

The Extraction and Stripping of Hg (II) from Produced Water via Hollow Fiber Contactor

Dolapop Sribudda, Ura Pancharoen

Abstract—The separation of Hg (II) from produced water by hollow fiber contactors (HFC) was investigated. This system included of two hollow fiber modules in the series connecting. The first module used for the extraction reaction and the second module for stripping reaction. Aliquat336 extractant was fed from the organic reservoirs into the shell side of the first hollow fiber module and continuous to the shell side of the second module. The organic liquid was continuously feed recirculate and back to the reservoirs. The feed solution was pumped into the lumen (tube side) of the first hollow fiber module. Simultaneously, the stripping solution was pumped in the same way in tube side of the second module. The feed and stripping solution was fed which had a countercurrent flow. Samples were kept in the outlet of feed and stripping solution at 1 hour and characterized concentration of Hg (II) by Inductively Couple Plasma Atomic Emission Spectroscopy (ICP-AES). Feed solution was produced water from natural gulf of Thailand. The extractant was Aliquat336 dissolved in kerosene diluent. Stripping solution used was nitric acid (HNO_3) and thiourea (NH_2CSNH_2). The effect of carrier concentration and type of stripping solution were investigated. Results showed that the best condition were 10 % (v/v) Aliquat336 and 1.0 M NH_2CSNH_2 . At the optimum condition, the extraction and stripping of Hg (II) were 98% and 44.2%, respectively.

Keywords—Hg (II), hollow fiber contactor, produced water, wastewater treatment.

I. INTRODUCTION

NATURAL gas condensate was the mixture of low density hydrocarbon liquid. The natural gas condensate was referred to natural gasoline. This was because it concludes the mixture of hydrocarbon to produced gasoline. In the production in offshore of natural gas and oil, it generated a large amount of produced water. The amount of produced water increased from the demand of petroleum oil and gas. Produced water contained of inorganic compound, toxic heavy metal and salt from the sea. It has the concentration of mercury about 500 ppb.

Mercury from produced water was the toxic heavy metal. It is a gray liquid at ambient temperature because of low vapor pressure. Mercury salt in the nature was concluded mercury (I), also called mercurous, and mercury (II) was called mercuric. The form of mercury is metallic from (Hg^0), inorganic mercury and organic mercury compound [1]. The nature mercury was stable in the environment and least toxicity. Inorganic mercury can be form methylated as methyl mercury (MeHg^+) by specific bacteria [2]. Inorganic mercury

was more toxic than organic mercury. The vapor of mercury has the severe dangerous. When inhaled its, mercury was permeated in the lung and distribution all of body. Then, it oxidized by bacteria to form Hg^{2+} that very reactive. It was deactivation of amino acid and enzyme. In addition, it was destroy brain, immune and nervous system [3].

Therefore, the ministry of industrial determined the maximum acceptable of wastewater discharged to surrounding having concentration of Hg (II) not exceeding 5 ppb [4]. Many researchers studied the extraction of mercury from various processes such as adsorption [5], liquid extraction (LLE) [6], [7]. The disadvantages of above methods were low selectivity, high operating cost, phase separation and solvent loss [8].

Liquid membrane is an interesting method metal ion removal because its can extract the trace metal ion. There are many type of liquid membrane. Supported liquid membrane (SLM) used to separation of metal ion from aqueous solution [9], emulsion liquid membrane (ELM) [10] and bulk liquid membrane (BLM) [11]. Hollow fiber supported liquid membrane (HFSLM) is the one of liquid membrane used to separated metal ion. Its can extract and strip in one step, high selectivity and low energy consumption [12]. It has some limitation of the instability of system which losing of organic liquid in the micro-pore [13].

The alternative method which improved long term operation time for extraction metal ion was Hollow fiber contactor (HFC). It used two connecting of hollow fiber modules. The first module used was the extraction reaction and the second module used for the stripping reaction. It has large interfacial area between the two contacting phases and obtain high efficient. In addition, it prevents the formation of emulsions [14], [15].

In this research studied the extraction and stripping of Hg (II) in the produced water via HFC. The extractant used was Aliquat336 dissolved in kerosene. The stripping solution used was thiourea and nitric acid. The effect of carrier concentration and type of stripping solution were investigated.

II. THEORY

HFC is the connecting series of two hollow fiber modules. The feed and stripping solution was pumped into the tube side of the first and second modules, respectively. The organic liquid was pumped into the shell side of both modules and recirculate to the reservoirs. Thus, in each module conclude of two phase. The first module concluded of feed solution phase and membrane phase. The metal ion reacts with the extractant at the interface of feed solution-membrane phase in the tube of the first hollow fiber module and generated metal complex

D. Sribudda and U. Pancharoen are with Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand (phone: +6622186755; fax: +6622186877, +6622186891; e-mail: akekung12@gmail.com, ura.p@chula.ac.th).

species. Then, it was diffused through the micro-pore of membrane to the extractant stream (shell side) by the driving force. Metal complex species was flowed into the shell side of the second module. Thus, it was generated stripping reaction at the interface of membrane-stripping solution phase. Metal ion was released to the stripping phase and the extractant transports back to the membrane phase. The transported mechanism of Hg (II) was shown in Fig. 1.

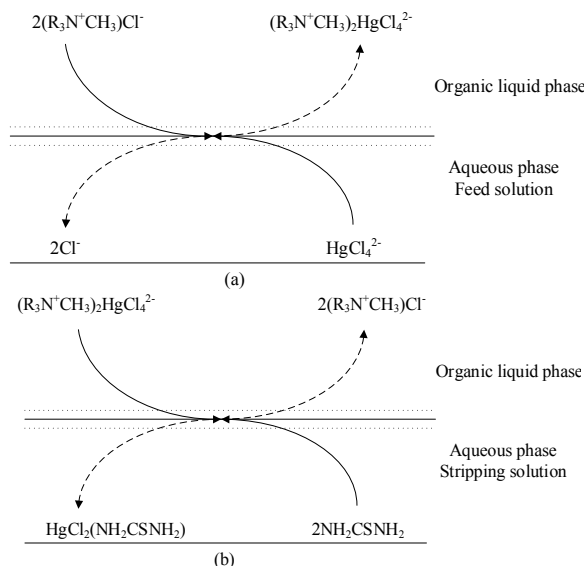
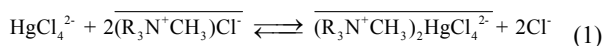
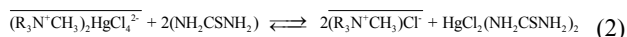


Fig. 1 Co-transportation of Hg (II) with Aliquat336 (a) in the first hollow fiber module (extraction reaction) (b) in the second hollow fiber module (stripping reaction)

The extraction reaction occurred at feed-membrane interface. The predominant form of Hg (II) in produced water is $HgCl_4^{2-}$. The mercury ion reacted with Aliquat336 to form the mercury-carrier complex species and chloride ion. The complex species diffused through the porous of membrane from the concentration gradient. The reaction is shown in (1) [7]:



When the stripping reaction occurs, the mercury complex species reacts with the stripping solution as thiourea at the interface of the membrane stripping phase. The stripping reaction is shown in (2) [7]:



Percentages of extraction and stripping of Hg (II) were obtained as shown in (3) and (4);

$$\% \text{Extraction} = \frac{[Hg^{2+}]_{f,in} - [Hg^{2+}]_{f,out}}{[Hg^{2+}]_{f,in}} \times 100 \quad (3)$$

$$\% \text{Stripping} = \frac{[Hg^{2+}]_{s,out}}{[Hg^{2+}]_{f,in}} \times 100 \quad (4)$$

III. EXPERIMENTS AND PROCEDURE

A. Chemical and Reagents

The produced water from natural Gulf of Thailand as the feed solution was obtained from Salamander energy (Bualuang) Co. Ltd. The initial pH of feed solution was about 6.2-6.7. The composition of produced water is shown in the Table I. Aliquat336 used was carrier with the 88% purity. It was the mixture of C_8 and C_{10} with the molecular weight about 442. It was supplied from Acros organic Co. Ltd. The stripping solution was thiourea and nitric acid solution. They were supplied from Qrec Co. Ltd., New Zealand. All of reagents were analytical grade.

TABLE I
COMPOSITION OF PRODUCED WATER FROM GULF OF THAILAND

Metal	Concentration (ppm)
Hg (II)	0.5
Na(I)	980.0
Fe(III)	1.0
Mg(II)	3.0
Ca(II)	15.0

B. Apparatus

The hollow fiber module used was the liqui-cel® Liquid-Liquid Extraction system. It was purchased from 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 II. The concentration of metal ion was measured by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

C. Procedure

The hollow fiber contactor module which continuous flow operation was used in this research as shown in Fig. 2. Aliquat336 dissolved in kerosene volume of 1000 mL was fed into the shell side of the first hollow fiber module and fed continuous in shell side of the second module. The feed solution was pumped in tube side of the first hollow fiber module. Simultaneously, the stripping solution was pumped in tube side of the second module. The feed and stripping solution was fed which had a countercurrent flow. Volume flow rate of feed solution, stripping solution and the extractant equaled about 150 ml/min. The samples were kept in the outlet feed and stripping solution. The concentration of mercury was analyzed by ICP-AES.

IV. RESULT AND DISCUSSION

A. The Effect of Carrier Concentration

The concentration of Aliquat336 and dissolved in kerosene was various about 4-14 % (v/v). Results are shown in Fig. 3. In the range of concentration of Aliquat336 was between 4-10 % (v/v). The extraction of Hg (II) increased when increased concentration of carrier. On the other hand, the removal efficiency was decreased significantly when the carrier concentration is increased over 10%. The maximum extraction and stripping of Hg (II) were 98.0% and 42.67%, respectively.

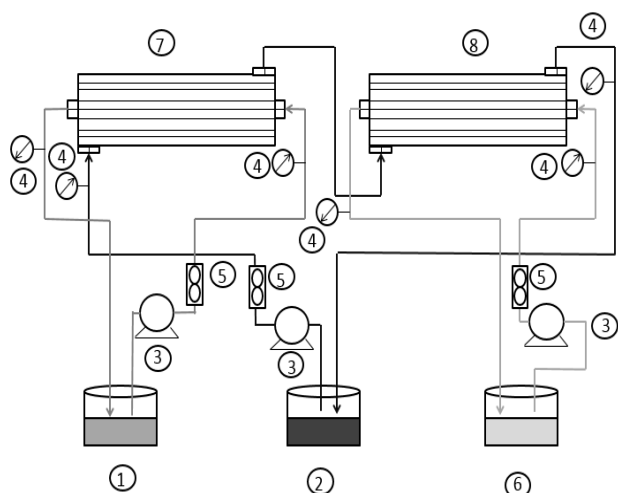


Fig. 2 Hollow fiber contactor module 1) inlet/outlet feed solution tank 2) inlet/outlet extractant tank 3) pump 4) pressure gauge 5) flow meter 6) inlet/outlet stripping solution tank 7) hollow fiber module for extraction 8) hollow fiber module for recovery.

TABLE II
PROPERTY OF HOLLOW FIBER MODULE

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

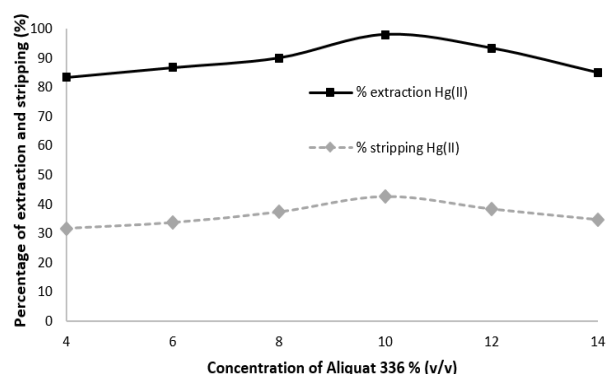


Fig. 3 Effect of concentration of Aliquat336 dissolved in kerosene on extraction and stripping yield: concentration of thiourea was 1.0 M

B. The Type of Stripping Solution

The stripping solution used was thiourea and nitric acid with concentration of 1.0 M. The result of stripping of Hg (II) from is shown in Fig. 4. The result shown that thiourea was stripped of Hg (II) more than nitric acid solution. Thiourea was the best stripping solution. The maximum stripping of Hg (II) was 44.2%.

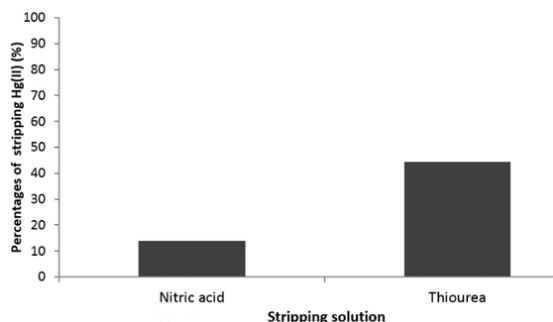


Fig. 4 Effect of type of stripping solution on stripping yield: concentration of Aliquat336 in kerosene was 10% (v/v)

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