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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

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1. Introduction

This chapter describes the merits of using hollow fiber supported liquid membrane (HFSLM), one of liquid membranes in supported structures, and the step-by-step mass transfer in removing arsenic (As) and mercury (Hg) ions from produced water in upstream petroleum operation from the Gulf of Thailand. Apart from the necessary fundamentals, the contents comply existing information and data based on our up-to-date publications in journals.

Arsenic (As) and mercury (Hg) are naturally trace components in petroleum reservoir. In certain Gulf of Thailand fields, the concentration levels vary widely and Hg, in particular, is drawing local statutory attention since its concentration is found typically higher than those found in the rest of the global petroleum production areas. A number of hypotheses have suggested the origin of As and Hg in the petroleum reservoirs laid underneath the Gulf. But one common fact agrees that mercury predominantly presents in an elemental form Hg(0) with the rest in an inorganic form ($HgCl_2$), organic forms (CH_3HgCH_3 and $C_2H_5HgC_2H_5$) and an organo-ionic form ($ClHgCH_3$). For arsenic, it presents as As(III) and As(V) (Korte & Fernando, 1991). The As(III) is normally in the form of H_3AsO_3 whereas As(V) is in either $H_2AsO_4^-$ or $HAsO_4^{2-}$. Arsenic and mercury are grouped in the most hazardous metals since arsenic compounds are carcinogens, both severe acute and chronic toxicity, while mercury can evaporate in soil or water; short-term exposure results in kidney damage; and a lifetime of exposure can lead to impairments in neurological functioning (U.S. EPA, 1984).

In the Gulf of Thailand, petroleum development and upstream production have been very active recently following an increasing domestic energy demand and a soaring global oil price. Accordingly, numbers of leading and national oil companies have been gathering in the Gulf for an interest of petroleum exploration and production. Figure (1) presents 2009 updated petroleum concessionaire map in the Gulf of Thailand where total gross production

per day has been reported around 680,000 barrels of oil equivalent [DMF, 2010] and hundreds of thousands of barrels daily for the produced water are generated. Trend of produced water production is increasing dramatically according to an exponential expansion of petroleum development to meet high domestic demand and maturity of production reservoir itself.

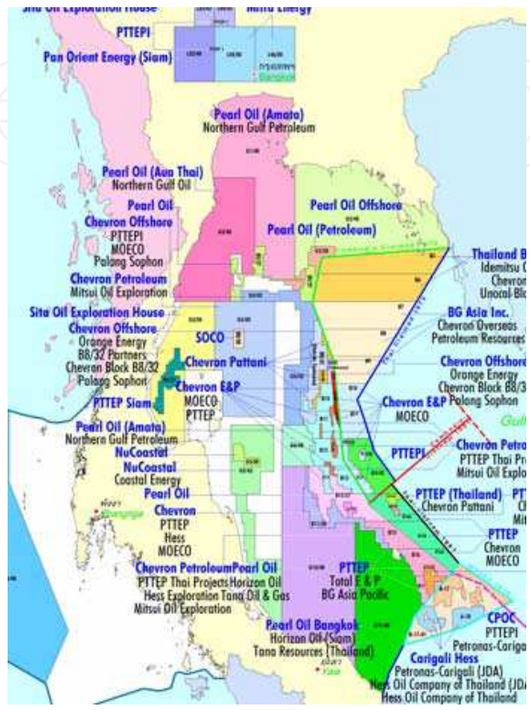


Fig. 1. Concessionaire map in the Gulf of Thailand (DMF, 2009)

To handle this massive daily generated amount of produced water, the oil company operators in the Gulf undertake an enduring path to pursue a "zero discharge" program enforced by Thai local authorities by injection of the produced water back into the formations. Nevertheless, overboard discharge of the produced water into the ocean is still necessitated when the re-injection facilities are in breakdown state or for some production fields where uncertainties in geological formations to receive such great volume of produced water hinder the feasibility. Pollution and biological impact to local marine environment is of concern when overboard discharge of arsenic and mercury contaminating produced water into the ocean. Various aspects of the potential environmental effects of arsenic and mercury have been assessed by local environmental control authorities. According to the overboard discharge limits made to reference with the Ministry of Industry and the Ministry of Natural Resources and Environment, Thailand, it is a must to remove arsenic and mercury from offshore waste discharges to no greater than 250 ppb and 5 ppb, respectively.

The conventional methods to treat heavy-metal-contaminated water are precipitation/co-precipitation, coagulation, electrolysis, reverse osmosis, carbon adsorption, membrane filtration, solvent extraction, ion exchange, etc (Arpa et al., 2000; Dabrowski et al., 2004; Van der Vaart et al., 2001). Nevertheless, those are reported to be ineffective at a very low concentration separation. Precipitation/co-precipitation is the most commonly used process.

It uses chemical additives to transform dissolved contaminants into insoluble solid which is then removed from the water phase by clarification or filtration. Adsorption is an alternative to precipitation/co-precipitation. However, it poses some constraints as it is effective for treating the water which has only mercury as a contaminant. The adsorption is likely to be affected by characteristics of the media and non-mercury contaminants (U.S. EPA, 2007).
Chevron Thailand Exploration and Production Ltd., one of the major oil company operators in the Gulf of Thailand, has applied a continuous chemical treatment process to comply with these regulations. However, the on-line As and Hg monitors have been problematic to achieve the desired discharge concentrations (Gallup & Strong, 2007). Apart from that, the use of chemical treatment has raised concerns from operation point of view. For instance, sodium hydroxide and ferric chloride in the process cause severe corrosion with the associated metal made pipeworks. Costly super alloy material is the only viable option for construction material of high pressure rating process but high capital cost. High toxicity from the chemicals deteriorates the circumstance by exposing personnel operators with health hazards when loading and unloading of the chemicals to the process.
To cope with the problems met by conventional methods and chemical treatment process, the removal by hollow fiber supported liquid membrane (HFSLM) has been applied. The modules of hollow fiber can be put in series after the conventional operation to scavenge the remaining arsenic/mercury down to the environmentally acceptable permits. The HFSLM technique is relatively recent. It can supplement or can replace the conventional separation techniques if the concentrations of As and Hg ions in produced water are very low and hardly handled by those conventional methods. To date based on the concept of mass transfer by using HFSLM with either a single extractant or a synergistic one, we published our remarkable works on effective removal of dilute arsenic/mercury concentration from the produced water in accordance with the discharge legislation.

2. Liquid membrane

The membrane is typically fabricated with hydrophobic microporous hollow fibers. With an organic extractant embedded in the micro pores of hydrophobic membrane, the membrane, therefore, acts as a semi barrier between two aqueous phases from contact but still allows the target component to diffuse across the membrane freely while simultaneously impedes the diffusion of other components. Thus, the advantage over solvent extraction method by the use of liquid membrane is non dispersive mass transfer. The flow rates of the phases can be varied independently over a wide range without any problem of flooding, loading, channeling or entrainment.
The system, shown in Figure (2), usually consists of feed phase, liquid membrane phase and stripping phase. The feed is a phase which consists of a mixture of components including the target component. The stripping phase is a phase which preferentially receives the target component from the feed through liquid membrane diffusion. The mechanism involves solvent extraction and a membrane-based mass transfer for the removal of the specific component from feed phase. It is renowned for its combined ability of extraction, diffusion, and stripping of the target component and can be treated as a simultaneous multistage extraction and stripping process (Mohapatra & Manchanda, 2008).
Common forms of liquid membrane are bulk, emulsion and supported liquid membranes. Each has different pros and cons, for example, bulk liquid membrane is easier to prepare and operate but offers less surface to volume ratio than others. Emulsion liquid membrane

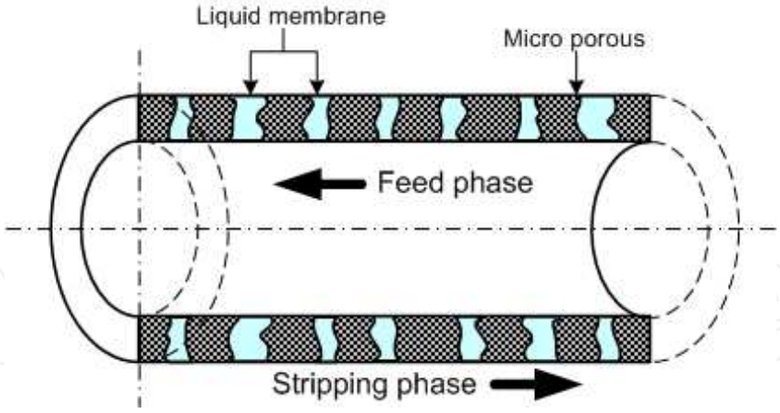


Fig. 2. The microporous hollow fiber liquid membrane

offers large surface to volume ratio but poor stability. Supported liquid membrane draws more industrial interests as it provides large surface to volume ratio to allow fast mass transfer while stability can be very well maintained. Moreover, supported liquid membrane is sustainable for a continuous flow operation. It has gained a broad range of separation applications and also demonstrated a promise in the removal of metal ions, such as nickel, uranium, chromium, copper, etc from the effluent streams (Lothongkum et al., 2009; 2009; Usapein et al., 2009; Pancharoen et al., 2005; Ramakul et al., 2009; 2007; 2006; 2006; 2004; 2003). The hollow fiber supported liquid membrane is, therefore, deployed in many of our study researches.

2.1 Diffusion transport in hollow fiber supported liquid membrane

HFSLM, or membrane contactor in many literatures, creates an immiscible layer between feed and stripping phases from an organic extractant in microporous hollow fibers. The target component reacts with the extractant at the feed-membrane interface to form complex species. Subsequently, the complex species diffuse across the liquid membrane (organic phase) to react with the stripping solution at the opposite interface of the membrane then are stripped into the stripping phase. Thus, the target component can be extracted and stripped simultaneously in a single step. The transportation rate of the target component is driven by the concentration gradient between feed and stripping phases. In this phenomenon of diffusion transport, it can be either a simple facilitated transport or a coupled facilitated transport. The simple facilitated transport occurs when the transport is independent of any other ions. It normally takes place in an application of neutral species extraction. As for ionic species extraction, the coupled transport occurs to maintain the solution electroneutrality (Bringas et al., 2009). The driving force to determine the transport rate is dependent on types and concentrations of co-ions in the feed.

Figure (3) schematically explains the transport of each case. The scheme depicts (A) as the target component, (B) co-ion, (C) the organic extractant, and ($\overline{AC}$ or $\overline{BC}$ or $\overline{ABC}$) the organic complex. In our study, the target component (A) can be arsenic and/or mercury ions. The straightforward mechanism is observed with the simple facilitated transport (Figure (3-a)) since the organic complex ($\overline{AC}$) is produced from the reaction between (A) and (C). Then, ($\overline{AC}$) is decomposed at the interface between the liquid membrane and the stripping phase, and (A) is recovered. The coupled facilitated transport can be classified into

co-transport (Figure (3-b)) and counter-transport (Figure (3- c)). For the coupled facilitated co-transport, the extractant reacts with the target component (A) and co-ion (*B*) to form the organic complex ($\overline{ABC}$). The ($\overline{ABC}$) diffuses across the liquid membrane to the stripping interface where both the target component and co-ion are simultaneously recovered. This mechanism has co-ion transporting along with the target component from feed phase to the stripping phase.

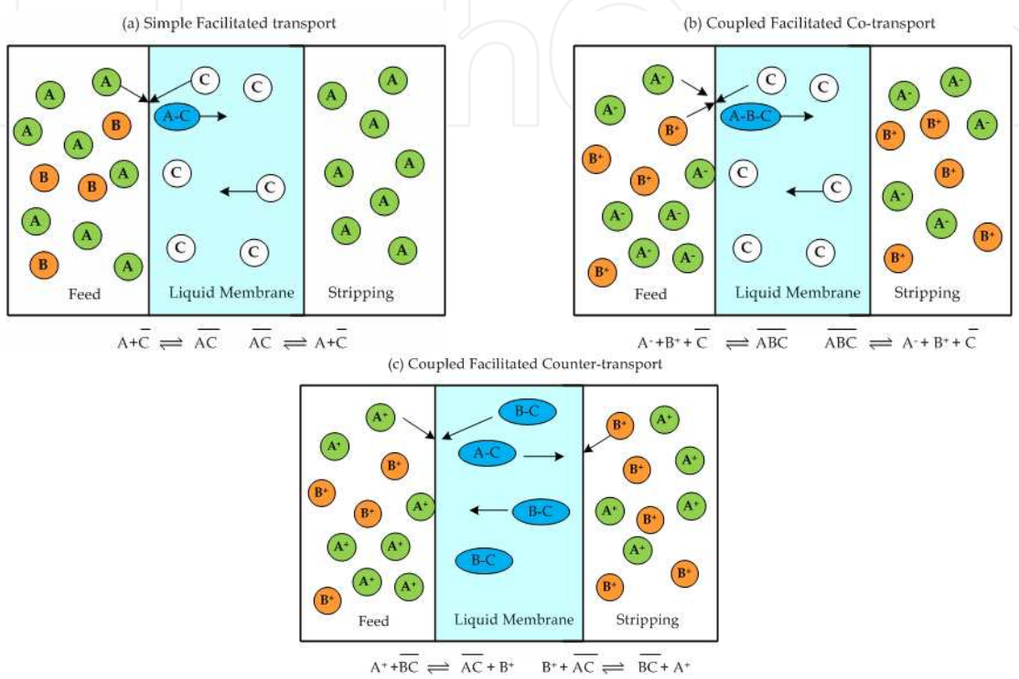


Fig. 3. Schematic pictures of liquid membrane systems (adopted from Bringas et al., 2009)

This coupled facilitated co-transport is common for neutral and basic extraction as schematized in Equation (1) for the reaction with neutral organic extractant, and Equation (2) for the reaction with basic organic extractant. The aqueous pH phase or hydrogen ion (H^+) in the system depicts as (H).

Coupled Co-transport, **Neutral** organic extractant

$$A^+_{(aq)} + B^-_{(aq)} + \overline{C}_{(org)} \Leftrightarrow \overline{ABC}_{(org)} \tag{1}$$

Coupled Co-transport, **Basic** organic extractant

$$A^{n+}_{(aq)} + mB^-_{(aq)} + (m-n)H^+_{aq} + \overline{(m-n)C_{(org)}} \Leftrightarrow \overline{(A_nB_m{}^{(m-n)-})((m-n)CH^+)_{(org)}} \tag{2}$$

The coupled facilitated counter-transport has reverse mechanism from the co-transport. The co-ion (B) transports from the stripping phase to feed phase, against the transport direction of the target component (A). The mechanism starts with the reaction between (A) and the organic extractant in terms of the organic complex ($\overline{BC}$) to form organic complex ($\overline{AC}$) and release co-ion (B) to feed phase. The organic complex ($\overline{AC}$), subsequently, diffuses across the liquid membrane to the stripping interface where the target component is released to

the stripping phase and co-ion is recovered to the organic extractant. The common case of the counter-transport is the reaction using acidic extractant as schematized by Equation (3).
Coupled Counter-transport, **Acidic** organic extractant

$$A^{+}_{(aq)} + \overline{HC_{(org)}} \Leftrightarrow \overline{AC_{(org)}} + H^{+}_{(aq)} \tag{3}$$

Uphill transport where the target component can be transported across the membrane against the concentration gradient of the target component is usually observed from the coupled transport. The uphill effects can continue until the target component diffuses across the liquid membrane to the stripping solution as long as the driving force in the coupled transport system is maintained. The driving force is often acquired from aqueous pH or H^{+} and/or co-ion (B) concentration gradient. Generally, research works in our laboratory shows that the removal of very dilute concentration of arsenic or mercury ions from produced water follows the mechanism of the coupled facilitated transport, and the uphill effects against the target component concentration is usually observed.
Key parameters to represent the performance of liquid membrane system are indicated in terms of the percentage of extraction (%), the percentage of stripping or recovery (%) and the distribution ratio (D). The percentage of extraction is the performance indicator which quantitatively identifies how much the target component, i.e., arsenic or mercury ions in our case is removed from produced water by the organic extractant. The percentage of recovery identifies how much the target component is recovered to the stripping solution. For the distribution ratio, it is a measurement of how much the target component is transferred to the next phase. It equals the concentration of the target component in the membrane phase divided by its concentration in the aqueous phase. Equations (4), (5) and (6) are provided for a better understating of these key parameters.

$$Extraction\ (\%) = \frac{(C_{f\mathbf{0}} - C_f)}{C_f} \tag{4}$$

$$Stripping\ (\%) = \frac{C_s}{C_{f\mathbf{0}}} \tag{5}$$

$$D = \frac{C_m}{C_{aq}} \tag{6}$$

2.2 HFSLM operation set up

The hollow fiber supported liquid membrane system is composed of two gear pumps, two variable flow rate controllers, two rotameters 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 properties of the hollow fiber module are shown in Table (1).
The one-through mode of a single-module HFSLM operation is shown in Figure (4). The selected organic extractant is filled in and subsequently circulated in shell and tube sides of the module for at least 20 minutes to ensure that the extractant is embedded in micro pores

Properties	Descriptions
Material	Polypropylene
Number of fibers	10,000
Module length	20.3 cm
Module diameter	6.3 cm
Porosity	30%
Pore size	0.05 mm
Contact area	1.4 m^2
Area per unit volume	29.3 cm^2/cm^3
Fiber ID	240 µm
Fiber OD	300 µm

Table 1. Properties of the hollow fiber module

of the fibers. The feed produced water and the stripping solution are then pumped counter-currently into the tube side and shell side of the HFSLM, respectively. A 10-mL sample is taken at the end of each separation cycle (about 40 min) from the feed and the stripping solutions to analyze the concentrations of arsenic and/or mercury ions by the inductively coupled plasma spectroscopy (ICP).

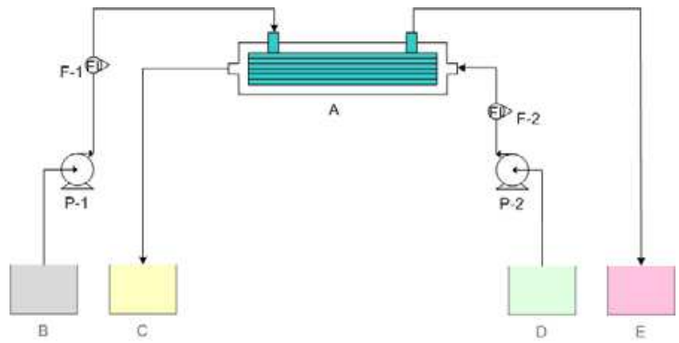


Fig. 4. Schematic counter-current flow diagram of one-through-mode separation by hollow fiber supported liquid membrane: A-HFSLM; B-inlet feed reservoir; C-outlet stripping solution reservoir; D-inlet stripping solution reservoir; E-outlet feed reservoir

3. Mass transfer mechanism in HFSLM

The mass transfer in HFSLM is the net diffusion of mass of arsenic/mercury ions across immiscible liquid membrane phase from feed phase to the stripping phase. The direction of mass transfer depends on the driving force across the liquid membrane. The driving force can be the concentration gradient of arsenic/mercury concentration itself or co-ion (B)/aqueous pH or H^+ concentration for the uphill transport in the case of the coupled facilitated transport as discussed earlier.

In engineering, the mass transfer coefficient is defined to quantify the mass transfer between the phases. It is a diffusion rate constant that relates among the mass transfer rate, mass transfer area and the concentration gradient. To determine the mass transfer coefficient for arsenic/mercury ions diffusion through HFSLM, the relationship between the mass transfer coefficient and permeability coefficient (P) is deployed. The permeability coefficient depends on mass transfer resistances and is reciprocal to the mass transfer coefficients as follows (Rathore et al., 2001).

$$\frac{1}{P} = \frac{1}{k_f} + \frac{r_i}{r_{lm}} \cdot \frac{1}{Dk_m} + \frac{r_i}{r_o}\frac{1}{k_s} \tag{7}$$

where

$$r_{lm} = \frac{r_o - r_i}{\ln(\frac{r_o}{r_i})} \tag{8}$$

Three mass transfer resistances in Equation (7) are in accordance with three steps of the transport mechanisms: first the resistance when arsenic/mercury ions diffuse across the feed interface; second the resistance when complex ions of arsenic/mercury diffuse across liquid membrane; and third the diffusion resistance across the stripping interface. The mass transfer resistance in the stripping interface can be disregarded since the mass transfer coefficient of the stripping solution (k_s) is higher than that of the feed phase (k_f) (Uedee et al., 2008) based on the following assumptions:

1. The film at feed interface is much thicker than that at the stripping interface. This is because of a combination of dense arsenic/mercury ions in the feed and co-ions from buffer solution at the feed interface, while there are only stripping ions and very lean arsenic/mercury ions at the stripping interface. From Equations (9) and (10), thick feed interfacial film (l_{if}) makes the mass transfer coefficient of the feed phase (k_f) much lower than that of the stripping solution (k_s).

Feed mass transfer coefficient $$k_f = \frac{D}{l_{if}} \tag{9}$$

Stripping mass transfer coefficient $$k_s = \frac{D}{l_{is}} \tag{10}$$

2. The arsenic/mercury concentration difference between the feed solution (C_f) and the feed-membrane interface (C_f^*) is higher than the difference between the membrane-stripping interface (C_s^*) and the membrane solution (C_s) (Porter, 1990). At equal flux by Equation (11), k_f is, therefore, much lower than k_s.

$$J = k_f(C_f - C_f^*) = k_s(C_s^* - C_s) \tag{11}$$

3. Only a stripping ion is used in the stripping side and it is directly in contact with the liquid membrane providing rapid dissolution. Thus, we can discard the third resistance in Equation (7) and obtain Equation (12).

$$\frac{1}{P} = \frac{1}{k_f} + \frac{r_i}{r_{lm}} \cdot \frac{1}{Dk_m} \tag{12}$$

The permeability coefficient (P) is also proposed by Danesi (Danesi, 1984) with the following Equations:

$$-V_f \ln\left(\frac{C_f}{C_{f,0}}\right) = AP\frac{\beta}{\beta+1}t \cdot \tag{13}$$

where $$\beta = \frac{Q_f}{PL\varepsilon\pi Nr_i} \quad (14)$$

The permeability coefficient is calculated from the slope of the plot between $-V_f ln\left(\frac{C_f}{C_{f,0}}\right)$ against t.

Theoretical model equations for mass transfer mechanism through hollow fiber supported liquid membrane system are defined for better understanding the system and to predict the behavior of the system under different operating condition applications. The accurate model is very useful to scale up the system for industrial applications. Developments of the models, for example, diffusion model, plug flow model, graphical model have been proposed by many researchers. One of the diffusion models which attracts interests of our research group is the model proposed by Huang (Huang et al., 2008) on Fick's law of mass transfer.

The following assumptions are made to simplify the model equations:

1. Pseudo steady state system with a constant operating temperature and constant physical properties.
2. The membrane phase is completely immiscible with the feed and stripping phases.
3. The volume of the liquid membrane phase can be neglected with reference to the bulk volume of feed phase or the stripping phase.
4. The reaction rates at both feed and stripping interfaces are rapid and can ignore the associated reaction resistances.

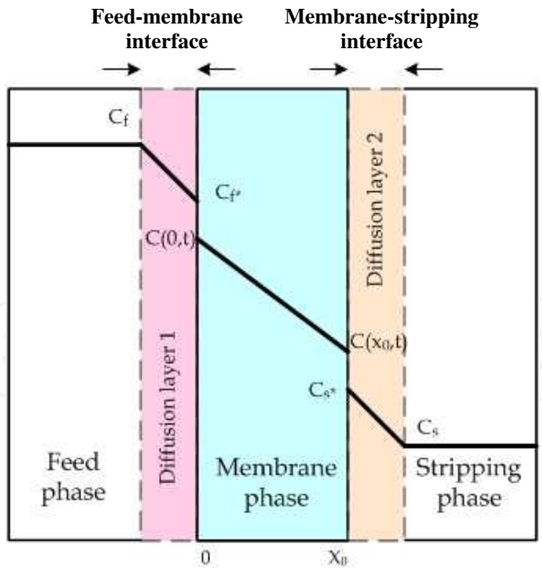


Fig. 5. The proposed steps in Huang's diffusion model

The diffusion transport at each step is described by Fick's law of diffusion as follows:

1. The target component diffuses across the interfacial layer between the feed and membrane.

$$j_f = k_f(C_f - C_f^*) \tag{15}$$

2. The target component reacts with the organic extractant to form the organic complex.

$$j_{r1} = k_1 C_f^* - k_{-1} C(0,t) \tag{16}$$

3. The organic complex diffuses across the membrane to the stripping interface.

$$j_{m1} = -D_e \frac{\partial C(0,t)}{\partial x} \tag{17}$$

$$j_{m2} = -D_e \frac{\partial C(x_0,t)}{\partial x} \tag{18}$$

4. The organic complex is decomposed at the stripping interface and the target component is released. Simultaneously, the organic extractant is regenerated and returns to the membrane phase.

$$j_{r2} = k_{-2} C(x_0,t) - k_2 C_s^* \tag{19}$$

5. The released target component diffuses across the interfacial layer between the membrane and is recovered to the stripping phase.

$$j_s = k_s(C_s^* - C_s) \tag{20}$$

where, k_f and k_s are obtained from the solution of Equation (7).
D_e is the effective diffusivity from Wilke-Chang's correlation, defined as follows

$$D_e = \frac{D\varepsilon'}{\tau'} \tag{21}$$

$$D = 7.4x10^{-8} \frac{(\varphi M_w)^{0.5} T}{\mu V_A^{0.6}} \tag{22}$$

By pseudo steady state assumption, the concentrations of the target component in the feed phase, membrane phase and stripping phase are achieved from the material balance equation.

$$V_f C_{f0} + V_s C_{so} = V_f C_f + V_s C_s + V_m C_m \tag{23}$$

$$C_m = C_f K_{ex} = C_s K_s \tag{24}$$

V_m can be neglected by the assumption that the membrane volume is very small relative to the bulk volume of feed and the stripping volume. The calculated results using the aforementioned proposed model equations show good agreement with the experimental results from various extraction applications via HFSLM by our group.

4. HFLSM applications for arsenic and mercury removal

Types of the extractants and stripping solutions are pivotal to the success of As and/or Hg separation. Iberhan and Wisniewski (Iberhan and Wisniewski, 2002) extracted As(III) and As(V) using the organic extractants of Cyanex 925, Cyanex 301 and a mixture between Cyanex 925 and Cyanex 301 at different volumetric ratios. The result showed that Cyanex 301 provided higher extraction of As(III) than As(V). The mixture of Cyanex 925 and Cyanex 301 helped remove As(V) significantly, while pure Cyanex 925 could extract As(V) a little better than As(III). Fabrega and Mansur (Fabrega & Mansur, 2007) extracted Hg(II) from HCl solution by Aliquat 336 dissolved in commercial Kerosene Exxol D-80. Mercury was almost extracted within 5 min at pH ≥ 1 and was satisfactorily stripped out about 99% by using thiourea as the stripping solution. Chakrabarty (Chakrabarty et al., 2010) found that by using triocthyamine (TOA) as the extractant in liquid membrane, Hg(II) could be extracted from pure solution more than lignosulfonate-mixed solution.

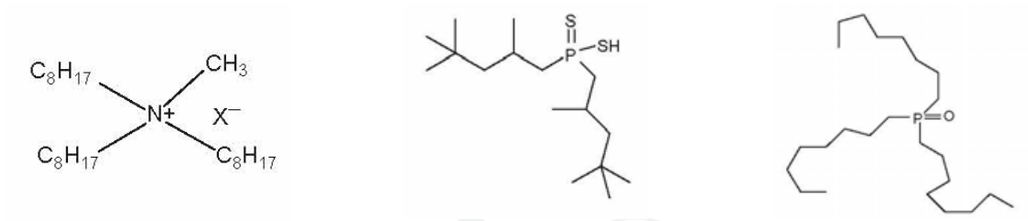
Knowledge from the past researches elicited our research group to progress further for the effective removal of arsenic/mercury ions from the produced water via HFSLM. Sangtumrong (Sangtumrong et al., 2007) simultaneously separated Hg(II) and As(III) ions from chloride media via HFSLM by TOA dissolved in toluene as the extractant and NaOH as the striping solution. Prapasawat (Prapasawat et al., 2008) used Cyanex 923 dissolved in toluene to separate As(III) and As(V) ions from sulphate media with water as the stripping solution via HFSLM. It was found that more As(V) could be extracted than As(III). Uedee (Uedee et al., 2008) obtained 100% extraction and 97% recovery of Hg(II) ions from chloride media via HFSLM using TOA dissolved in kerosene as the extractant and NaOH as the stripping solution. Recently, Pancharoen (Pancharoen et al., 2009; 2010) separated arsenic and mercury ions from the produced water from different gas fields in the Gulf of Thailand by HFSLM. Aliquat 336 dissolved in kerosene was a proper extractant with 91% arsenic extraction for the produced water without mercury contamination.

The discussions of the results from our research group are provided in the following sub topics (1) selective arsenic removal, (2) selective mercury removal and (3) simultaneous arsenic and mercury removal.

4.1 Selective arsenic removal

A number of researchers sought the organic extractants to remove arsenic ions, mostly they worked in a lab scale using synthetic feeds. Cyanex 301, Cyanex 923, Cyanex 925, a mixture of Cyanex 301 and Cyanex 925, tri-n-butylphosphate (TBP), hydrophobic glycol and hydroxamic acids were used to remove As(III) and As(V) from sulfuric acid solution by liquid–liquid extraction. The acidic reagent, Cyanex 301, could extract As(III) better than As(V). Cyanex 925 and Cyanex 923 were found more suitable for As(V) extraction than As(III) (Wisniewski, 1997; Meera et al., 2001).

Arsenic in the produced water is predominantly in the species of arsenite As(III) and arsenate As(V). The As(III) normally occurs as H_3AsO_3 and $H_2AsO_3^-$complexes. While As(V) occurs as H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}. But for the produced water from the Gulf of Thailand, As(III) usually presents in un-dissociated neutral H_3AsO_3 and As(V) presents in dissociated anion complexes of $H_2AsO_4^-$ and $HAsO_4^{2-}$ (Wilson et al., 2007). The As(V) takes majority part of total arsenic in the produced water where the pH is found in the range of 6-6.5. It appears that the removal of arsenic from produced water has to deal with spectroscopic range of arsenic in the water. Therefore, three different types of potential organic extractants for arsenic removal have been investigated in which the summary resultsare provided herewith.



(a) (b) (c)

Fig. 6. Chemical structures of the organic extractants: (a) Aliquat 336, (b) Cyanex 301, and (c) Cyanex 923 (Mohapatra and Manchanda, 2008)

4.1.1 Arsenic extraction using aliquat 336 (basic extractant)

Aliquat 336 (CH_3R_3NCl) is the basic organic extractant which has an ability to react with both dissociated forms ($H_2AsO_4^-$ and $HAsO_4^{2-}$) and un-dissociated form (H_3AsO_3) of the arsenic ions. The transport mechanism for arsenic removal is driven by the concentration gradient of hydroxide ion (OH-) in counter with arsenic ion transport direction. For clear illustration, the schematic transport mechanism is provided in Figure (7) for the extraction of $H_2AsO_4^-$ using Aliquat 336. The extraction reaction and recovery reaction are demonstrated in Equations (25) – (30). Term X^- in the equations is denoted as Cl^- in feed and membrane phases for the first cycle, and OH^- (a counter ion in the stripping phase) will take over the place of Cl^- in the next cycles (Porter, 1990).

Extraction reactions of dissociated arsenic forms by Aliquat 336

$$H_2AsO_4^- + \overline{CH_3R_3N^+ \cdot X^-} \rightleftharpoons \overline{(CH_3R_3N^+)(H_2AsO_4^-)} + X^- \quad (25)$$

$$HAsO_4^{2-} + \overline{2(CH_3R_3N^+ \cdot X^-)} \rightleftharpoons \overline{(CH_3R_3N^+)_2(HAsO_4^{2-})} + 2X^- \quad (26)$$

Extraction reactions of un-dissociated arsenic forms by Aliquat 336

$$H_3AsO_3 + \overline{CH_3R_3NCl} \rightleftharpoons \overline{(CH_3R_3NCl)(H_3AsO_3)} \quad (27)$$

Recovery reactions of arsenic-Aliquat 336 complex

$$\overline{(CH_3R_3N)(H_2AsO_4)} + NaOH \rightleftharpoons \overline{CH_3R_3N \cdot OH} + NaH_2AsO_4 \quad (28)$$

$$\overline{(CH_3R_3N)_2(HAsO_4)} + 2NaOH \rightleftharpoons \overline{2CH_3R_3N \cdot OH} + Na_2HAsO_4 \quad (29)$$

$$\overline{(CH_3R_3NCl)(H_3AsO_3)} + 3NaOH \rightleftharpoons \overline{CH_3R_3NCl} + Na_3AsO_3 + 3H_2O \quad (30)$$

Using 0.75 M (35% v/v) Aliquat 336 as the organic extractant and 0.5 M NaOH as the stripping solution, successful reduced arsenic to meet the permissible limit (< 250 ppb). The percentage of the recovery of arsenic ions increased with the concentration of sodium hydroxide up to 0.5 M. After 3-cycle operation, 91% of arsenic extraction from the produced water and 72% of arsenic recovery were achieved (Pancharoen et al., 2009).

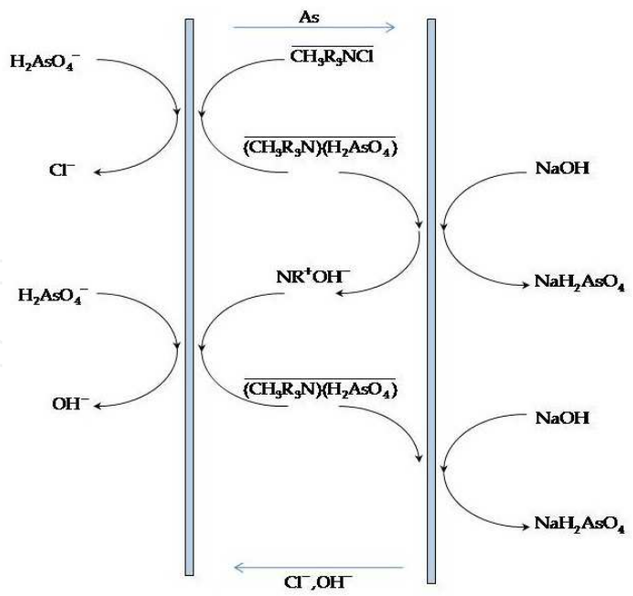


Fig. 7. Schematic representation of $H_2AsO_4^-$ coupled transport with Aliquat 336

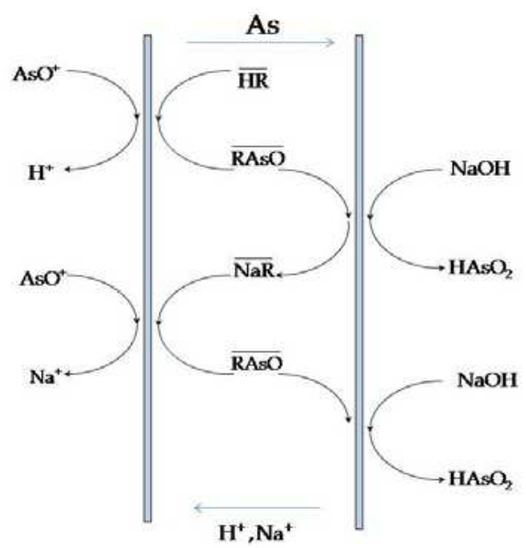


Fig. 8. Schematic representation of AsO^+ coupled transport with Cyanex 301

4.1.2 Arsenic extraction using cyanex 301 (acidic extractant)

Cyanex 301 is an acidic organic extractant which is recommended as an effective extractant for cation arsenic such as AsO^+ from the dissolution of H_3AsO_3 (Iberhan & Wisniewski, 2002). The transport mechanism is schematically illustrated in Figure (8). The process is driven by the hydrogen ion in counter with arsenic ion transport. The extraction and recovery reactions are described in the following equations:

$$AsO^+ + \overline{HR} \quad \rightleftharpoons \quad \overline{RAsO} + H^+ \tag{31}$$

$$\overline{RAsO} + NaOH \rightleftharpoons \overline{NaR} + HAsO_2 \quad (32)$$

For arsenic extraction using Cyanex 301 via HFSLM, the results were reported with relatively high percentage of extraction but with very low percentage of recovery (Pancharoen et al., 2009). The poor performance of recovery is explained by the strong bond that arsenic ions (AsO^+) make with Cyanex 301 and it is difficult for the stripping solution to break the bond (Iberhan & Wisniewski, 2002). This finding does not promote the favor of using Cyanex 301 as it offers an effective extraction while obtaining unacceptable recovery.

4.1.3 Arsenic extraction using cyanex 923 (neutral extractant)

Cyanex 923 or trialkylphosphine oxides (TRPO) is a neutral extractant which is recommended to use for the removal of un-dissociated neutral arsenic ions (Wisniewski, 1997; Meera et al., 2001). In the produced water, $HAsO_2$ is the neutral species of As(III) and H_3AsO_4 is the neutral species of As(V). The extraction of As(III) and As(V) by Cyanex 923 is proposed in Equations (33) and (34), respectively.

$$HAsO_2 + H^+ + \overline{TRPO} \rightleftharpoons \overline{HAsO_2 \cdot H^+ \cdot TRPO} \quad (33)$$

$$H_3AsO_4 + H^+ + \overline{TRPO} \rightleftharpoons \overline{H_3AsO_4 \cdot H^+ \cdot TRPO} \quad (34)$$

Using water as the stripping solution in the study, the recovery reactions are described as follows:

$$\overline{HAsO_2 \cdot H^+ \cdot TRPO} + H_2O \rightleftharpoons HAsO_2 + H^+ + \overline{TRPO} \quad (35)$$

$$\overline{H_3AsO_4 \cdot H^+ \cdot TRPO} + H_2O \rightleftharpoons H_3AsO_4 + H^+ + \overline{TRPO} \quad (36)$$

All equations above can be presented in the schematic diagram of arsenic transport as shown in Figure (9). Our work (Prapasawat et al., 2008) reported the study of using Cyanex 923 (30% v/v) diluted in toluene as the organic extractant and water as the stripping solution, the maximum arsenic extraction was 38% for As(III) species and 45% for As (V) species. Poor arsenic extraction performance was observed from Cyanex 923. This should be attributed to the low contribution of neutral arsenic in the feed and Cyanex 923 can work with neutral species only.

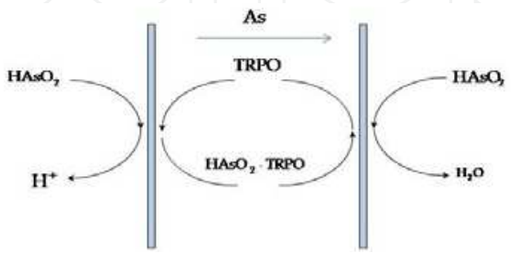


Fig. 9. Schematic representation of neutral As(III) with Cyanex 923

Of all three investigated extractants, Aliquat 336 attains high percentages of extraction and recovery of arsenic ions. This is due to its ability to react with both dissociated forms

($H_2AsO_4^-$ and $HAsO_4^{2-}$) and un-dissociated form (H_3AsO_3) of the arsenic which takes the majority part of total arsenic contribution in the produced water.

4.2 Selective mercury removal

Most of mercury in the produced water is an elemental form Hg(0) with the rest of inorganic form such as $HgCl_2$ or Hg(II). To remove mercury, the elementary mercury is normally taken by a chemical treatment process using an oxidant, ferric ions and flocculent to form a removable sludge containing mercury, which is known as an effective solution for the removal of mercury of high concentration. The residual mercury after the chemical treatment will be diluted and extracted via HFSLM subsequently. Uedee (Uedee et al., 2008) revealed that high extraction and recovery performances of mercury using HFSLM could be constantly maintained under the dilute mercury concentration system.

Normally, the mercury species after chemical treatment are in the form of Hg(II). The existence of Hg(II) comes from inorganic mercury $HgCl_2$ originally in the produced water and the undesired conversion of elementary mercury in the chemical treatment process. For the latter, the oxidation reduction potential is the contributory factor for the conversion. If the oxidation reduction potential exceeds the controlled limit, the elementary mercury is often converted to ionic mercury form of Hg(II) resulting in seriously degradation in the overall treatment process (Frankiewicz & Gerlach, 2000).

Sangtumrong (Sangtumrong et al., 2007) and Uedee (Uedee et al., 2008) removed Hg(II) from Hg(II) contaminated synthetic chloride water using tri-n-octylamine (TOA) by HFSLM. Pancharoen (Pancharoen et al., 2010) succeeded a similar work but used the produced water as the feed. The results corresponded closely; implying that the predominant Hg(II) species in the produced water is valid.

TOA is a basic organic extractant and its chemical structure can be referred to Figure (6). TOA in toluene is found to be the most selective mercury extractant (Sangtumrong et al., 2007; Uedee et al., 2008). However, feed pretreatment is necessary in order to deprotonate the Hg(II) of neutral $HgCl_2$ to anion form which is suitable for the function of the basic extractant (Ramakul & Panchareon, 2003). Equation (37) shows the Hg(II) deprotonation by HCl.

$$HgCl_2 + 2HCl \rightarrow HgCl_4^{2-} + 2H^+ \tag{37}$$

Subsequent to the feed pretreatment, mercury ions in the form of $HgCl_4^{2-}$ will react with the organic extractant (TOA, shown as R_3N) to form the complex species as seen in Equation (38):

$$HgCl_4^{2-} + 2H^+ + 2\overline{R_3N} \rightleftharpoons \overline{(R_3NH)_2 \cdot HgCl_4} \tag{38}$$

The mercury complex species diffuse to the opposite side of the liquid membrane by the concentration gradient and react with NaOH, a stripping solution. The $HgCl_4^{2-}$ ions are recovered to the stripping phase, shown in Equation (39):

$$\overline{(R_3NH)_2 \cdot HgCl_4} + 2OH^- \rightleftharpoons 2\overline{R_3N} + HgCl_4^{2-} + 2H_2O \tag{39}$$

After the stripping reaction, TOA is diffused back to the feed-membrane interface according to its concentration gradient, and again TOA is reacted with $HgCl_4^{2-}$ ions from the feed.

Thus, the transport mechanism of Hg(II) ions in the produced water through liquid membrane can be illustrated in Figure (10).

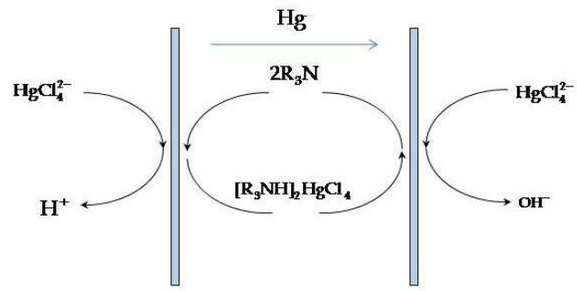


Fig. 10. Co-transport scheme of $HgCl_4^{2-}$ by TOA extractant

Pancharoen (Pancharoen et al., 2010) found that the highest percentages of extraction and recovery of 99.8% and 62%, respectively were achieved in 300 min by a 6th-cycle operation, pH of the feed solution of 2.5, 2% (v/v) TOA, 0.5 M NaOH using 50 mL/min of feed and stripping solutions.

4.3 Simultaneous arsenic and mercury removal

A successive attempt on simultaneous removal of arsenic and mercury from the produced water was investigated. The focused species to be extracted were dissociated As(V) as $H_2AsO_4^-$ and Hg(II) as $HgCl_2$ since they were key contaminated arsenic/mercury in the produced water. To enhance the separation of arsenic and mercury, the synergistic extraction by using the mixture of the organic extractant was examined. Equation (40) defines the synergistic extent in terms of synergistic coefficient (R) relating to the distribution coefficients (Luo et al., 2004).

$$R = \frac{D_{max}}{(D_1 + D_2)} \tag{40}$$

D_{max} is the maximum distribution coefficient or the distribution ratio of the synergistic system to extract the specifed ions, and (D_1 + D_2) is the summation of the distribution coefficient from each single extraction system. The greater synergistic coefficient means that the mixture of the extractant has synergistic effect on arsenic/mercury extraction. Figure (11) shows a comparative plot of the maximum percentages of the extraction of arsenic and mercury ions from the produced water against the different extractants. The sequences of the percentages of extraction are as follows.

As: Aliquat 336+Cyanex 471 > Aliquat 336 > Bromo-PADAP > Cyanex 471 > Cyanex 923,

Hg: Aliquat 336+Cyanex 471 > Aliquat 336 > Cyanex 923 > Bromo-PADAP ≈ Cyanex 471

It was reported that the mixture of 0.22 M Aliquat 336 and 0.06 M Cyanex 471 provided the highest extraction of both arsenic and mercury. The calculated synergistic coefficient (R) to arsenic ions of Cyanex 471 was 2.8; the value greater than 1 indicated that the mixture of Aliquat 336 and Cyanex 471 had the synergistic effect on arsenic extraction.

Among the stripping solutions used in this work, i.e., NaOH, DI water, HNO_3 and H_2SO_4, thiourea (NH_2CSNH_2) was found to be the best stripping solution for arsenic and mercury. Thiourea with large anion in the structure was strong enough to strip mercury complex ion from Aliquat 336, which was composed of a large organic cation associated with a chloride

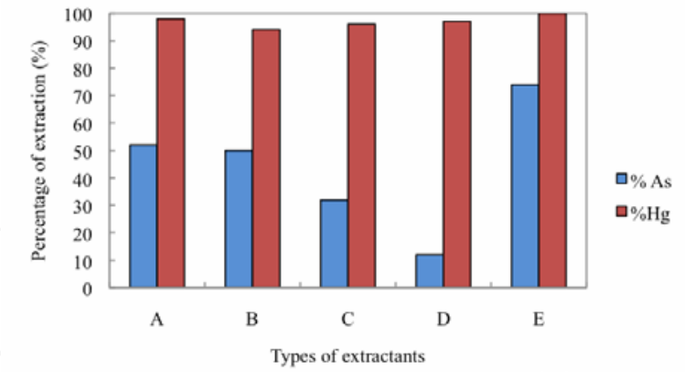


Fig. 11. The maximum percentages of arsenic and mercury ions extraction from produced water against types of the extractants: (A) 0.22 M Aliquat 336, (B) 0.002 M Bromo-PADAP, (C) 0.06 M Cyanex 471, (D) 0.51 M Cyanex 923, (E) 0.22 M Aliquat 336 + 0.06 M Cyanex 471

ion. Moreover, water in aqueous thiourea also contributed to the recovery performance according to the report of using water as the stripping solution for As(III) and As(V) separation (Prapasawat et al., 2008). Using thiourea, no trace of the precipitates was observed unlike NaOH which produced the precipitates with Hg resulting in membrane fouling and poor transport performance in the membrane phase. The discharge concentrations of mercury and arsenic in the produced water to the environment complied with the legislation limits determined by the Ministry of Industry within 1-cycle separation and 3-cycle separation, respectively.

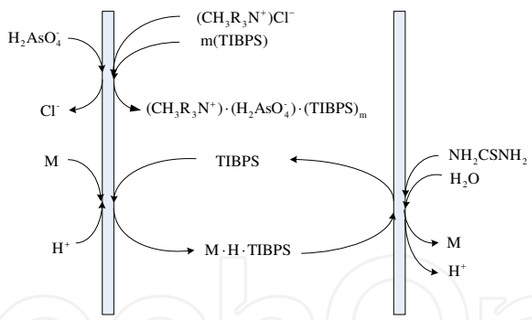


Fig. 12. Schematic extraction and stripping mechanisms of $H_2AsO_4^-$ by the synergistic extractant of Aliquat 336 and Cyanex 471 (TIBPS) with thiourea as the stripping solution

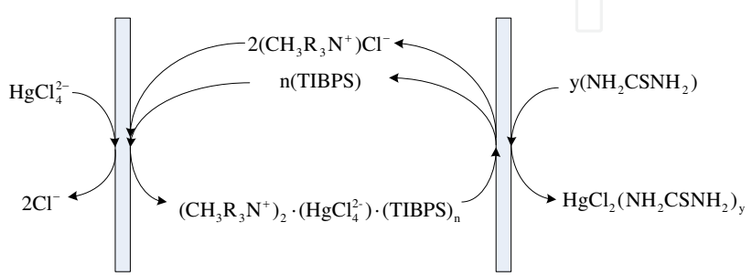


Fig. 13. Schematic extraction and stripping mechanisms of $HgCl_4^{2-}$ by the synergistic extractant of Aliquat 336 and Cyanex 471 (TIBPS) with thiourea as the stripping solution

The descriptive illustrations of the extraction and stripping mechanisms of arsenic/mercury ions by the mixture of Aliquat 336 ($(CH_3R_3N^+)Cl^-$) and Cyanex 471 (TIBPS) as the synergistic extractant, and thiourea (NH_2CSNH_2) as the stripping solution, are shown in Figures (12) and (13).
The synergistic extraction reactions are shown in Equations (41) - (44).
Extraction by Aliquat 336

$$\text{As(V)} \qquad H_2AsO_4^- + \overline{CH_3R_3N^+Cl^-} \rightleftharpoons \overline{(CH_3R_3N^+)\cdot(H_2AsO_4^-)} + Cl^- \tag{41}$$

$$\text{Hg(II)} \qquad HgCl_4^{2-} + 2\overline{CH_3R_3N^+Cl^-} \rightleftharpoons \overline{(CH_3R_3N^+)_2\cdot(HgCl_4^{2-})} + 2Cl^- \tag{42}$$

Extraction by the mixture of Aliquat 336 and Cyanex 471 (TIBPS)

$$\text{As(V)} \qquad H_2AsO_4^- + \overline{CH_3R_3N^+} + m\overline{(TIBPS)} \rightleftharpoons \overline{(CH_3R_3N^+)\cdot(H_2AsO_4^-)\cdot(TIBPS)_m} \tag{43}$$

$$\text{Hg(II)} \qquad HgCl_4^{2-} + 2\overline{(CH_3R_3N^+)} + n\overline{(TIBPS)} \rightleftharpoons \overline{(CH_3R_3N^+)_2\cdot(HgCl_4^{2-})\cdot(TIBPS)_n} \tag{44}$$

where, the stoichiometric coefficients of m and n were calculated from the distribution coefficients of the relevant components at various concentrations of the extractant used.
Extraction by Cyanex 471 (TIBPS) for un-dissociated arsenics

$$\text{As (III \&V)} \qquad M + H^+ + \overline{TIBPS} \rightleftharpoons \overline{M\cdot H\cdot TIBPS} \tag{45}$$

where, M stands for H_3AsO_3 (As(III)) or H_3AsO_4 (As(V)). Cyanex 471 (TIBPS) is the neutral organic extractant and effective for un-dissociated ions (Wisniewski, 1997) including un-dissociated arsenic such as H_3AsO_3 (As(III)) and H_3AsO_4 (As(V)) in the produced water. Accordingly, it is regarded as an enhancement to arsenic extraction, on top of primarily focused species of dissociated $H_2AsO_4^-$.

4.3.1 Distribution coefficients and extraction equilibrium constants

Subject to the mass transport analysis, the following terms of the extraction equilibrium constant (K_{ex}) and the distribution ratio are expressed by Equations (46) – (49).
The extraction equilibrium constants (K_{ex}) of arsenic and mercury ions:

$$K_{ex,As} = \frac{\overline{[(CH_3R_3N^+)\cdot(H_2AsO_4^-)\cdot(TIBPS)_m]}}{[H_2AsO_4^-][\overline{CH_3R_3N^+}][\overline{TIBPS}]^m} \tag{46}$$

$$K_{ex,Hg} = \frac{\overline{[(CH_3R_3N^+)_2\cdot(HgCl_4^{2-})\cdot(TIBPS)_n]}}{[HgCl_4^{2-}][\overline{CH_3R_3N^+}]^2[\overline{TIBPS}]^n} \tag{47}$$

The distribution coefficients (D) for arsenic and mercury extractions by the mixture of Aliquat 336 and Cyanex 471 (TIBPS):

$$D_{As} = \frac{\overline{[(CH_3R_3N^+)\cdot(H_2AsO_4^-)\cdot(TIBPS)_m]}}{[H_2AsO_4^-]} = K_{ex,As}\overline{[CH_3R_3N^+]}\overline{[TIBPS]}^{\,m} \quad (48)$$

$$D_{Hg} = \frac{\overline{[(CH_3R_3N^+)_2\cdot(HgCl_4^{2-})\cdot(TIBPS)_n]}}{[HgCl_4^{2-}]} = K_{ex,Hg}\overline{[CH_3R_3N^+]}^{2}\overline{[TIBPS]}^{\,n} \quad (49)$$

The distribution coefficients (D) of arsenic and mercury from the extraction by HFSLM, shown in Table (2), are estimated from Equations (48) and (49). The increase of the distribution coefficient indicates the enhancement of the extractability. From Table (2), the distribution coefficients increased with the concentration of Cyanex 471. The maximum distribution coefficients of arsenic and mercury were attained at 0.06 M Cyanex 471 and 0.07 M Cyanex 471, respectively.

Cyanex 471 (M)	Distribution coefficients	
	Arsenic	Mercury
0.02	0.63	-
0.04	1.13	4.52
0.05	1.32	5.57
0.06	1.47	6.59
0.07	-	8.72

Table 2. The distribution coefficients at Cyanex 471 concentration of 0.02 – 0.07 M mixed with 0.22 M Aliquat 336 (0.5 M NaOH as the stripping solution)

The distribution coefficients in Equations (48) and (49) were rewritten as follows:

$$\log D_{As} = \log (K_{ex,As}\cdot\overline{[CH_3R_3N^+]}) + m\log\overline{[TIBPS]} \quad (50)$$

$$\log D_{Hg} = \log (K_{ex,Hg}\cdot\overline{[CH_3R_3N^+]}^{2}) + n\log\overline{[TIBPS]} \quad (51)$$

The stoichiometric coefficients (m and n) were calculated from the plots of log D_{As} and log D_{Hg} against log [TIBPS]. The linear relationships with slopes m = 0.7917 or 4/5 for arsenic extraction and n = 1 for mercury extraction were observed. The slopes, m and n, were substituted in the synergistic extraction Equations (43) and (44). The extraction equilibrium constants of arsenic ions ($K_{ex,As}$) and mercury ($K_{ex,Hg}$) were determined by Equations (46) and (47). The equilibrium constant of mercury (1,622 (L/mol^3)) was much higher than that of arsenic (62.7 ($L/mol^{9/5}$) suggesting that the extraction of mercury was higher than arsenic, which was in accordance with the results obtained from the study.

4.3.2 Permeability coefficients

The permeability coefficients of arsenic and mercury, which related to the concentration of Cyanex 471 from 0.02 – 0.07 M, were obtained from Equations (13) and (14) and the slopes (AP $\beta/(\beta+1)$) of the plot between $-V_f \ln(C_f/C_{f,o})$ versus t in Figure (14). From Table (3), it could be observed that the permeability coefficients increased when the concentration of Cyanex 471 increased. The permeability coefficients of mercury were higher than those of arsenic, implying higher mass transfer or higher extraction of mercury ions.

Cyanex 471 (M)	P x 10^3 (cm/s)	P x 10^3 (cm/s)
	Arsenic	Mercury
0.02	5.47	-
0.04	8.90	33.98
0.05	9.81	40.94
0.06	11.54	48.37
0.07	-	53.14

Table 3. The permeability coefficients at Cyanex 471 concentration of 0.02 – 0.07 M mixed with 0.22 M Aliquat 336

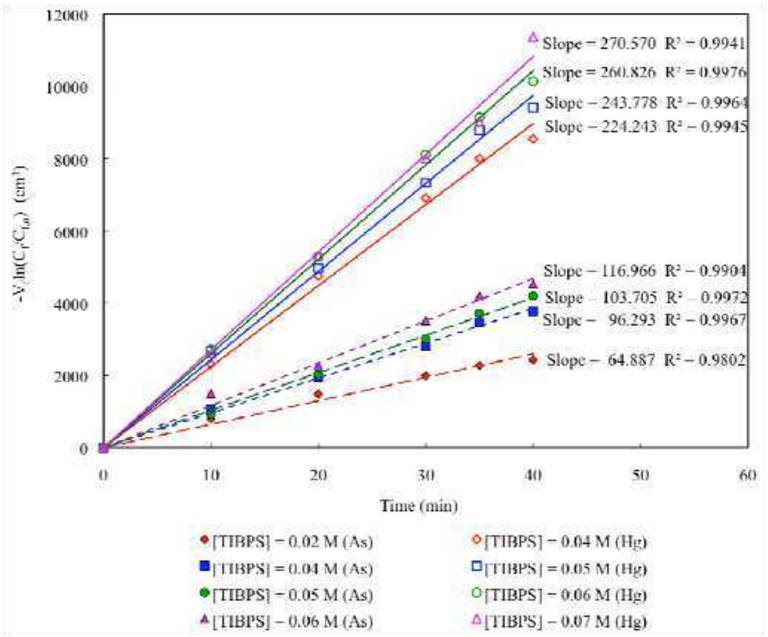


Fig. 14. Plot of $-V_f \ln (C_f / C_{f,o})$ of arsenic and mercury ions in feed solution against time with different concentrations of Cyanex 471 mixed with 0.22 M Aliquat 336 for synergistic organic extractant

4.3.3 Mass transfer coefficients

Equations (52) and (53) were defined assuming the stripping reactions of arsenic and mercury were instantaneous and no contribution of resistance in the stripping phases.

$$\frac{1}{P_{As}} = \frac{1}{k_i} + \frac{r_i}{r_{lm}} \cdot \frac{1}{K_{ex,As} k_m \overline{[CH_3R_3N^+]} \overline{[TIBPS]}^{4/5}} \tag{52}$$

$$\frac{1}{P_{Hg}} = \frac{1}{k_i} + \frac{r_i}{r_{lm}} \cdot \frac{1}{K_{ex,Hg} k_m \overline{[CH_3R_3N^+]}^2 \overline{[TIBPS]}} \tag{53}$$

where, P_{As} and P_{Hg} were the permeability coefficients of arsenic and mercury, respectively. The organic-phase and aqueous-phase mass transfer coefficients (k_m and k_i) of arsenic were determined from the plot of 1/P against $1/([CH_3R_3N^+][TIBPS]^{4/5})$. The slope and the ordinate were $(r_i/r_{lm})(1/K_{ex}k_m)$ and $1/k_i$. Accordingly, k_m and k_i of arsenic were obtained at $1.02x10^{-4}$ and 0.0392 cm/s. Similarly, the values of mercury were obtained at $1.27x10^{-5}$ and 2.210 cm/s from the plot of 1/P against $1/([CH_3R_3N^+]]^2$ [TIBPS]). According to the calculated k_m and k_i where the organic-phase mass transfer coefficient was lower than the aqueous-phase mass transfer coefficient, thus, the mass transfer within membrane was the rate controlling step of this extraction system.

5. Conclusions

The outstanding feature of HFSLM technique is its ability to treat metal ions of a very low concentration that are hardly treated or impractical by the conventional techniques. Therefore, based on the concept of mass transfer we, for example, deployed the HFSLM to remove low concentrations of arsenic and mercury in the produced water. The result was successfully achieved by using the HFSLM in conjunction with the selection of the suitable single or synergistic organic extractant, and the stripping solution. The removal of mercury contamination was very effective. In many cases, the mercury content could be reduced to meet the permissible discharge limit to the environment from only single extraction cycle. The removal of arsenic was found inferior to the mercury. More than one extraction cycles were required to treat arsenic in the produced water. Of all the potential organic extractants in the study for arsenic treatment, Aliquat 336 was the best extraction since it could extract both dissociated and un-dissociated arsenic under a basic or weak acidic condition.

Synergism extraction was much of interest aiming for the simultaneous removal of arsenic and mercury. By using the mixture of 0.06 M Cyanex 471 and 0.22 M Aliquat 336, it promoted the synergistic effect on arsenic extraction. The calculated synergistic coefficient to arsenic ions was 2.8, implying 2.8 times of arsenic being extracted by the synergistic extractant more than by the single organic extractant. The 0.1 M thiourea was found to be the best stripping solution. The arsenic/mercury contaminated in the effluent produced water complied with the legislation limit after 1-cycle extraction for mercury and 3-cycle extraction for arsenic. Mass transfer during the whole extraction process starting from feed phase through the stripping phase was followed the Fick's law diffusion mass transport. The parameters describing mass transport were determined, i.e., (1) equilibrium constant (K_{eq}), (2) distribution ratio (D), (3) permeability coefficient (P), (4) mass transfer coefficient in the feed phase stagnant layer (k_f) and (5) mass transfer coefficient in the immobilized liquid membrane (k_m). In this extraction via HFSLM system for the simultaneous removal of arsenic and mercury, the rate controlling step was found at the membrane phase.

6. Acknowledgments

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7. Notation

A	Membrane area (cm^2)
C	Concentration within the membrane (mol / cm^3)
C_{aq}	Concentration in the aqueous phase (mol / cm^3)
C_f	Concentration in the feed phase (mol / cm^3)
$C_{f\,0}$	Initial concentration in the feed phase (mol / cm^3)
C^*_f	Concentration at the feed interface with liquid membrane (mol / cm^3)
C_m	Concentration in the liquid membrane phase (mol / cm^3)
C_s	Concentration in the stripping phase (mol / cm^3)
$C_{s\,0}$	Initial concentration in the stripping phase (mol / cm^3)
C^*_s	Concentration at the stripping interface with the liquid membrane (mol / cm^3)
D	Distribution ratio
D_e	Effective diffusivity (cm^2/s)
D_0	Free bulk diffusion coefficient (cm^2/s)
HFSLM	Hollow Fiber Supported Liquid Membrane
J	Flux (mol/cm^2.s)
j_f	Flux across the feed interface film (mol/cm^2.s)
j_{m1}	Flux at feed-liquid membrane interface (mol/cm^2.s)
j_{m2}	Flux at liquid membrane-stripping interface (mol/cm^2.s)
j_{r1}	Flux following the extraction reaction (mol/cm^2.s)
j_{r2}	Flux following the recovery or stripping reaction (mol/cm^2.s)
j_s	Flux across the stripping interface film (mol/cm^2.s)
K_e	Equilibrium constant of the interfacial reaction in the feed phase
K_s	Equilibrium constant of the interfacial chemical reaction in stripping phase
K_f	Dimensionless form of mass transfer coefficient in the feed phase
K_s	Dimensionless form of mass transfer coefficient in the stripping phase
k_1	Forward interfacial reaction rate constant in the feed phase (m/s M)
k_{-1}	Backward interfacial reaction rate constant in the feed phase (m/s M)
k_2	Forward interfacial reaction rate constant in the stripping phase (m/s M)
k_{-2}	Backward interfacial reaction rate constant in the stripping phase (m/s M)
k_f	Mass transfer coefficient in the extraction boundary layer (cm/s)
k_s	Mass transfer coefficient in the stripping boundary layer (cm/s)
L	Length of the hollow fiber (cm)
l_{if} and l_{is}	Thickness of feed interface film and stripping interface film (cm)
M_w	Molecular weight (g/mol)
N	Numbers of hollow fibers in the module
m, n	Stoichiometric coefficient
P	Permeability coefficient (cm/s)
Q_f	Volumetric flow rate of feed solution (cm^3/s)

R	Synergy coefficient
r_i	Internal radius of the hollow fiber (cm)
r_o	External radius of the hollow fiber (cm)
r_{lm}	Log-mean radius of the hollow fiber
T	Absolute temperature (K)
V_A	Molar volume of the target component at its normal boiling temperature (cm^3/mol)
V_f	Volume of the feed phase (cm^3)
$V_{f\,0}$	Initial volume of the feed phase (cm^3)
V_m	Volume of the membrane phase (cm^3)
$V_{s\,0}$	Initial volume of the stripping phase (cm^3)
V_s	Volume of the stripping phase (cm^3)
x_0	Membrane thickness (cm)
ε	Porosity of the hollow fiber (%)
φ	Association factor of solvent (dimensionless)
μ	Viscosity (cP)
Subscripts	
aq	Aqueous
f	Feed phase
m	Membrane phase
org	Organic
s	Stripping phase

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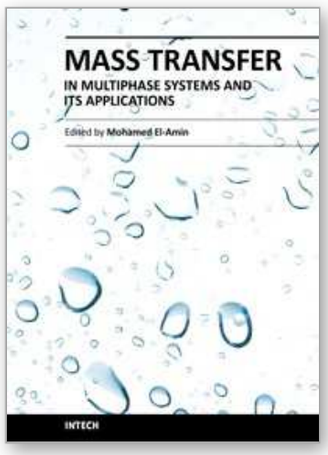
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This book covers a number of developing topics in mass transfer processes in multiphase systems for a variety of applications. The book effectively blends theoretical, numerical, modeling and experimental aspects of mass transfer in multiphase systems that are usually encountered in many research areas such as chemical, reactor, environmental and petroleum engineering. From biological and chemical reactors to paper and wood industry and all the way to thin film, the 31 chapters of this book serve as an important reference for any researcher or engineer working in the field of mass transfer and related topics.

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