one component of a mixture to permeate the membrane freely, while impeding permeation of other components. Liquid membrane system has been widely applied to a large variety of systems including the extraction and recovery of metal ions from solutions because they contain an organic extractant or a carrier to facilitate selective transport of gases or ions [6,8,9]. One promising technique of liquid membrane is the use of micro porous hollow fiber modules as liquid–liquid phase contactors. It is effective for low-level metal removal. Metal ions can move from low to high concentration solutions by simultaneous extraction and recovery operation. The basic principle of hollow fiber supported liquid membrane (HFSLM) is the immobilizaion of organic extractant into the pores of a hydrophobic membrane [10,11]. The hollow fiber system provides rapid transportation from its surface area and membrane thickness. Some other advantages of HFSLMs over traditional separation techniques are low energy and low extractant consumption, high fluxes compared to solid membranes, suitably for high pressure operation and ease of scaling up [2,8,10,11]. There are a few problems associated with the hollow fiber system, i.e., high hydrophobic membrane solvents are required to maintain integrity, hollow fibers are notoriously prone to pore fouling thus the hollow fiber system must be cleaned between uses to maintain its stability otherwise there will be aqueous and contaminant buildup [2].

Due to the aforementioned advantages, the HFSLM is being looked into industrial applications, notably in the areas of recovery of dilute precious metals or removal of heavy metals from industrial wastewaters [10,12–14]. In this study work, a lab-scale HFSLM was employed to extract and recover Hg(II) ions from produced water obtaining from the PTT Exploration and Production Public Co. Ltd. In certain oil and gas fields in the Gulf of Thailand, the concentrations of arsenic and mercury in produced water are high. The maximum permissible concentration of mercury in discharged industrial water according to the Ministry of Industry, Thailand is not higher than 0.005 mg/L [15]. Emulsion liquid membrane (ELM) with different types of extractants and solvents was initially used to select the extractant of high mercury ions selectivity and extractability for further experiments using HFSLM system. In case of arsenic but from a different gas field was studied by Pancharoen et al. [16].

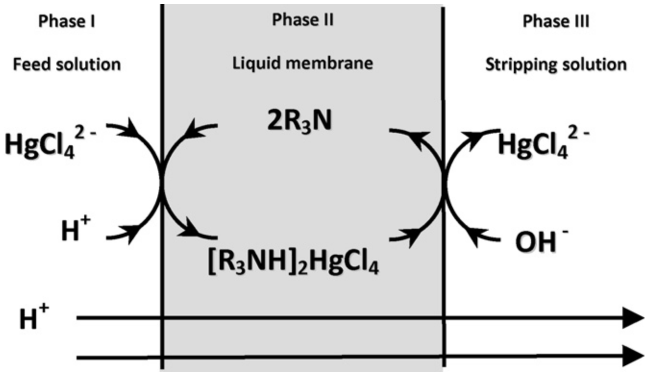


Fig. 1. Co-transport scheme of $HgCl_4^{2-}$ extraction and stripping by TOA extractant.

2. Theory

Liquid membrane (LM) was extensively studied in previous works to remove heavy and toxic metals from synthetic waters as well as to recover precious metals. Several extractants were selected for highly separation. Our research group, therefore, applied the HFSLM system to remove arsenic from synthetic water by Cyanex 923, cerium by TOA [17,18] and to highly selective extract yttrium ions from the mixture of rare earths by the synergistic effect of Cyanex 272 and TBP [19]. The HFSLM system was successfully remove chromium and nickel from wastewater of the stainless steel industry by Aliquat 336 and LIX 860-I, respectively [20,21], and arsenic from produced water from a gas separation plant [16]. Recently, the consecutive extraction of uranium from trisodium phosphate solution, a by-product from monazite processing, via HFSLM by Aliquat 336 and TBP was published [22]. Apart from liquid membrane to remove mercury, ion exchange [23–25], solid phase extraction [26,27], chemical precipitation [28,29] were studied. In LM and HFSLM systems, several extractants such as Cyanex 923 [26,30], *N*-benzoyl-*N′*,*N′*-diheptadecylthiourea [13], Aliquat 336 [31], LIX 34 [32], Cyanex 471X [33] Dicyclohexyl-18-crown-6 (DC18C6) [34] and TOA [35,36] were investigated. Details of feeds, types of extractants and extracted ions were listed in Table 1.

Tri-*n*-octylamine (TOA), a basic extractant used in this work, was in the liquid membrane which was trapped in the hydrophobic microporous hollow fiber module. Liquid membrane was between feed and stripping solutions which flowed counter-currently. The transport mechanism of mercury ions through the liquid membrane is shown in Fig. 1. Mercury ions in produced water which served as feed solution appeared in anion form of $HgCl_4^{2-}$ [36,37]. $HgCl_4^{2-}$ ions in feed solution were reacted with the extractant (TOA, shown as R_3N) to form complex species as shown in Eq. (1):

$$HgCl_4^{2-} + 2H^+ + 2R_3N \rightleftarrows (R_3NH)_2\cdot HgCl_4 \tag{1}$$

Table 1
Examples of methods to remove mercury(II) ions and others.

Author	Type of feed	Ions in feed	Extractant	Method
Arpa et al. [23]	Wastewater from mining industry	Pb(II), Hg(II), Cd(II)	–	Ion exchange
Dabrowski et al. [24]	Industrial wastewater	Pb(II), Hg(II), Cu(II), etc	–	Ion exchange
Oehmen et al. [25]	Synthetic water	As(III), As(V), Hg(II)	–	Ion exchange
Starvin and Prasada Rao [26]	Synthetic water, hazardous brine sludge effluent	Hg(II)	TAN	SPE
Duan et al. [27]	City lake and deep well waters	Hg(II)	Cyanex 923	SPE
Meera et al. [30]	Synthetic water	Hg(II)	Cyanex 923	LM
Fabrega et al. [31]	Synthetic water	Hg(II)	Aliquat 336	LM
Huebra et al. [32]	Wastewater	Hg(II), Fe(III), etc	LIX 34	LM
Francis et al. [33]	Industrial wastewater	Hg(II)	Cyanex 471X	LM
Jabbari et al. [34]	Synthetic water	Hg(II), Ca(II), Fe(III), etc	DC18C6	LM
Fontas et al. [13]	Synthetic water, sea water	Hg(II), Cd(II), Pb(II)	*N*-benzoyl-*N*′,*N*′-diheptadecylthiourea	HFSLM
Sangtumrong et al. [35]	Synthetic water	Hg(II), As(III)	TOA	HFSLM
Uedee et al. [36]	Synthetic water	Hg(II)	TOA	HFSLM
This work	Produced water from natural gas well	Hg(II)	TOA, Aliquat 336, Cyanex 923	HFSLM

Note: SPE, solid phase extraction; LM, liquid membrane; HFSLM, hollow fiber supported liquid membrane.

The mercury complex species diffused to the opposite side of the liquid membrane by the concentration gradient and reacted with the stripping solution, NaOH, to strip $HgCl_4{}^{2-}$ ions into the stripping phase as shown in Eq. (2):

$$(R_3NH)_2HgCl_4 + 2OH^- \rightleftarrows 2R_3N + HgCl_4{}^{2-} + 2H_2O \quad (2)$$

$HgCl_4{}^{2-}$ ions were transferred in to the stripping solution while the extractant moved back to liquid membrane and diffused to the opposite side of the liquid membrane by the concentration gradient to react again with $HgCl_4{}^{2-}$ ions in feed solution.

The percentages of extraction and stripping were determined as follows:

$$\%\,\text{extraction} = \frac{C_{f,in} - C_{f,out}}{C_{f,in}} \times 100 \quad (3)$$

$$\%\,\text{stripping} = \frac{C_{s,out}}{C_{s,in}} \times 100 \quad (4)$$

The selectivity was defined as:

$$S_i = \frac{C^i_{out,s}}{\sum_{i=1}^{n} C^i_{out,s}} \quad (5)$$

where $C_{f,in}$, $C_{f,out}$ is the inlet and outlet feed concentrations of component *i* (ppm); $C_{s,in,}$ $C_{s,out}$ is the inlet and outlet stripping concentrations of component *i* (ppm).

The extraction equilibrium constant (K_{ex}) of mercury (II) ions extracted by TOA in Eq. (1) was derived from the experimental data and calculated by the following equation:

$$K_{ex} = \frac{[(R_3NH)_2HgCl_4]}{[HgCl_4^{2-}][H^+]^2[R_3N]^2} \quad (6)$$

The distribution ratio for mercury was given by

$$D = \frac{[(R_3NH)_2HgCl_4]}{[HgCl_4^{2-}]} = K_{ex}[H^+]^2[R_3N]^2 \quad (7)$$

The distribution ratio as a function of the extraction equilibrium constant became

$$D = K_{ex}[H+]^2[R_3N]^2 \quad (8)$$

Determining the permeability coefficient, fast interfacial reactions and the distribution of mercury (II) between the membrane phase and the stripping phase, was much lower than that between feed phase and membrane phase. The permeability coefficient expressed by Denesi [38].

$$-V_f \ln\left(\frac{C_f}{C_{f,0}}\right) = AP\frac{\beta}{\beta+1}t \quad (9)$$

$$\beta = \frac{Q_f}{PL\varepsilon\pi N r_i} \quad (10)$$

where *P* is the permeability coefficient (cm/s); V_f is the volume of the feed (cm^3); $C_{f,0}$ is the mercury ion concentration at time 0 (mol/L); C_f is the mercury ion concentration at time *t* (mol/L); *A* is the effective area of the hollow fiber module (cm^2); *t* is the time (min); Q_f is the volumetric flow rate of feed solution (cm^3/s); *L* is the length of the hollow fiber (cm); ε is the porosity of the hollow fiber (%); *N* is the numbers of hollow fibers in the module; r_i is the internal radius of the hollow fiber (cm).

$AP(\beta/\beta+1)$ is the slope of the plot between $-V_f \ln(C_f/C_{f,0})$ versus *t* in Eq. (9), and *P* can be obtained by Eq. (10). To determine mass transfer coefficients for mercury (II) ions separation by HFSLM, the mass transfer model and permeability coefficient (*P*) are employed. The permeability coefficient depends on mass transfer resistance which is reciprocal to the mass transfer coefficients as follows [39].

$$\frac{1}{P} = \frac{1}{k_i} + \frac{r_i}{r_{lm}}\frac{1}{P_m} + \frac{r_i}{r_o}\frac{1}{k_s} \quad (11)$$

where r_{lm} is the log–mean radius of the hollow fiber; r_o is the external radius of the hollow fiber (cm); k_i is the aqueous mass transfer coefficient in tube side; k_s is the stripping mass transfer coefficient in shell side; P_m is the membrane permeability coefficient.

The relation between P_m and the distribution ratio (*D*) is as follows [39]:

$$P_m = Dk_m \quad (12)$$

Combining Eqs. (7) and (12), thus

$$P_m = K_{ex}k_m[R_3N]^2[H^+]^2 \quad (13)$$

where k_m is the mass transfer coefficient of the membrane.

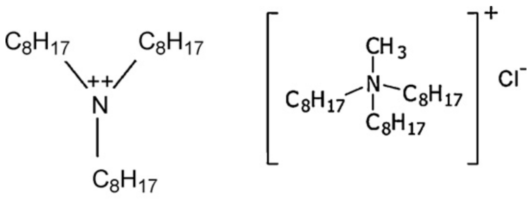
The value of liquid membrane permeability coefficient (P_m) from Eq. (13) is substituted into Eq. (11). Assuming that the stripping reaction is instantaneous and the contribution of the stripping phase is neglected, Eq. (11) becomes:

$$\frac{1}{P} = \frac{1}{k_i} + \frac{r_i}{r_{lm}}\frac{1}{K_{ex}k_m[R_3N]^2[H^+]^2} \quad (14)$$

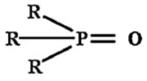
where k_i is the mass transfer coefficient of feed solution.

Table 2
Compositions of the produced water (pH ≈ 7).

Metal ions	Concentration (ppm)
As(III)	1.988
Hg(II)	1.248
Fe(III)	0.756
Mg(II)	2.414
Ca(II)	11.64
Na(I)	1022.75



(a) TOA [18] (b) Aliquat 336 [40]



(c) Cyanex 923 [41]

Fig. 2. Chemical structures of the extractants: (a) TOA (b) Aliquat 336 [40] and (c) Cyanex 923 [41] where R is a mixture of C_6H_{13} and C_8H_{17}.

3. Experimental

3.1. Feed and chemicals

In this work, feed solution is the produced water from the gas separation plant of the PTTEP Public Co. Ltd. having pH about 6.5–7. The pH of feed solution was then adjusted by hydrochloric acid (HCl), analytical grade from Merck Ltd. The compositions of the produced water, shown in Table 2, were analyzed by the inductively coupled plasma spectroscopy (ICP). TOA (Tri-*n*-octylamine) and Aliquat 336 (methyltrioctyl ammonium chloride) extractants were supplied by Merck Ltd., and Cyanex 923 was supplied by the Cytec Industries Inc. The extractants were diluted in toluene supplied by the Fisher Scientific UK Ltd., and kerosene by the JPI grade from the PTT Public Co., Ltd., without further purification. The structures of the extractants were shown in Fig. 2. Sodium hydroxide, analytical grade from Merck Ltd., was used as the stripping solution.

3.2. Apparatus

The hollow fiber module (Liqui-Cel Extra-flow module) as shown in Fig. 3 was manufactured by the Hoechst Celanese. The module uses Celgard microporous polypropylene fibers that are woven into fabric and wrapped around a central tube feeder that supplied the shell side fluid. The woven fabrics provided more uniform fiber spacing, which in turn leads to higher mass transfer coefficients than those obtained with individual fibers [42]. The properties of the hollow fiber module were specified in Table 3. The fibers were potted into a solvent-resistant polyethylene tube sheet and shell casing in polypropylene.

Table 3
Properties of hollow fiber module.

Property	Description
Material	Polypropylene
Inside diameter of hollow fiber	240 μm
Outside diameter of hollow fiber	300 μm
Pore size	0.05 μm
Number of fiber	240
Porosity	30%
Contact area	1.4 m^2
Area per unit volume	29.3 cm^2/cm^3
Module diameter	6.3 cm
Module length	20.3 cm

3.3. Procedures

Different types of extractants and solvents, i.e., TOA, Aliquat 336 and Cyanex 923 in kerosene, and TOA in toluene were applied with emulsion liquid membrane (ELM) to select the extractant of high mercury ions selectivity and extractability for the HFSLM system. The single-module operation is shown in Fig. 4. The selected extractant in selected solvent of 800 ml was simultaneously pumped into tube side and shell side of the hollow fiber module for 40 min to assure the extractant embedded in micropores of the hollow fibers. Subsequently, 5 L of feed solution and stripping solution were fed counter-currently into the tube side and the shell side, respectively. The pH of feed solution was varied to achieve the highest mercury extraction. The concentration of extractant in liquid membrane, concentration of stripping or recovery solution (sodium hydroxide), volumetric flow rates of feed and stripping solutions, numbers of separation cycles, and stability of HFSLM were investigated. The operating time for one run was 50 min. The concentrations of mercury ions in samples from feed and stripping solutions were analyzed by the inductively coupled plasma spectroscopy (ICP) to estimate the percentages of extraction and stripping. To achieve higher separation and less mercury concentration in discharged produced water to meet the regulation of discharged industrial water and to study membrane stability, the numbers of separation cycles were studied. The feed of the second cycle was obtained from the first outlet feed solution and so on, whereas the inlet stripping solution was fresh.

4. Results and discussion

4.1. Effects of pH of feed solution and types of extractants

By varying the pH of feed solution in Fig. 5, the results were clearly seen that the percentage of Hg(II) extraction decreased with the pH of feed solution. The highest selective extraction of Hg(II) than As(III) and Fe(III) by TOA in a single-module operation of 79% was obtained at the pH of 2.5. However, the pH values reported by Lothongkum et al. for nickel separation from wastewater of the stainless steel industry by HFSLM [21], and Arpa et al. for mercury separation by ion exchange from wastewater of mining industry were about 4 [23].

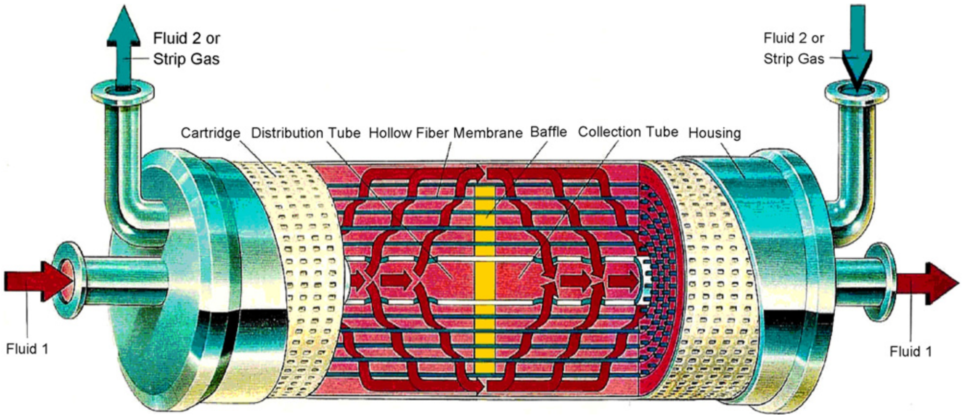


Fig. 3. Liqui-Cel Extra-Flow module.

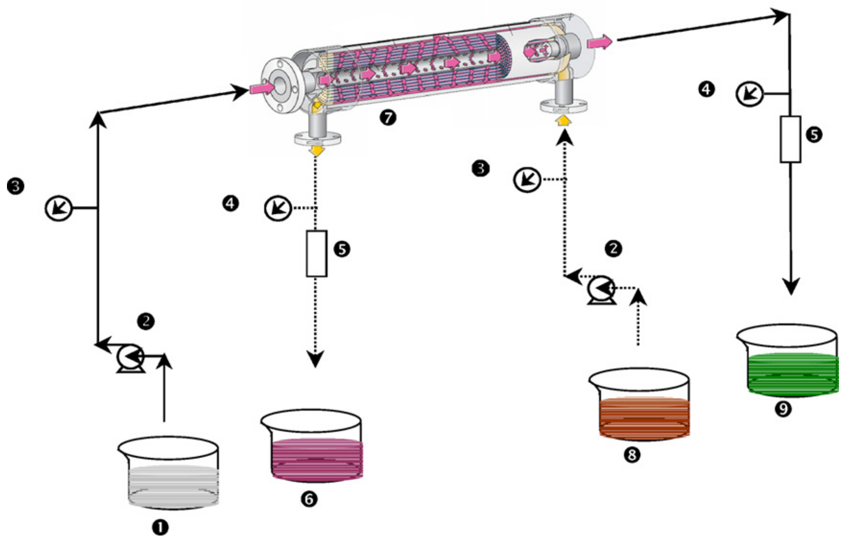


Fig. 4. Schematic counter-current flow diagram for one-through-mode operation in hollow fiber supported liquid membrane. (1) Feed reservoir; (2) gear pumps; (3) inlet pressure gauges; (4) outlet pressure gauges; (5) flow meters; (6) outlet stripping reservoir; (7) hollow fiber module; (8) inlet stripping reservoir; (9) outlet stripping reservoir.

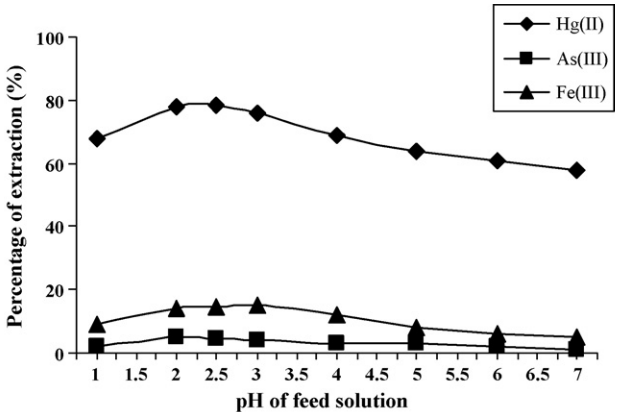


Fig. 5. Percentage of extraction at different pH: TOA 2% (v/v), stripping solution [NaOH] = 0.5 M and $Q_{feed} = Q_{strip} = 100$ ml/min.

According to the experiments by emulsion liquid membrane, tri-*n*-octylamine (TOA) in toluene was found to be the most suitable extractant for higher selective mercury extraction than other metal ions, particularly As(III) and Fe(III) ions, as shown in Fig. 6.

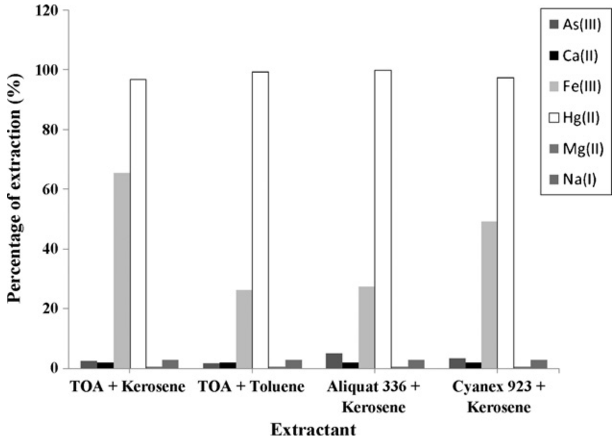


Fig. 6. Selective Hg(II) extraction by emulsion liquid membrane: [TOA, Aliquat and Cyanex 923 in kerosene] = 0.1 M, [TOA in toluene] = 0.1 M.

4.2. Effect of the extractant concentration

The concentration of TOA were studied in the ranges of 0.5–6% (v/v) same as using with the synthetic waters [35,36]. Mercury extraction increased with the extractant concentration, as seen in Fig. 7. The highest percentage of mercury extraction was obtained at the extractant concentration of 2% (v/v). This result is in accordance with that studied by our group with the synthetic waters. It can be explained by Le Chatelier's principles that the increase in extractant concentration in the liquid membrane results in higher fluxes. However, in this work, the extractant concentration higher than 2% (v/v) showed no significant change in mercury extraction although theoretically, the fluxes decreased at higher extractant concentration because the viscosity of the film between feed solution and liquid membrane increased and obstructed mass transfer.

4.3. Effect of the stripping solution concentration

The concentration of stripping solution (NaOH) was studied at 0.2–1.4 M same as using with the synthetic waters [35,36]. The progressive increase in the percentage of mercury stripping was found when the concentration of stripping solution increased. This indicated that NaOH accelerated the extraction and stripping processes. From Figs. 8 and 9, for a single-module operation, the highest mercury extraction and stripping of about 79% and 48% were achieved at NaOH concentration of 0.5 M.

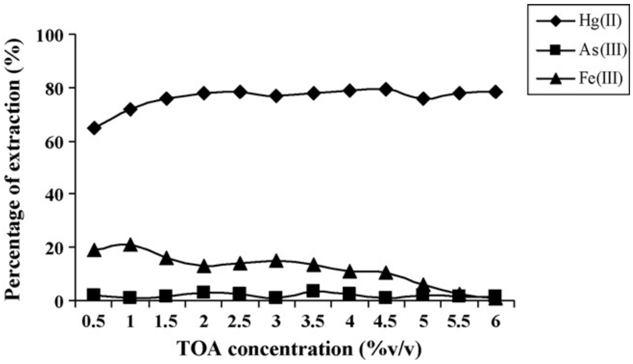


Fig. 7. Percentage of extraction against TOA concentration: pH of feed solution = 2.5, stripping solution [NaOH] = 0.5 M and $Q_{feed} = Q_{strip} = 100$ ml/min.

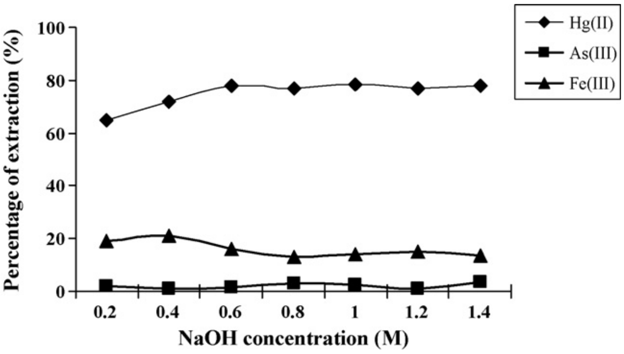


Fig. 8. Percentage of extraction against NaOH concentration: TOA 2% (v/v), pH of feed solution = 2.5 and $Q_{\mathrm{feed}} = Q_{\mathrm{strip}}$ = 100 ml/min.

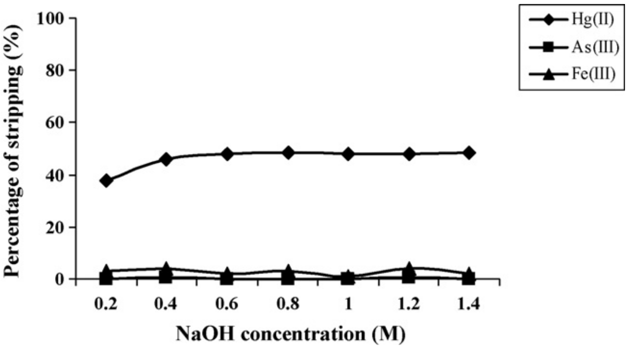


Fig. 9. Percentage of stripping against NaOH concentration: TOA 2% (v/v), pH of feed solution = 2.5 and $Q_{\mathrm{feed}} = Q_{\mathrm{strip}}$ = 100 ml/min.

4.4. Effects of the flow rates of feed and stripping solutions

Fig. 10 shows the relationship between the percentage of extraction and stripping of mercury at different equal flow rates of feed and stripping solutions. The results indicated that by using a single-module operation for 50 min at the flow rates of feed and stripping solutions of 50 ml/min, the highest percentages of mercury extraction and stripping of 79 and 48, respectively were obtained. However, the percentages of mercury extraction and stripping decreased with the flow rates of feed and stripping solutions due to less resident time of the solutions to stay in the hollow fiber module.

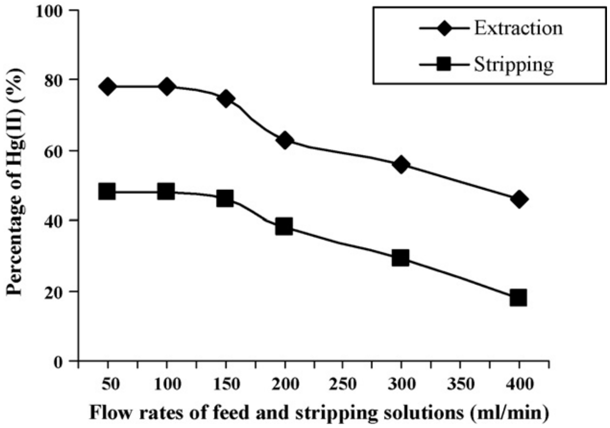


Fig. 10. Percentages of Hg(II) extraction and stripping against flow rate of feed and stripping solution: TOA 2% (v/v), stripping solution [NaOH] = 0.5 M and pH of feed solution = 2.5.

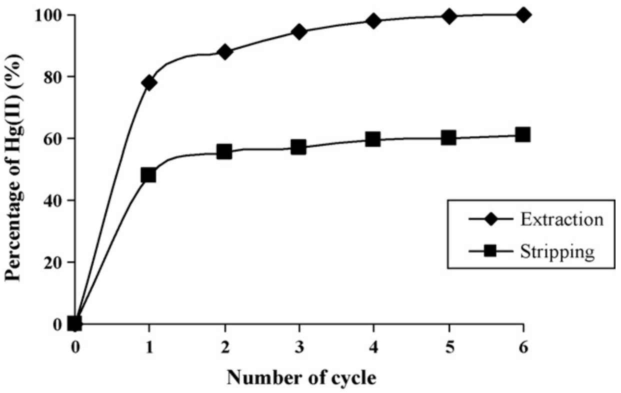


Fig. 11. Percentages of Hg(II) extraction and stripping against number of separation cycle: TOA 2% (v/v), stripping solution [NaOH] = 0.5 M, pH of feed solution = 2.5 and $Q_{\mathrm{feed}} = Q_{\mathrm{strip}}$ = 100 ml/min.

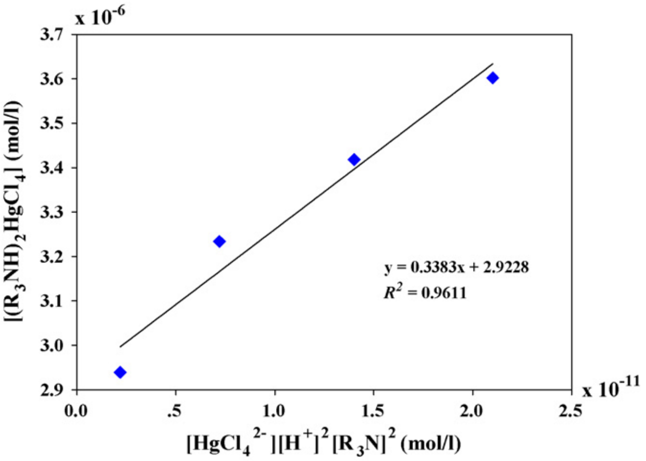


Fig. 12. Mercury extraction with [TOA] as a function of equilibrium $[\mathrm{HgCl_4}^{2-}][\mathrm{H}^+]^2[\mathrm{R_3N}]^2$.

4.5. Effects of the numbers of separation cycles

The numbers of separation cycles were studied using the optimum conditions in a single-module operation to expect higher separation and less mercury concentration in discharged produced water as well as to inspect the membrane stability. Fig. 11 shows that the highest percentages of mercury extraction and stripping was obtained at 6-cycle operation for 300 min. The extraction and stripping reached 99.8% and 62%, resulting in mercury concentration about 0.0025 mg/L which was less than the permissible limit of 0.005 mg/L. The membrane stability was verified.

4.6. The extraction equilibrium constant and distribution ratio

The extraction equilibrium constants (K_{ex}) was calculated by the slope of the graph in Fig. 12 and found to be 3.383×10^{-1} (L/mol)^4. The distribution ratios (D) at the TOA concentration of 0.5–2% (v/v) were calculated by Eqs. (6) and (7) as shown in Table 4. It was noted

Table 4
The distribution ratio (D) at TOA concentration of 0.5–2.0% (v/v).

[TOA] (% (v/v))	D ($\times 10^2$)
0.5	0.361
1.0	0.722
1.5	1.08
2.0	1.44

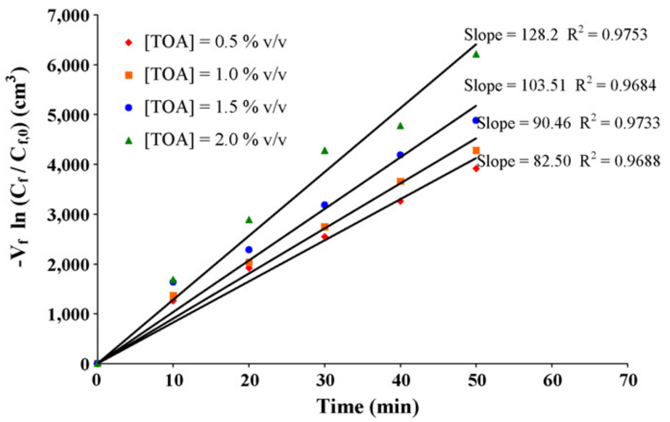


Fig. 13. Plot of $-V_f \ln(C_f/C_{f,0})$ of mercury ions in feed solution against time with different TOA concentrations.

Table 5
The permeability coefficient (P) at TOA concentration of 0.5–2.0% (v/v).

[TOA] (% (v/v))	P (cm/s × 10^2)
0.5	2.59
1.0	3.20
1.5	4.45
2.0	5.97

that the distribution ratio increased with the extractant concentration same as the results stated earlier [36].

4.7. *Permeability coefficient*

The permeability coefficients for mercury separation at TOA concentration of 0.5–2.0% (v/v) were calculated by the slope obtained in Fig. 13 as shown in Table 5. The results show that the permeability coefficient increased with the extractant concentration same as the results stated earlier [36].

4.8. *The mass transfer coefficients*

The aqueous phase mass transfer coefficient (k_i) and organic phase mass transfer coefficient (k_m) were evaluated by Eq. (14). The plot of $1/P$ as a function of $1/([R_3N]^2[H^+]^2)$ against TOA concentration was shown in Fig. 14. The slope and the ordinate were $(r_i/r_{lm})(1/K_{ex}k_m)$ and $1/k_i$, respectively. Thus, k_i and k_m were 0.011 and 0.413 cm/s. As a result, the membrane mass transfer coefficient (k_m) was much higher than that of the aqueous phase implying that the rate controlling step was the diffusion of mercury ions through the film layer between feed solution and liquid membrane.

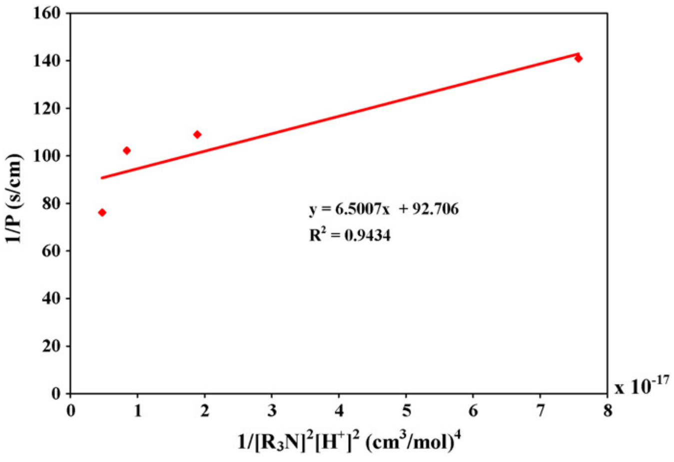


Fig. 14. Plot of $1/P$ as a function of $1/([R_3N]^2[H^+]^2)$.

5. Conclusions

Progressive research over the period of time helps reduce the risks associated with toxic discharge from industrial operations to human health and the environment. The optimum values of the parameters used with the produced water to attain high percentages of mercury extraction and stripping agree with those used with the synthetic water. This implies that the coexisting contamination of As(III) and Fe(III) ions in produced water has no significant effect on Hg(II) extraction by TOA, which is a basic extractant. In fact, a basic extractant can extract only anion forms of Hg(II) and is not suitable for cation forms containing in feed solution. In this work, for 300 min at 6-cycle operation via HFSLM system, the mercury percentages of extraction and stripping were 99.8% and 62% at the pH of feed solution of 2.5, 2% (v/v) TOA, 0.5 M NaOH and 50 ml/min of feed and stripping solutions. The concentration of mercury ions met the discharge permit issued by the Ministry of Industry, Thailand. The mass transfer coefficients of the aqueous phase (k_i) and organic phase (k_m) were 0.011 and 0.413 cm/s therefore, the rate controlling step was the diffusion of mercury ions through the film layer between feed solution and liquid membrane.

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