State of the Art Hollow Fiber Supported Liquid Membrane on Pd (II) Separation from Wastewater Using Alamine 336

Kraiwith Wongkaew, Natchanun Leepipatpiboon, and Ura Pancharoen

Abstract—**A hollow fiber supported liquid membrane (HFSLM), having unique characteristics in the separation and stripping of trace species from dilute aqueous solutions, was applied to separate trace Pd(II) of approximately 1 ppm from wastewater. Optimum values of the parameters influencing the extraction and stripping of Pd(II) were investigated i.e. types of extractants (Alamine 336 and Aliquat 336), types of stripping agents (H$_2$SO$_4$, HCl, NH$_2$CSNH$_2$, NH$_4$Cl and a mixture of NH$_2$CSNH$_2$ and HCl), as well as types of diluents. The experimental results indicated that Alamine 336 and a mixture of NH$_2$CSNH$_2$ and HCl were the extractant and stripping solution, respectively. Under the most favorable operating conditions, Pd(II) was successfully separated from Pt(IV), Au(III), Cu(II) and Zn(II). Percentages of Pd(II) extraction and stripping were achieved reaching 95% and 88% respectively. Reproducibility of the HFSLM system was found to be ±2%.**

Index Terms—**Palladium, Alamine 336, Aliquat 336, wastewater, HFSLM.**

I. Introduction

Platinum group elements (PGEs) are very expensive, high quality materials and are utilized in industries such as automobiles, petroleum, dental, catalyst, medicine and jewelry. Extraction and recovery of PGMs are difficult and complicated due to their chemical properties and formation of many chemical species in chloride media. Moreover, some platinum group compounds have been reported as potential health risks to humans [1] together with high price levels [2]. Thus, it is very important to investigate the best and most efficient method to recover Pd(II) from wastewater. Wastewater from the gold-refining process containing Pd(II) is used as the feed solution [3]. Palladium contaminates the wastewater along with other metal ions such as Pt(IV), Au(III), Zn(II) and Cu(II). The concentration of Pd(II) is about 1 ppm in solution where the original pH ranges from 6 to 7.

Conventional methods for the extraction and recovery of palladium from solution are commercially operated e.g. chemical precipitation [4] and solvent extraction [5]. Nevertheless, these methods have some shortcomings [6], [7]. Therefore, HFSLM is recommended due to its various advantages compared with conventional methods. In particular, it has low capital and operational costs [8], low energy consumption [9] and high overall separation factors [10]. Moreover, HFSLM is also easily scalable [11] and it can improve the lifetime of the liquid membrane system due to their hydrodynamic characteristics [12]. Many works concerned with simultaneous extraction and recovery of metal ions via HFSLM have recently been reported [13]-[15].
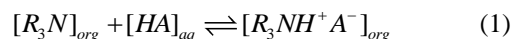
The main objective of this work is to report on the simultaneous extraction and recovery of trace Pd(II) in chloride media from gold-refining plant wastewater via HFSLM in a single operation. The various effects of the parameters on the percentages of Pd(II) extraction and stripping such as types of extractants, stripping agents and different diluents were investigated.
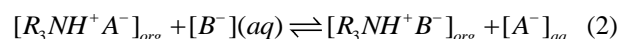
II. Theory

A. Transport of Pd(II) across the Liquid Membrane Phase

The general reaction of Alamine 336 is presented below in two steps: protonation and exchange

Protonation reaction:

$$[R_3N]_{org} + [HA]_{aq} \rightleftharpoons [R_3NH^+A^-]_{org} \qquad (1)$$

Exchange reaction:

$$[R_3NH^+A^-]_{org} + [B^-](aq) \rightleftharpoons [R_3NH^+B^-]_{org} + [A^-]_{aq} \quad (2)$$

Alamine 336 in the presence of the selected diluent is trapped in the hydrophobic micropores of the hollow fibers as the liquid membrane. The feed and stripping solution, having a capacity for palladium ions and the mixture of thiourea and hydrochloric acid utilized as the stripping phase, is normally circulated counter- currently through the tube and shell sides of the hollow fiber module. The transport of palladium ions is illustrated in Fig. 1.
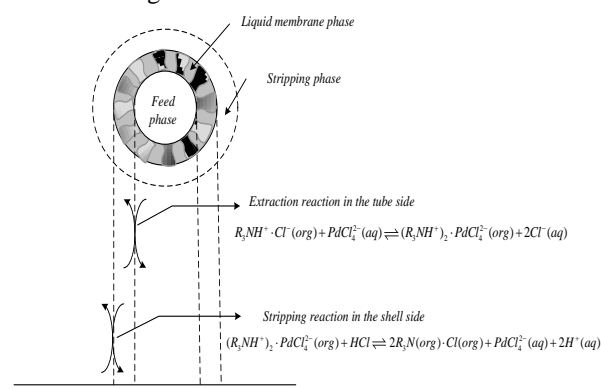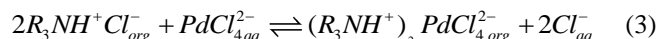

Fig. 1. Transport mechanism of M representing Pd(II) across the liquid membrane phase.

The tertiary amine forms an amine salt which reacts with an excess amount of hydrochloric acid. Two molecules of amine salt react with palladium tetrachloride complex to form the complex species as shown in Eq (3) [16].

$$2R_3NH^+Cl^-_{org} + PdCl^{2-}_{4aq} \rightleftharpoons (R_3NH^+)_2 PdCl^{2-}_{4org} + 2Cl^-_{aq} \quad (3)$$

B. The Efficiency of Extraction and Stripping

In this work, the efficiency of Pd(II) extraction was determined as follows:

$$\% \, Extraction = \frac{[C]_{f,in} - [C]_{f,out}}{[C]_{f,in}} \times 100 \quad (4)$$

The stripping efficiency of Pd(II) was determined as follows:

$$\% \, Stripping = \frac{[C]_{s,out}}{[C]_{f,in}} \times 100 \quad (5)$$

where $[C]_{f,in}$ and $[C]_{f,out}$ are the inlet and outlet of feed concentration, respectively; $[C]_{s,out}$ is the outlet stripping concentration.

III. EXPERIMENT

A. Feed and Stripping Solution Preparation

Alamine 336 (trialkyl (C8–C10) amine) was obtained from Cognis Company. Aliquat 336 is a commercial extractant containing a mixture of C8 (octyl) and C10 (decyl) chains with C8 predominating. The pH of the aqueous feed solution was adjusted by hydrochloric acid from Qrec (USA). All other chemicals such as thiourea (NH_2CSNH_2) from RFLC (New Zealand), sodium perchlorate ($NaClO_4$) from ACROS (USA), sodium hydroxide (NaOH) and sodium thiosulfonate ($Na_2S_2O_3$) from Merck Ltd (Germany) were used as stripping solutions. Hexane, cyclohexane, benzene, 1, 2-dichloromethane and chloroform without further purification, supplied by Sigma-Aldrich, were used as diluents. All substances used were of analytical grade. Doubly deionized water was used throughout the experiments.

The wastewater from the gold-refining plant containing several metal ions as shown in Table I with the original pH value (6-7) was used as feed solution.

TABLE I: THE COMPOSITIONS OF GOLD-REFINING WASTEWATER

Compositions	Concentration (ppm)
Pt(IV)	4.578
Pd(II)	0.876
Au(III)	0.943
Cu(II)	0.549
Zn(II)	0.120

B. Apparatus

A microporous polypropylene hollow fiber module (Liqui-Cel®Extra-Flow 2.5 in.×8 in. membrane contactor, Hoechst Celanese, USA) was used to prepare the HFSLM system. The specifications of the module are given in Table II.

TABLE II: PHYSICAL CHARACTERISTICS OF THE HOLLOW FIBER MODULE

Characteristics	Descriptions
Material	polypropylene
Number of fibers	35,000
Fiber inside diameter (μm)	240
Fiber outside diameter (μm)	300
Effective length (cm)	19.8
Surface area (m^2)	1.4
Area per unit volume ($cm^2\,cm^{-3}$)	29.3
Membrane porosity (%)	25
Average pore size (μm)	0.03
Membrane tortuosity	2.6
Module diameter (cm)	6.3
Module length (cm)	20.3
Operating temperature (°C)	1~60

C. Procedure

The single-module operation in recirculation mode is set up in Fig. 2. At first, the liquid membrane is prepared by mixing Alamine 336 dissolved in kerosene. Then, it is circulated into the lumen and shell sides of the HFSLM system for at least 50 min to ensure the complete soaking of membrane pores. The excessive liquid membrane is completely washed out with sufficient distilled water for 10 min, prior to the pumping of the feed and stripping solutions into the HFSLM system. Thereafter, the feed solution was pumped counter-currently into the lumen side, and at the same time the stripping solution was passed through the shell side. The metal ions from the aqueous solution were transported across the liquid membrane to the stripping phase and were collected in the stripping reservoir. The flow rate for both feed and stripping solutions was kept the same in all experiments.
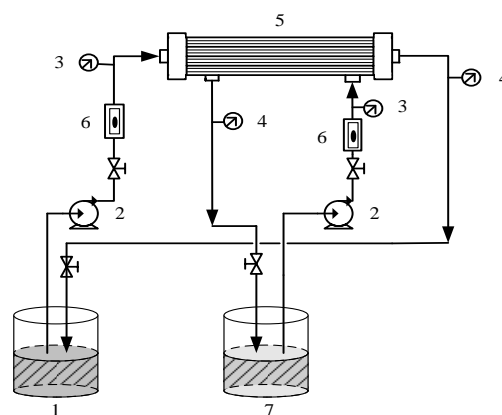

Fig. 2. Schematic counter-current flow diagram for a single-module operation in the HFSLM: 1) feed reservoir 2) gear pumps 3) inlet pressure gauges 4) outlet pressure gauges 5) hollow fiber module 6) flow meters and 7) stripping reservoir.

D. Analytical Instruments

Palladium sampling analysis, from the aqueous feed and stripping solution phases, was undertaken by an inductively coupled plasma optical emission spectrometer (ICP-OES) by JY 2000, JY JOBIN YVON (HORIBA). The pH values of the feed solution were measured by a professional pH Meter PP-50.

IV. RESULTS AND DISCUSSION

A. Influence of Types of Extractants

From the previous literature reviews, Aliquat 336 [17] and

Alamine 336 [16], [18] showed high performance in the extraction of Pd(II). Consequently, these extractants were selected to investigate the selective extraction of Pd(II) from the feed solution. The experiment was carried out by using a single-module hollow fiber with the mixture of thiourea and HCl as stripping solution. As shown in Fig. 3, Alamine 336 was the most suitable extractant for the selective extraction of Pd(II) at pH 2 of the feed solution. This corresponded to the fact that Alamine 336 is a basic extractant which reacts well with anion of $PdCl_4^{2-}$ at pH 2 of feed solution. The previous report was reported by P. P. Sun, M. S. Lee [19], regarding the separation of platinum and palladium from chloride solution by solvent extraction, using Alamine 336 as an extractant. The results indicate that 99.9% purity of platinum was obtained at the optimizing conditions. However, more steps in the extraction and recovery, high energy consumption are required. Moreover, this system is still suffered from the separation difficulty of aqueous phase and organic phase.
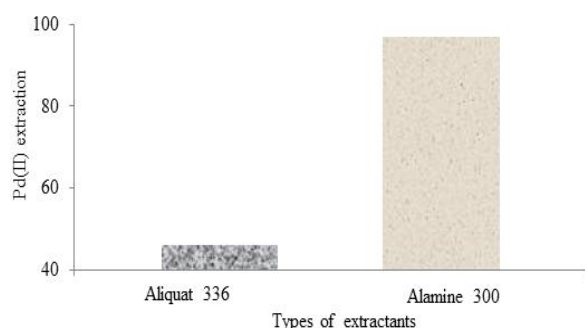

Fig. 3. Percentage of Pd(II) extraction versus types of extractants, using 9% (v/v) individual extractant concentration.

B. Influence of Types of Stripping Agents

A number of stripping agents were used for Pd(II) stripping from a complex species. Certainly, the fundamental principle is dependent on the characteristics of the selected extractant. In this work, the investigation of stripping agent influence on Pd(II) stripping from the membrane phase was carried out by testing stripping agents which were able to form complex species with Pd(II) strong enough to strip Pd(II) from Alamine 336 chlorocomplex. The stripping agents selected – H_2SO_4, HCl, NH_2CSNH_2, NH_4Cl and a combination of NH_2CSNH_2 and HCl – were chosen because of their Pd(II) stripping efficiency. The results as shown in Fig. 4 indicated that the stripping efficiency of Pd(II) decreased in the order of NH_2CSNH_2+HCl > NH_4Cl > NH_2CSNH_2 > HCl > H_2SO_4. The combination of NH_2CSNH_2 and HCl achieved a stripping percentage of approximately 70%. This can be attributed to the fact that NH_2CSNH_2 + HCl has stronger decomplexation ability for Pd(II) compared with other reagents.

C. Influence of Diluents

Diluents e.g. hexane, cyclohexane, benzene, 1,2-dichloromethane and chloroform were investigated using Alamine 336 as an extractant via HFSLM in a single operation while keeping the pH value of the feed solution at 2. Polarity parameters were taken into consideration in order to select diluents for Pd(II) extraction and stripping as well as to enhance membrane stability as shown in Table III. As reported in Table III, the extraction and stripping

performances of the different kinds of organic diluents was quite high. The results showed that 1, 2-dichloromethane gave the highest percentage of extraction reaching 73.2%, with a relative error of approximately 1.5%.
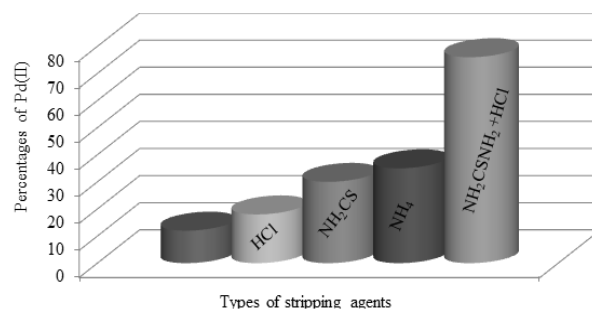

Fig. 4. The influence of the types of stripping agent on the percentage of stripping of Pd(II) using the concentration of 9% (v/v) Aliquat 336.

TABLE III: PERCENTAGES OF EXTRACTION AND STRIPPING OF PD(II)

Diluents	Extraction (%)	Stripping (%)
Hexane	70.51	61.80
Cyclohexane	71.78	62.64
Benzene	72.82	63.00
1,2-dichloromethane	73.21	66.64
Chloroform	70.45	46.41

D. Validation of the Method and Analysis of Real Samples

The separation of Pd(II) from other metal ions from gold-refining wastewater which contains Pt(IV), Au(III),Cu(II) and Zn(II). Under optimum conditions, experimental results indicate that Pd(II) is selectively extracted by Alamine 336 dissolved in kerosene. On the other hand, Pd(II), Au(III),Cu(II) and Zn(II) were not extracted. Percentages of Pd(II) extraction and stripping were achieved reaching 95% and 88% respectively.

E. Reproducibility of the HFSLM System

The reproducibility of the HFSLM method, impregnated with Alamine 336 was studied by performing five replicate transport experiments. The relative standard deviation was found to be ±2%. Thus, it can be concluded that HFSLM is an efficient and reliable system for the extraction and stripping of Pd(II) in chloride media.

V. CONCLUSIONS

Alamine 336 and a mixture of thiourea and hydrochloric acid were used as an extractan and a stripping agent, respectively. Pd(II) was successfully separated from the feed solution under optimum conditions. Percentages of Pd(II) extraction and stripping were achieved reaching 95% and 88% respectively. Therefore, the HFSLM method can be successfully applied for the extraction and stripping of Pd(II) from the gold-refining wastewater (GRW).

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