Separation of mercury and arsenic from produced water via hollow fiber contactor: Kinetic and mass transfer analysis

Dolapop Sribudda*, Thanaporn Wannachod*, Prakorn Ramakul**, Ura Pancharoen*,†, and Suphot Phatanasri*,†

*Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
**Department of Chemical Engineering, Faculty of Engineering and Industrial Technology,
Silpakorn University, Nakhon Pathom 73000, Thailand

Abstract−The separation of Hg(II) and As(V) from produced water by hollow fiber contactors was investigated. Two identical hollow fiber modules were employed. The first module was used for extraction, while the second module was used for stripping. The optimum conditions achieved were 14% (v/v) of Aliquat336, 0.07 M thiourea, volumetric flow rate of 100 mL/min for aqueous solution and 0.02 M HCl of stripping solution. At such conditions, the maximum extraction of Hg(II) and As(V) attained 100% and 78.78%, respectively. Concurrently, the maximum stripping of Hg(II) and As(V) reached 47.88% and 6.66%, respectively. The overall mass transfer coefficients of Hg(II) and As(V) extraction were 2.31×10^{-6} and 1.15×10^{-6} m/s, while the Hg(II) and As(V) stripping exhibited the overall mass transfer coefficients of 8.37×10^{-7} m/s and 9.05×10^{-7} m/s, respectively. Mass transfer coefficients of the organic layer diffusion (k_0) had the most effect on the overall mass transfer coefficients.

Keywords: Hg(II), As(V), Hollow Fiber Contactor, Mass Transfer Coefficients, Kinetic

INTRODUCTION

Mercury poisoning is a global concern due to its highly toxic, carcinogenic and non-biodegradable nature. Mercury and its compounds, especially methyl mercury, are extremely toxic. Inorganic mercury is the most prevalent form of mercury in aquatic ecosystems. However, its biochemical conversion (methylation) into more toxic methyl mercury (organic form) by micro-organisms is kinetically feasible both in water and soil [1]. In addition, mercury is easily absorbed through skin, respiratory and gastro-intestinal tissues. Long-term exposure to mercury causes brain damage, chromosome breakage and dysfunction of liver, kidney and central nervous system [2-4].

Arsenic (As) is considered highly toxic to human beings. Thus, it is vital to eliminate arsenic from natural sources and industrial work. Arsenic toxicity is closely related to its oxidation state. The most common forms of As found in natural water are the inorganic forms: arsenate [As(V)] and arsenite [As(III)]. In general, in a highly acidic solution (at pH value lower than 2), As(V) exists in the form of uncharged arsenic acid, H_3AsO_4. Anionic $H_2AsO_4^-$ predominates in the pH range of 3 to 6 and $HAsO_4^{2-}$ in the pH range of 8 to 11. In the pH range from 6.9 to 9.2, uncharged arsenite species prevail as H_3AsO_3. In a highly basic solution (at pH value more than 12), As(V) exists as AsO_4^{3-} [5]. It can destroy the brain, causing behavior change and loss of memory. In addition, heart disease, lung and liver cancer will occur [6].

Production of oil and gas generates large volumes of produced water that contains numerous dissolved and particulate organic and inorganic substances with a concentration largely depending on reservoir characteristics. These substances include inorganic salts, toxic heavy metals, radio-isotopes and organic compounds [7]. The growing demand for petroleum oil and gas means that the amount of produced water highly increases. Thus, toxic levels of mercury and arsenic in produced water also increase. The ministry of Natural Resources and Environment has determined that the mandatory discharge limit for mercury and arsenic into the environment should not exceed 5 and 250 µg/L, respectively [8]. In practice, toxic metal ions in produced water are treated by using precipitation, coagulation, ion exchange and carbon adsorption. However, sometimes the system has been problematic in achieving the permissible limits of discharge concentrations of metal ions. It is reported that these conventional treatments are mostly ineffective at a very low concentration of metal ions e.g. lower than 100 mg/L [9].

Many researchers have studied the separation of toxic metal ions by various processes via the liquid-liquid extraction (LLE) method [10-12] (see Table 1). Although this method has a good performance for extraction, its disadvantages are low selectivity, high operating costs, phase separation and solvent loss [13-15]. Furthermore, liquid membrane (LM) is a highly integrated separation technique that combines extraction and stripping processes in one step. The advantages of LM include the ease of scale-up, high selectivity, low consumption of extractant and no flooding [16,17]. Supported liquid membrane (SLM) is a promising separation method for wastewater treatment [18-20]. The SLM has attraction as an alternative for conventional LLE method owing to suppression of emulsification, loss of solvent, phase engagement and large solvent inventory [21]. Hollow fiber supported liquid membrane (HFSLM) is

Table 1. Literature review of various studies

Authors	Feed solution	Ion removal	Extractant	Methods	Ref.
Francis et al.	Synthesis water	Hg(II)	Cyanex 471x	LL	[10]
Meera et al.	Synthesis water	Hg(II)	Cyanex 923	LL	[11]
Fábrega et al.	Synthesis water	Hg(II)	Aliquat 336	LL	[12]
Perez et al.	Synthesis	As(V)	Cyanex 921	SLM	[18]
Güell et al.	Synthesis water	As(III), As(V)	Aliquat 336	SLM	[19]
Chakrabarty et al.	Synthesis water	Hg(II)	TOA	SLM	[20]
Mafu et al.	Industrial wastewater	As(III)	Undecane : dodecane 3 : 1	HFSLM	[22]
This work	Co-produced wastewater	Hg(II), As(V)	Aliquat336	HFC	

HFC=hollow fiber contactor, HFSLM=hollow fiber supported liquid membrane, LL=liquid liquid extraction,
SLM=supported liquid membrane

Table 2. Comparative studies of HFSLM and HFC system

Items	HFSLM			HFC		
	Guell et al. [36]	Yang et al. [37]	Saikia et al. [38]	Ortiz et al. [39]	Lin et al. [40]	Escalante et al. [41]
Target ion	Cr(VI)	Cu(II)	L-Phenyl alanine	Cr(VI)	Cu(II)	L-Phenyl alanine
Extractant	Aliquat336	LIX54	Aliquat336	Aliquat336	LIX 64N	Aliquat336
Diluent	N/A	Kerosene	Xylene	N/A	Kerosene	Kerosene
Stripping solution	HNO_3	H_2SO_4	HCl	N/A	HCl	H_2SO_4
Extraction (%)	92.4	99	80	99	99	99
Stripping (%)	92.4	27.78	40	N/A	30	N/A

another supported liquid membrane system s used to separate metal ions [5,22]. The limitation of HFSLM is the instability of impregnation of the solvent (and extractant) inside the pores of the hollow fiber: showing the loss of membrane liquid with its solubility, progressive wettability of the support pores induced by interfacial tension and the differential pressure existing between tube and shell sides caused by pumping of the flow streams [23-25].

The method for the extraction of metal ions which improved the long-term stability of the HFSLM system was found to be the hollow fiber contactor (HFC) [26-29]. It consists of two identical hollow fiber modules. The first module is used for extraction and the other module is used for stripping. The feed and the stripping aqueous solutions were pumped through the lumen (tube side) of the hollow fibers within the first and second modules, respectively. The organic liquid was filled up in the shell side of the two modules and continuously circulated in a close loop. According to the mentioned procedure, extraction and stripping were connected and carried out simultaneously. It has been noted that the integration of extraction and stripping substantially increases the performance characteristics of the HFSLM system [30]. The HFC method can eliminate equilibrium limitation and is highly efficient. Moreover, it provides the enhancement of the process rate and mass transport compared to the HFSLM system. This is due to the larger interfacial area of HFC about twenty to one-hundred times more surface area per volume between the two contacting phases [31-33]. In addition, the most stable mass-transfer process using hollow fibers can be realized by means of two separate membrane modules [30]. Other advantages of the HFC are independence of density differences and dispersion between the two phases and the backmixing as well as the prevention of formation of stable emulsion

[34,35]. Moreover, the HFC has a long-term stability of the extraction and stripping performances which leads to the continuous operation without or less system shutdown. Therefore, HFC has an economic feasibility due to its prolonged stable operation period [26-28]. Some articles studying various target ion extractions such as Cr(VI), Cu(II) and L-phenylalanine using HFC and HFSLM methods are shown in Table 2 [36-41].

In this research, the separation of Hg(II) and As(V) in produced water via HFC was studied. Feed solution was produced water from the natural gulf of Thailand. Aliquat336 was selected as an extractant because it is a quaternary ammonium salt that has a permanent positive charge which can form salts with anions over wider pH range [12]. It has a high performance for Hg(II) and As(V) extractions as reported in the literature [5,12,19]. Kerosene was used as the diluent because it was the one that most commonly adopted [42]. The stripping solutions used were thiourea, sodium hydroxide, sodium thiosulfate, DI water and nitric acid. The effect of carrier concentration, type and concentration of stripping solution, volumetric flow rate of feed and stripping solution and hydrochloric acid in feed solution were investigated. In addition, the kinetic rate reaction order and mass transfer coefficients in series including aqueous diffusion, membrane diffusion and organic-layer diffusion were calculated and identified mass transfer coefficient that had the most effect on the overall mass transfer process.

THEORY

HFC consists of two identical hollow fiber modules connected in series. In module one, the feed solution was pumped into the tube side of the hollow fibers. Likewise, in module two, the strip-
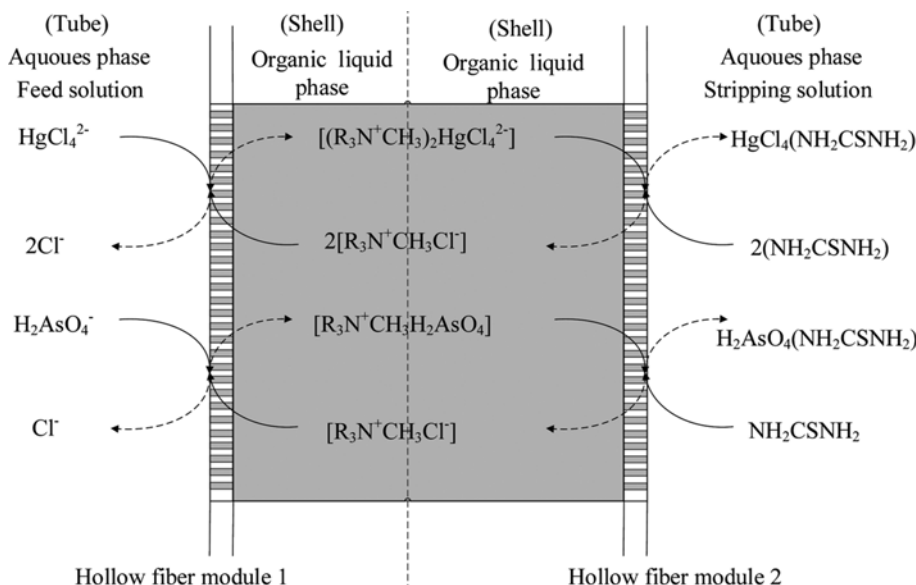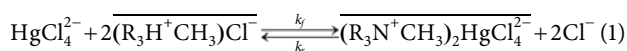
Fig. 1. Co-transport of Hg(II) and As(V) in the HFC system using Aliquat336.

ping solution was pumped into the tube side of the hollow fibers. The organic liquid filled up in the shell side of both modules. So, both hollow fiber modules included the aqueous solution and organic liquid phase. The feed solution consisted of toxic heavy metal such as Hg(II) and As(V). At the initial pH of produced water of 6.5, the formation of As(V) was $H_2AsO_4^-$ and the predominance of mercury(II) ion was $HgCl_4^{2-}$. In the first module, the target metal ion from the feed solution reacted with the extractant Aliquat336 at the interface of the feed-organic liquid phase in the tube side and generated the metal complex species. Thereafter, the metal complex species diffused through the membrane to the extractant stream (shell side) by the concentration gradient and then flowed into the shell side of the second module. Subsequently, stripping reaction occurred at the interface of the organic liquid-stripping phase. Thus, metal ions were released into the stripping phase while the extractant was transported back to the organic liquid phase. A schematic of the mass transport of target metal ions (Hg(II) and As(V)) is shown below in Fig. 1.
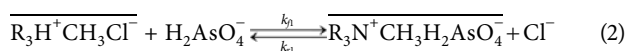
1. The Extraction Equilibrium

The extraction of Hg(II) by n-methyl-n,n-dioctyloctan-1-ammonium chloride (Aliquat336) at the feed-organic liquid interface, as shown in Eq. (1), is described by [12]:

$$HgCl_4^{2-} + 2\overline{(R_3H^+CH_3)Cl^-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \overline{(R_3N^+CH_3)_2HgCl_4^{2-}} + 2Cl^- \quad (1)$$
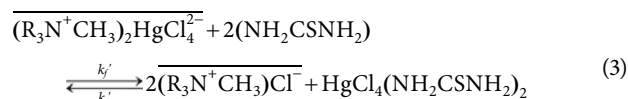
The overbar represents the species in the organic liquid phase.

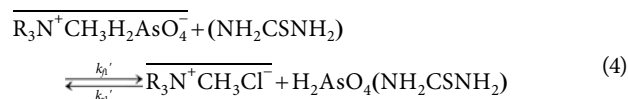The extraction of As(V) by Aliquat336 at the feed-organic liquid interface, as shown in Eq. (2), is described by [5]:

$$\overline{R_3H^+CH_3Cl^-} + H_2AsO_4^- \underset{k_{r1}}{\overset{k_{f1}}{\rightleftharpoons}} \overline{R_3N^+CH_3H_2AsO_4} + Cl^- \quad (2)$$

When the stripping reaction occurs, the mercury complex species react with the stripping solution as thiourea (NH_2CSNH_2) at the interface of the organic liquid-stripping phase. Then, Hg(II) is released into the stripping phase as shown in Eq. (3). The stripping reaction is described by [12]:

$$\overline{(R_3N^+CH_3)_2HgCl_4^{2-}} + 2(NH_2CSNH_2)$$
$$\underset{k_r'}{\overset{k_f'}{\rightleftharpoons}} 2\overline{(R_3N^+CH_3)Cl^-} + HgCl_4(NH_2CSNH_2)_2 \quad (3)$$

At the organic liquid-stripping interface, the arsenic complex species continuously react with thiourea. Then, As(V) is released into the stripping phase as shown in Eq. (4). The stripping reaction is described by [5]:

$$\overline{R_3N^+CH_3H_2AsO_4} + (NH_2CSNH_2)$$
$$\underset{k_{r1}'}{\overset{k_{f1}'}{\rightleftharpoons}} \overline{R_3N^+CH_3Cl^-} + H_2AsO_4(NH_2CSNH_2) \quad (4)$$

Percentages of extraction and stripping of Hg(II) and As(V) were obtained as shown in Eqs. (5)-(8):

$$\% \text{ Hg(II) extraction} = \frac{[Hg^{2+}]_{f,in} - [Hg^{2+}]_{f,out}}{[Hg^{2+}]_{f,in}} \times 100 \quad (5)$$

$$\% \text{ Hg(II) stripping} = \frac{[Hg^{2+}]_{s,out}}{[Hg^{2+}]_{f,in}} \times 100 \quad (6)$$

$$\% \text{ As(V) extraction} = \frac{[As^{5+}]_{f,in} - [As^{5+}]_{f,out}}{[As^{5+}]_{f,in}} \times 100 \quad (7)$$

$$\% \text{ As(V) stripping} = \frac{[As^{5+}]_{s,out}}{[As^{5+}]_{f,in}} \times 100 \quad (8)$$

2. Determination of Mass Transfer Coefficients

In this work, the flow through the hollow fibers is laminar (Re< 2400). Within this region, the mass transfer coefficient in aqueous phase (k_t) for the tube side, as shown in Eq. (9), is described by [40]:

$$k_t = 1.62 \frac{D}{2r_i} \left(\frac{4r_i^2 u_{tube}}{DL} \right)^{1/3} \quad (9)$$

where k_t is the mass transfer coefficients of aqueous diffusion in the tube side of both two modules, k_t is either k_f (feed) or k_s (strip-

ping). D is diffusion coefficient of the aqueous solution, u is flow velocity and r_i is inner radius of the hollow fibers.

Mass transfer coefficient of the membrane diffusion (k_m) for Aliquat336 extractant and the complex can be expressed in the following Eq. (10) [43]:

$$k_m = \frac{\varepsilon D_m}{\tau r_i \ln(r_o/r_i)} \tag{10}$$

where ε is porosity of the hollow fibers, D_m is diffusion coefficient of membrane phase, τ is tortuosity of the hollow fibers, r_i and r_o is radius of inner and outer of the hollow fibers, respectively.

In the case of shell side, the mass transfer coefficient as shown in Eq. (11) [40]:

$$k_o = \frac{0.245D}{4r_H}\left(\frac{4r_H u_{shell}}{\upsilon}\right)^{2/3}\left(\frac{\upsilon}{D}\right)^{1/3} \tag{11}$$

where D is diffusivity coefficient, u_{shell} is velocity in the shell side, υ is kinematic viscosity of the medium, r_H is hydraulic radius of shell side. Hydraulic radius was 5.97×10^{-8} m as calculated from Eq. (12) [44]:

$$d_H = \frac{d_a^2 - d_c^2 - nd_o^2}{nd_o} \tag{12}$$

where d_a is the diameter of the fiber bundle, d_c is the diameter of the distribution/collection tube in the Liqui-Cel extra-flow contactor and d_o is the outer diameter of hollow fibers.

From the Wilke-change equation [45], the diffusion coefficient of Hg(II) in feed solution phase and the diffusion coefficient of Hg(II) in membrane phase is given in Eqs. (13) and (14):

$$D_{aq}^* = \frac{7.4 \times 10^{-8}(M)^{0.5}T}{\eta V_A^{0.6}} \tag{13}$$

$$D_m^* = \frac{7.4 \times 10^{-8}(M)^{0.5}T}{\eta V_A^{0.6}} \tag{14}$$

where D_{aq}^* is the diffusion coefficient in feed solution phase (cm^2/s), D_m^* is diffusion coefficient in membrane (cm^2/s), M is molecular weight of solvent (g/mol), T is temperature (K), η is viscosity (cP) and V_A is molar volume of solute (cm^3/mol).

The overall mass transfer resistances of the extraction and stripping module of Hg(II) can be expressed as follows in Eqs. (15) and (16) [40]:

$$\frac{1}{K_E} = \frac{1}{k_{Hg,f}} + \frac{[Cl^-]_f}{k_f[(R_3H^+CH_3)Cl^-]_{oi}}$$
$$+ \frac{[Cl^-]_f^2}{k_{\overline{(R_3N^+CH_3)_2HgCl_4^{2-}},m}K_{ex}[\overline{(R_3H^+CH_3)Cl^-}]_{fi}^2}$$
$$+ \frac{[Cl^-]_f^2}{k_{\overline{(R_3N^+CH_3)_2HgCl_4^{2-}},o}K_{ex}[\overline{(R_3H^+CH_3)Cl^-}]_{fi}^2} \tag{15}$$

$$\frac{1}{K_S} = \frac{1}{k_{Hg,s}} + \frac{1}{k_f[NH_2CSNH_2]_s} + \frac{1}{k_{\overline{(R_3N^+CH_3)_2HgCl_4^{2-}},m}}$$
$$+ \frac{K_{ex}[R_3H^+CH_3Cl^-]_{si}^2}{k_{\overline{(R_3N^+CH_3)_2HgCl_4^{2-}},o}[NH_2CSNH_2]_s^2} \tag{16}$$

The overall mass transfer resistances of the extraction and stripping module of As(V) can be expressed as follows in Eqs. (17) and (18) [40]:

$$\frac{1}{K_E} = \frac{1}{k_{As,f}} + \frac{[Cl^-]_f}{k_{f1}[\overline{(R_3H^+CH_3)Cl^-}]_{oi}}$$
$$+ \frac{[Cl^-]_f}{k_{\overline{(R_3N^+CH_3)H_2AsO_4^-},m}K_{ex}[\overline{(R_3H^+CH_3)Cl^-}]_{fi}^2}$$
$$+ \frac{[Cl^-]_f}{k_{\overline{(R_3N^+CH_3)H_2AsO_4^-},o}K_{ex}[\overline{(R_3H^+CH_3)Cl^-}]_{fi}} \tag{17}$$

$$\frac{1}{K_S} = \frac{1}{k_{As,s}} + \frac{1}{k_{f1}[NH_2CSNH_2]_s} + \frac{1}{k_{\overline{(R_3N^+CH_3)H_2AsO_4^-},m}}$$
$$+ \frac{K_{ex}[R_3H^+CH_3Cl^-]_{si}}{k_{\overline{(R_3N^+CH_3)H_2AsO_4^-},o}[NH_2CSNH_2]_s} \tag{18}$$

where K_E and K_S are the overall mass transfer coefficients of the extraction module (first module) and stripping module (second module), respectively. The mass transfer resistance in the right term of Eqs. (15)-(18) consisted of the four individual resistance terms including resistance of aqueous layer diffusion in the tube side, resistance of chemical reaction, membrane resistance and resistance of organic layer in the shell side, respectively. The value of K_{ex} is equilibrium constant. k_f and k_{f1} are the extraction reaction rate constant of Hg(II) and As(V).

EXPERIMENTAL

1. Chemical and Reagents

The produced water from the Gulf of Thailand as the feed solution was obtained from Salamander Energy (Bualuang) Co. Ltd. The initial pH of feed solution was 6.5. The composition of produced water is shown in Table 3. Aliquat336 (n-methyl-n-dioctyloctan-1-ammonium chloride) was used as extractant. It was supplied from Acros Organics Co. Ltd., USA. The diluent used in this work was kerosene with purity of 99%. It was purchased from Thai Oil Co. Ltd., Thailand. The stripping solution used, i.e., thiourea, thiosulfate and sodium thiosulfate was supplied by Qrec company, New Zealand. Another stripping solution was deionized water as well as nitric acid with purity of 65%. All reagents were of analytical grade.

2. Apparatus

The hollow fiber modules used in this work were the Liqui-Cel® Liquid-Liquid Extraction (LLE) system. It was purchased from

Table 3. The composition of produced water from natural gulf Thailand (pH about 6.5)

Metal	Concentration (ppm)
Hg(II)	1.1
As(V)	0.9
Na(I)	1020.0
Fe(III)	0.8
Mg(II)	2.4
Ca(II)	11.6

Table 4. The properties of hollow fiber module

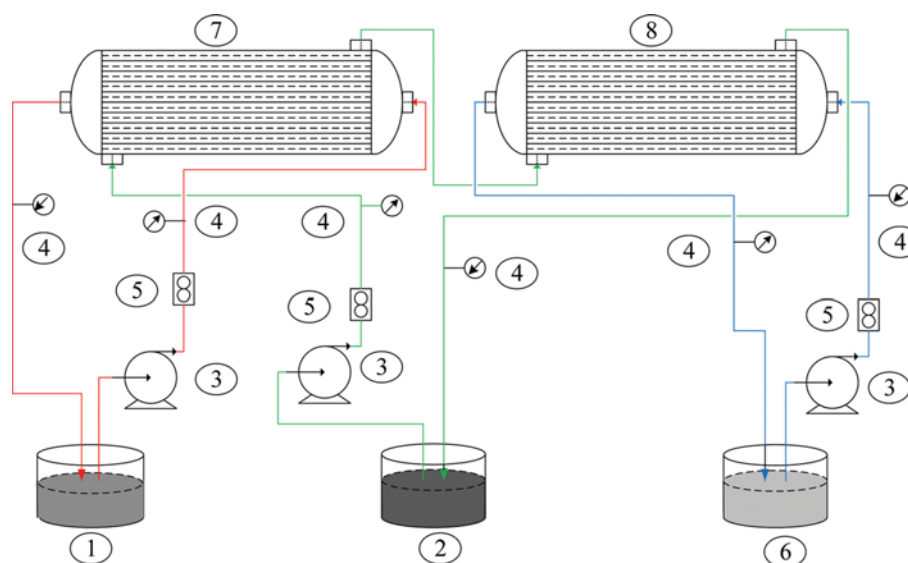| Properties	Descriptions
Material[a]	Polypropylene
Inner diameter of hollow fibers (d_i)[a]	240×10^{-4} cm
Outer diameter of hollow fibers (d_o)[a]	300×10^{-4} cm
Fiber bundle diameter (d_a)[b]	4.70 cm
Distribution tube diameter (d_c)[b]	2.20 cm
Shell diameter (d_s)[a]	6.30 cm
Effective length of hollow fiber (L)[a]	15 cm
Number of hollow fibers (n)[a]	35,000
Average pore size[a]	0.03 μm
Porosity (ε)[a]	25%
Tortuosity (τ)[a]	2.60
Effective surface area (A)[a]	1.40×10^{4} cm^2
Area per unit volume[a]	29.30 cm^2/cm^3
Module diameter[a]	6.30 cm
Module length[a]	20.30 cm
Operating temperature[a]	273-333 k

[a] is [46] and [b] is [44]

Hoechst Celanese Corporation, Japan. Celgard® X-30 polypropylene pores were wrapped by the supported module. All properties of the hollow fiber module are shown in Table 4 [44,46]. The concentration of metal ions was measured by Inductively coupled plasma optical emission spectrometry (ICP-OES). The instrument used was JY 2000-2 from Horiba scientific, France.

3. Procedure

The HFC system which involved a continuous flow operation was used in this research as shown in Fig. 3. The aqueous solutions (feed and stripping) were each 1,000 mL in volume. Both solutions circulated from their respective reservoirs through the tube side of the hollow fibers and then back into the reservoirs. The feed

Fig. 2. Chemical structure of Aliquat336.

and stripping solutions were pumped into the tube side of hollow fibers of the module one and module two, respectively. The organic liquid (extractant) with volume of 500 mL was circulated countercurrently in the shell side of both modules and then flowed back into the organic liquid reservoir. This method (HFC) eliminated the equilibrium limitation and proved to be highly efficient, more than the HFSLM system. The HFC system has a large interfacial and surface area between the aqueous solution and organic liquid in each module resulting in the improvement of process rate. No mixing and no phase separation problems occur after the mass-transfer between the liquids. The volume flow rates of feed and stripping solutions equaled about 100 mL/min. The volume flow rate of organic liquid was 50 mL/min. The pressure of the aqueous phase was maintained higher than the pressure of the organic phase, as the hydrophobic fibers are preferentially wetted by the organic extractant. The pressure was adjusted by using the four valves at the inlet and outlet of the modules, ensuring that no displacement of the organic phase and emulsion formation took place. Samples were kept of the outlet feed and stripping solutions and their concentration of metal ions was analyzed by ICP-OES.

Fig. 3. Schematic circulated counter-current flow diagram in the HFC system.

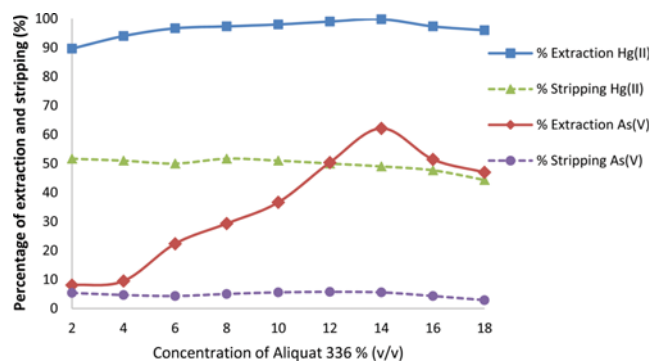|			
1. Feed reservoir	3. Gear pumps	5. Flow meters	7. Extraction module
2. Extractant reservoir	4. Pressure gauges	6. Stripping reservoir	8. Stripping module

Fig. 4. Extraction and stripping percentages against Aliquat336 concentration: Stripping concentration of 0.05 M and 100 mL/min of feed and stripping flow rates.

RESULTS AND DISCUSSION

1. Effect of Extractant Concentration

The effect of Aliquat336 concentration on separation of Hg(II) and As(V) was studied between the range of 2-18%. Results are shown in Fig. 4. In the range of Aliquat336 concentration between 2-14% (v/v), the extraction of Hg(II) and As(V) reached its maximum at 14%. As revealed by Eqs. (1) and (3), an increase in Aliquat336 concentration can improve extraction efficiency. From Le Chatelier's principle the increase in extractant concentration in the liquid membrane results in higher fluxes. On the other hand, removal efficiency decreased significantly when extractant concentration increased over 14%. It can be explained by using Wilke-Change equation in Eq. (14). This reduction in removal efficiency can be attributed to the increase in viscosity of the organic liquid, which leads to a decrease in transport [47]. When Aliquat336 concentration was more than 14%, the percentage of extraction and stripping of Hg(II) and As(V) slightly decreased.

Therefore, by using 14% (v/v) of Aliquat336 as extractant, the maximum extraction of Hg(II) and As(V) achieved 99.80% and 62.14%, respectively. Concurrently, the maximum stripping of Hg(II) and As(V) reached 49.00% and 5.53%, respectively.

2. Type of Stripping Solutions

The stripping solutions used in this work were thiourea (NH_2 $CSNH_2$), sodium thiosulfate ($Na_2S_2O_3$), sodium hydroxide (NaOH), nitric acid (HNO_3) and deionized water. The results of the stripping of Hg(II) and As(V) from various stripping solutions are shown in Fig. 5. Results showed that thiourea was the best stripping solution. It can be explained by the chemical structure of Aliquat336 as shown in Fig. 2. Aliquat336 is a water insoluble quaternary ammonium salt composed of a large organic cation associated with a chloride ion. When Aliquat336 reacted with Hg(II) and As(V), it generated a strong complex species which was difficult to strip as shown in Eqs. (1) and (3). To attract the anion and release the quaternary ammonium (extractant) into the organic liquid phase, the interaction between stripping agent and anion must overcome that of anion-extractant complex [12]. The deionized water and hydrochloric acid gave lower stripping percentages of target metal ions from the process. In case of basic solution, thiourea was able to strip Hg(II) and As(V) more than sodium thiosulfate and sodium hydrox-
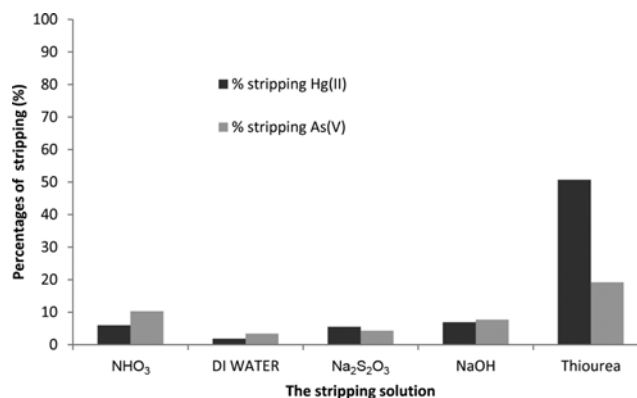

Fig. 5. Stripping percentage against type of stripping solutions: 14% (v/v) of extractant concentration and 100 mL/min of feed and stripping flow rates.
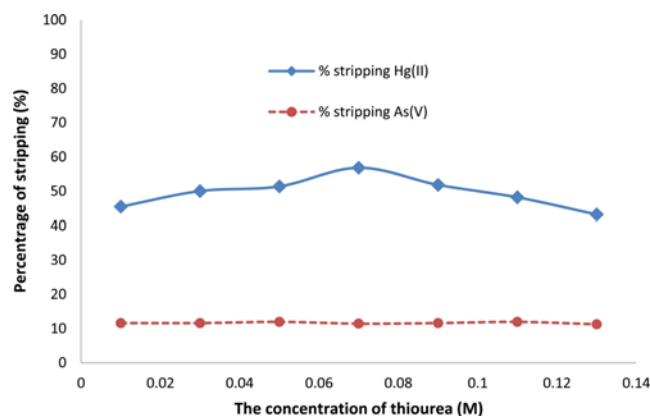

Fig. 6. Stripping percentage against stripping concentration: 14% (v/v) of extractant concentration and 100 mL/min of feed and stripping flow rates.

ide due to its strong basic solution resulting from the large anion of thiourea [12]. Thus, thiourea proved to be the best stripping solution and was used in further experiments. By using thiourea as stripping solution, the maximum stripping of Hg(II) and As(V) obtained was 50.69% and 19.21%, respectively.

3. Concentration of Stripping Solution

The effect of thiourea concentration in the range of concentration at 0.01 to 0.13 M was studied. Results are shown in Fig. 6. The percentage of stripping of Hg(II) increased when concentration of the stripping agent increased to 0.07 M. When concentration increased more than 0.07 M, there was a significant decrease in the stripping of Hg(II). This is because the stripping reaction is a reversible process as shown in Eq. (2). The adverse effect of the higher concentration was due to the saturation solubility of thiourea in the stripping phase. The reversible nature of the stripping reaction also led to the back-extraction of Hg(II) to the organic liquid [48]. In the case of As(V), results showed that the percentage of stripping solution remained stable. Therefore, by using 0.07 M of thiourea as stripping solution, the maximum stripping of Hg(II) and As(V) obtained was 56.82% and 11.42%, respectively.

4. The Volumetric Flow Rates of Feed and Stripping Solutions

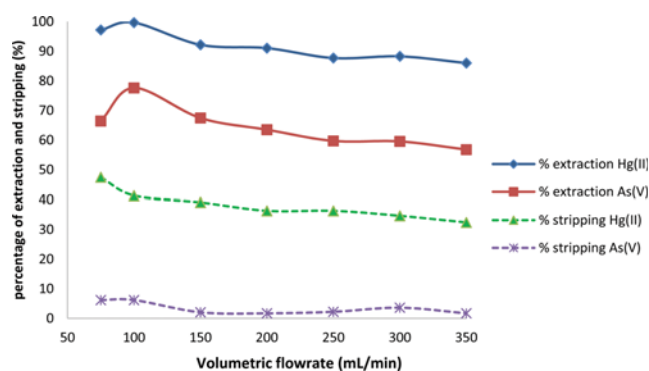In this work, the volumetric flow rates of feed and stripping solu-

Fig. 7. Extraction and stripping percentages against feed and stripping flow rates: 14% (v/v) of extractant concentration and stripping concentration of 0.07 M.

tions varied from 75-350 mL/min (the result is shown in Fig. 7). Percentages of extraction of Hg(II) and As(V) increased when volumetric flow rates were increased from 75-100 mL/min., because the thickness of the boundary layer at the interface of aqueous and organic liquid phases decreased. Consequently, the permeability at the interface of the feed solution and organic liquid phases increased [49]. Optimum volumetric flow rate was 100 mL/min. At a higher volumetric flow rates, there was less residence time of the aqueous solution to contact with the extractant for extraction and stripping reactions. In addition, the organic liquid can be lost from the hollow fibers and slip through to the aqueous solution due to the strength of lateral shear force at the interface of aqueous and organic liquid phases [50]. Thus, the percentage of extraction and stripping decreased.

Thus, by using each 100 mL/min of feed and stripping solutions, the maximum extraction of Hg(II) and As(V) attained 100% and 77.62%, respectively. Meanwhile, the maximum striping of Hg(II) and As(V) reached 41.34% and 6.19%, respectively.

5. The Effect of HCl in Feed Solution

From Fig. 8, the concentration of hydrochloric acid in feed solution varied from 0.01 to 0.06 M. The extraction of Hg(II) continuously decreased with the increasing hydrochloric acid concentration in the feed solution higher than 0.02 M. This was due to the formation of species $HgCl_3^-$ and $HgCl_4^{2-}$ in feed solution with the in-
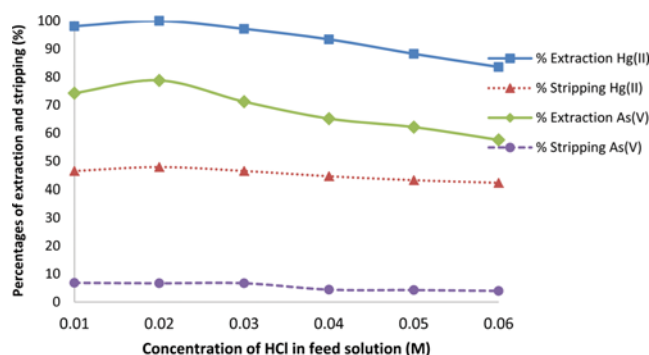

Fig. 8. Extraction and stripping percentages against concentration of HCl in feed solution: 14% (v/v) of extractant concentration and stripping concentration of 0.07 M.
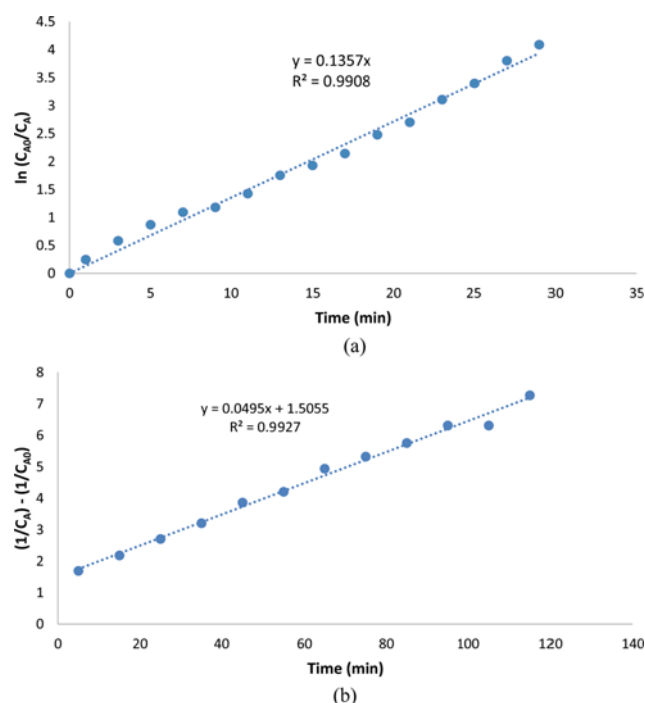

(a)

(b)

Fig. 9. Reaction rate order for extractions of (a) Hg(II) and (b) As(V).

crease of hydrochloric acid concentration [10,11]. The extraction of As(V) increased when the concentration of hydrochloric acid increased from 0.01 to 0.02 M. When the concentration of hydrochloric acid was higher than 0.02 M, the percentages of As(V) extraction decreased with the increasing acid concentration, because Aliquat336 effectively performed in weak acidic solution (low acid concentration in feed solution) [51].

By maintaining concentration of hydrochloric acid in feed solution at 0.02 M, the maximum percentage of Hg(II) and As(V) extraction attained 100% and 78.78%, respectively. The maximum percentages of stripping of Hg(II) and As(V) reached 47.88% and 6.66%, respectively.

6. The Reaction Rate Order of Extraction

The reaction rate order of extraction of Hg(II) and As(V) with Aliquat336 as extractant is shown in Fig. 9 and Table 5. Results showed that the reaction rate order of extraction of Hg(II) and As(V) by Aliquat336 exhibited, respectively, first-order and second-order reaction with best fit of the correlation coefficient. The experimental data showed that Hg(II) was extracted more rapidly by Aliquat336

Table 5. The reaction rate order of extraction of Hg(II) and As(V)

Reaction order	Equations	Hg(II) extraction	As(V) extraction
0	$C_{A0} - C_{A(t)}$ vs time	0.7894	0.6058
1	$\ln (C_{A0}/C_{A(t)})$ vs time	*0.9908	0.3639
2	$(1/C_{A(t)}) - (1/C_{A0})$ vs time	0.7172	*0.9927

*Rate reaction order of extraction Hg(II) and As(V) by Aliquat336 with the best fit of correlation coefficient were first and second order, respectively

Table 6. The mass transfer coefficients in HFC system

Solute/phase	Hg(II)	As(V)
Toxic metal/ feed (m/s)	$k_{Hg,f}=2.32\times10^{-6}$	$k_{As,f}=2.93\times10^{-6}$
Toxic metal/stripping (m/s)	$k_{Hg,s}=2.28\times10^{-6}$	$k_{As,s}=2.87\times10^{-6}$
Metal-complex species/membrane (m/s)	$k_{\overline{(R_3N^+CH_3)_2HgCl_4^{2-}},\,m}=1.31\times10^{-6}$	$k_{\overline{(R_3N^+CH_3)H_2AsO_4^-},\,m}=1.31\times10^{-6}$
Metal-complex species/shell side (m/s)	$k_{\overline{(R_3N^+CH_3)_2HgCl_4^{2-}},\,o}=7.06\times10^{-6}$	$k_{\overline{(R_3N^+CH_3)H_2AsO_4^-},\,o}=8.93\times10^{-6}$
Overall mass transfer coefficient of extraction reaction (m/s)	$K_E=2.31\times10^{-6}$	$K_E=1.15\times10^{-6}$
Overall mass transfer coefficient of stripping reaction (m/s)	$K_S=8.37\times10^{-7}$	$K_S=9.05\times10^{-7}$

than As(V). The percentage of extraction of Hg(II) and As(V) reached a maximum at 30 min and 115 min, respectively. From the results, the value of the rate reaction constant of extraction reaction of Hg(II) (k_f) was 1.36×10^{-1} min^{-1}. The rate reaction constant of extraction reaction of As(V) (k_{fl}) was 4.95×10^{-2} L·mol^{-1} min^{-1}. Thus, the values of both constants were used to calculate the overall mass transfer coefficients.

7. The Mass Transfer Coefficients

The values of k_t, k_m and k_o can be calculated using Eqs. (9)-(11) under optimum conditions where the initial concentrations of Hg(II) and As(V) were 1.1 and 0.9 ppm, respectively. The concentration of Aliquat336 was 14% (v/v) and the concentration of thiourea was 0.07 M with volumetric flow rate of aqueous solution 100 mL/min. The overall mass transfer coefficient can be calculated by using Eqs. (15)-(18). The results of the calculated individual mass transfer coefficients and overall mass transfer coefficients of extraction and stripping of toxic metal ions are shown in Table 6.

The results showed that the mass transfer coefficients of the aqueous layer diffusion (feed and stripping phase) and mass transfer coefficient of the organic layer diffusion were much higher than membrane diffusion. This means that for the extraction and stripping process of Hg(II) and As(V) in the HFC system, the mass transfer coefficient of membrane diffusion in both modules has little effect on the overall mass transfer coefficients. So, the mass transfer coefficient of organic layer diffusion is the most important for separation of Hg(II) and As(V) from the HFC system.

CONCLUSION

The separation of Hg(II) and As(V) from produced water via HFC was investigated. The best conditions found were at extractant concentration of 14% (v/v), 0.07 M thiourea and volumetric flow rate of 100 mL/min for both feed and stripping solutions in each module and 0.02 M HCl in feed solution. At such conditions, the extraction percentage of Hg(II) and As(V) were 100% and 78.78%, respectively, while the stripping percentage of Hg(II) and As(V) was 47.88% and 6.66%, respectively. Results showed that the best performance for separation of toxic Hg(II) and As(V) ions from produced water was attained via HFC. The final concentrations of Hg(II) and As(V) after extraction process were 0 and 0.19 ppm, respectively. In addition, the results indicated the higher extraction of Hg(II) than that of As(V). It could be supported by the extraction equilibrium constants of Hg(II) and As(V) that were 3.89×10^{-5} and 5.85×10^{-6}, respectively.

Extraction of Hg(II) by Aliquat336 exhibited first-order reaction, and extraction of As(V) exhibited second-order reaction. At optimum conditions, the mass transfer coefficients of organic layer diffusion proved to be the most important. Furthermore, the mass transfer coefficients from membrane layer diffusion had little effect on the overall mass transfer coefficients process. The overall mass transfer coefficients of extraction of Hg(II) and As(V) extractions were 2.31×10^{-6} and 1.15×10^{-6} m/s, respectively. The overall mass transfer coefficients of stripping of Hg(II) and As(V) stripping were 8.37×10^{-7} and 9.05×10^{-7} m/s, respectively.

NOMENCLATURE

A   : effective area of the membrane [cm^2]
D   : diffusion coefficient [cm^2/s]
d_a : diameter of the fiber bundle [m]
d_c : diameter of the distribution/collection tube in the Liqui-Cel extra-flow contactor [m]
d_H : hydraulic diameter of shell [m]
d_i : inner diameter of hollow fibers [m]
D_m : mass diffusivity [m^2/s]
d_o : outer diameter of hollow fibers [m]
d_s : shell diameter of hollow fiber module [m]
k_t : mass transfer coefficient in the tube side [m/s]
k_m : mass transfer coefficient in the organic liquid phase [m/s]
k_o : mass transfer coefficient in the shell side [m/s]
K_{ex} : equilibrium constant
K_E : overall mass transfer coefficient of extraction module [m/s]
K_S : overall mass transfer coefficient of stripping module [m/s]
k_f : extraction reaction rate of extraction Hg(II) [min^{-1}]
k_{fl} : extraction reaction rate of extraction As(V) [L·mol^{-1} min^{-1}]
L   : effective length of hollow fiber [cm]
M   : molecular weight [g/mol]
N   : number of hollow fibers in the module

r_i : inner radius of the hollow fibers [m]
r_o : outer radius of the hollow fibers [m]
r_H : hydraulic radius of the shell side [m]
T   : temperature [k]
u_{tube} : flow rate of solution in the tube side [m/s]
u_{shell} : flow rate of solution in the shell side [m/s]
V_a : molar volume [cm^3/mol]

Greek Letters

ε : porosity of hollow fiber
τ : tortuosity
η : viscosity [cp]
υ : kinematic viscosity [m^2/s]

Subscripts

ex   : extraction
f   : feed phase
fi   : feed interface
aq   : aqueous phase
m   : membrane
s   : stripping
si   : stripping interface

<div align="center">

REFERENCES

</div>

1. H.-B. Lia, S. Yu, G.-L. Li, H. Deng, B. Xu, J. Ding, J.-B. Gao, Y.-W. Hong and M.-H. Wong, *Sci. Total. Environ.*, **445-446**, 117 (2013).

2. S. Díez, *Rev. Environ. Contam. Toxicol.*, **198**, 111 (2009).

3. C. Deng, D. Zhang, X. Pan, F. Chang and S. Wang, *J. Photoch. Photobio. B.*, **127**, 1 (2013).

4. X. Wang, R. Sun and C. Wang, *Colloids Surf., A.*, **441**, 51 (2014).

5. S. Bey, A. Criscuoli, A. Figoli, A. Leopold, S. Simone, M. Benamor and E. Drioli, *Desalination*, **264**, 193 (2010).

6. Y. Fujino, X. Guo, J. Liu, L. You, M. Miyatake, T. Yoshimura and Japan Inner Mongolia Arsenic Pollution (JIAMP) Study Group, *Soc. Sci. Med.*, **59**, 1969 (2004).

7. L. Camus, S. Brooks, P. Geraudie, M. Hjorth, J. Nahrgang, G. H. Olsen and M. G. D. Smit, *Ecotox. Environ. Safe.*, **113**, 248 (2015).

8. Thailand regulatory discharge standards, Ministry of Industry, Thailand (1996).

9. B. S. Inbaraj, J. S. Wang, J. F. Lu, F. Y. Siao and B. H. Chen, *Bioresour. Technol.*, **100**, 200 (2009).

10. T. F. Rao, T. P. Rao and M. L. P. Reddy, *Hydrometallurgy*, **57**, 263 (2000).

11. R. Meera, T. Francis and M. L. P. Reddy, *Hydrometallurgy*, **61**, 97 (2001).

12. F. B. M. Frabega and M. B. Mansur, *Hydrometallurgy*, **87**, 83 (2007).

13. A. Gabelman and S.-T. Hwang, *J. Membr. Sci.*, **159**, 61 (1999).

14. S. A. Ansari, P. K. Mohapatra, M. Iqbal, P. Kandwal, J. Huskens and W. Verboom, *J. Membr. Sci.*, **430**, 304 (2013).

15. N. Leepepatpiboon, U. Pancharoen and P. Ramamkul, *Korean J. Chem. Eng.*, **30**, 194 (2013).

16. Z. Hao, Z. Wang, W. Zhang and W. S. Winston Ho, *J. Membr. Sci.*, **468**, 90 (2014).

17. P. Ramakul, W. Pattaweekongka and U. pancharoen, *Korean J. Chem. Eng.*, **23**, 85 (2006).

18. M. E. Martinez Perez, J. A. Reyes-Aguilera, T. I. Saucedo, M. P. Gonzalez, R. Navarro and M. Avila-Rodriguez, *J. Membr. Sci.*, **302**, 119 (2007).

19. R. Güell, C. Fontàs, V. Salvadó and E. Anticó, *Sep. Purif. Technol.*, **72**, 319 (2010).

20. K. Chakrabarty, P. Saha and A. K. Ghoshal, *J. Membr. Sci.*, **350**, 395 (2010).

21. P. Zaheri, H. Abolghasemi, T. Mohammadi and M. G. Maraghe, *Korean J. Chem. Eng.*, **32**(8), 1642 (2015).

22. L. D. Mafu, T. A. M. Msagati and B. B. Mamba, *Phys. Chem. Earth.*, **50-52**, 121 (2012).

23. M. S. Manna, P. Saha and A. K. Ghoshal, *J. Membr. Sci.*, **471**, 219 (2014).

24. M. F. San Roman, E. Bringas, R. Ibanez and I. Ortiz, *J. Chem. Technol. Biotechnol.*, **85**, 2 (2010).

25. H.-D. Zheng, B.-Y. Wang, Y.-X. Wu and Q.-L. Ren, *Colloids Surf, A.*, **351**, 38 (2009).

26. B. Galan, M. Calzada and I. Ortiz, *Chem. Eng. J.*, **124**, 71 (2006).

27. A. K. Pabby and A. M. Sastre, *J. Membr. Sci.*, **430**, 263 (2013).

28. D. N. Ambare, S. A. Ansari, M. Anitha, P. Kandwal, D. K. Singh, H. Singh and P. K. Mohapatra, *J. Membr. Sci.*, **446**, 106 (2013).

29. F. Zhang, W. Sun, J. Liu, W. Zhang and Z. Ren, *Korean J. Chem. Eng.*, **31**(6), 1049 (2014).

30. Z. Lazarova, B. Syska and K. Schügerl, *J. Membr. Sci.*, **202**, 151 (2002).

31. I. M. Coelhoso, M. M. Cardoso, R. M. C. Viegas and J. P. S. G. Crespo, *Sep. Purif. Technol.*, **19**, 183 (2000).

32. A. B. de Haan, P. V. Bartels and J. de Graauw, *J. Membr. Sci.*, **45**, 281 (1989).

33. I. Ortiz, B. Galan and A. Irabien, *J. Membr. Sci.*, **118**, 113 (1996).

34. I. M. Coelhoso, E. Silvestre, R. M. C. Viegas, J. P. S. G. Crespo and M. J. T. Carrondo, *J. Membr. Sci.*, **134**, 19 (1997).

35. A. Gugliuzza and A. Basile, *Membrane contactors: Fundamentals, membrane materials and key operations, Handbook of Membrane Reactors*, Woodhead Publishing, England (2013).

36. R. Guell, E. Antico, V. Salvado and C. Fontas, *Sep. Purif. Technol.*, **62**, 389 (2008).

37. Q. Yang and N. M. Kocherginsky, *J. Membr. Sci.*, **286**, 301 (2006).

38. B. Saikia, N. N. Dutta and N. N. Dass, *J. Membr. Sci.*, **225**, 1 (2003).

39. I Ortiz, B. Galan and A. Irabien, *J. Membr. Sci.*, **118**, 213 (1996).

40. S.-H. Lin and R.-S. Juang, *J. Membr. Sci.*, **188**, 251 (2001).

41. H. Escalante, A. I. Alonso, I. Ortiz and A. Irabien, *Sep. Sci. Technol.*, **33**, 119 (1998).

42. Pawel-Dzygiel and Piotr P. Wieczorek, Supported Liquid Membranes and Their Modifications: Definition, Classification, Theory, Stability, Application and Perspectives, *Liquid Membranes Principles and Applications in Chemical Separations & Wastewater Treatment*, Elsevier B.V., Oxford, U.K. (2010).

43. Q. Yang and N. M. Kocherginsky, *J. Membr. Sci.*, **297**, 121 (2007).

44. A. Baudot, J. Floury and H. E. Smorenburg, *AIChE J.*, **47**, 1780 (2001).

45. V. S. Kislik, *Liquid Membranes: Principles and Applications in Chemical Separations and Wastewater Treatment*, Elsevier B.V., Oxford, U.K. (2010).

46. S. Chaturabul, T. Wannachod, V. Mohdee, U. Pancharoen and S. Phatanasri, *Chem. Eng. Process.*, **89**, 35 (2015).

47. H. R. Mortaheb, A. Zolfaghari, B. Mokhtarani, M. H. Amini and
    V. Mandanipour, *J. Hazard. Mater.*, **177**, 660 (2010).
48. K. K. Bhatluri, M. S. Manna, P. Saha and A. K. Ghoshal, *J. Membr.
    Sci.*, **459**, 256 (2014).
49. S. Gupta, M. Chakraborty and Z. V. P. Murthy, *J. Ind. Eng. Chem.*,

20, 2138 (2014).
50. X. J. Yang and A. G. Fane, *J. Membr. Sci.*, **156**, 251 (1999).
51. A. W. Lothongkum, S. Suren, S. Chaturabul, N. Thamphiphitb and
    U. Pancharoen, *J. Membr. Sci.*, **369**, 350 (2011).