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MODELING AND SIMULATION OF PALLADIUM-ION EXTRACTION VIA HOLLOW FIBER SUPPORTED LIQUID MEMBRANE

Laisua Nattaya, Kittisupakorn Paisan
Department of Chemical Engineering, Faculty of Engineering
Chulalongkorn University
Bangkok, Thailand

***Abstract*— A hollow fiber supported liquid membrane has been applied to separate precious compounds at a very low concentration with the specific characteristic of high selectivity. The modeling of the palladium ions extraction via the hollow fiber supported liquid membrane has been studied. LIX84-I dissolved in kerosene and hydrochloric acid is specified as a stripping solution in this work. Models developed give good dynamic behavior under a recycling operation mode. In addition, the sensitivity of process parameters including axial convection, axial diffusions, chemical reactions at the feed-liquid membrane and the accumulation of palladium ions in the system are also carried out in the simulation study. Simulation results show that the final predicted concentration of the palladium ions in feed solution is good agreement compared to the experiment data (average percentage deviation of 4.69%) .**

***Index Terms*— Palladium, Modeling, Simulation, Extraction, Hollow fiber, Liquid membrane.**

I. INTRODUCTION

The electronic equipments such as the mobile phone, computer, television etc. became a part of daily life. The flexible printed circuit board plays an important role in electronic equipments; therefore a flexible printed circuit board industry rapidly grows at this moment. In an industry, wastewater generates direct effect to the natural water resource; however the wastewater released by flexible printed circuit board production contains palladium ions, which is a precious metal. For this reason, the extract method is a challenging method to recover of palladium ions from aqueous solution [1].

Hollow fiber supported liquid membrane (HFSLM), one of liquid membrane in supported structure, was used to separate metal ions from an aqueous solution. The membranes contain an extractant or a carrier which possesses the potential for selective permeation by using the facilitated transport mechanism. There are several reasons for the hollow fiber supported liquid membrane is that used widely. Firstly, extraction and stripping can be carried out simultaneously in one equipment. Secondly, backmixing effects and loss of complexing agent can be minimized. Next, only small amounts of complexing agent are required due to the continuous regeneration associated with the reversible reaction. Finally, highly selective separation is possible [2].

In this work, an extraction of palladium ions from flexible printed circuit board wastewater by hollow fiber supported liquid membrane was examined. LIX84-I was used as the extractant and hydrochloric acid was used as the stripping solution. The influences of two variables such as concentration of extractant in feed solution and flow rate of feed solution were investigated. Fluid-flow model describing the transport phenomena of palladium ions at unsteady-state condition were studied. The MATLAB software was used to solve these models. The final calculated concentration of palladium ions in feed solution was validated with the experimental data.

II. THEORY

A. Membrane structure, materials and modules

The performance of membrane relates closely to structures, material and module [3].

In case of membrane material, polymeric or organic membranes made of various polymers (e.g., cellulose acetate, polyamide, polypropylene, etc) are cheap, easy to manufacture and available of a wide range of pore sizes. However, some limitations like pH, temperature, pressure, etc, can impede the applications of polymeric membrane.

In terms of membrane modules, the development of membrane module with large surface areas of membrane at a relatively low manufacturing cost is very important. Resistance to fouling, which is particularly critical problem in liquid separation, depends on the membrane module. Hollow fiber module Fig. 1, has the greatest surface area-to-volume ratio resulting in high mass transfer coefficient and is the most efficient type of membrane separation. Hollow fiber module is obviously the lowest cost design per unit membrane area.

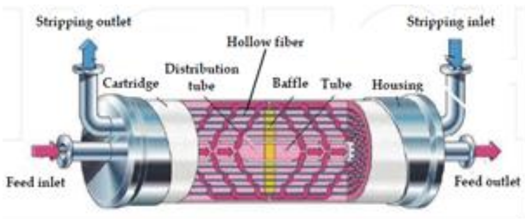

Fig. 1. The hollow fiber module [3]

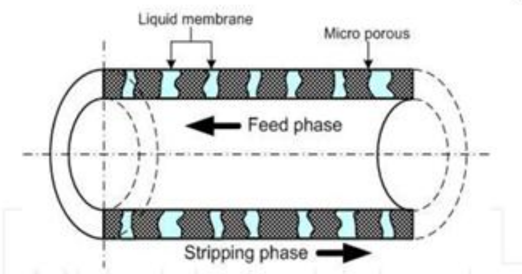

Fig. 2.The microporous hollow fiber liquid membrane [4]

The system, shown in Fig. 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 [4].

B. Hollow fiber supported liquid membrane (HFSLM)

The characteristics of the hollow fiber modules are shown in Table 1. And the parameter values used for calculation of the concentration of palladium ions in feed solution are shown in Table 2.

TABLE I. CHARACTERISTICS OF THE HOLLOW FIBER MODULE USED FOR EXTRACTION EXPERIMENTS

Characteristics	Description	
	Shell values (unit)	***Fiber values (unit)***
Material	Polypropylene	-
Length	2.03 (dm)	-
Inner diameter	0.63 (dm)	-
Outer diameter	0.77 (dm)	-
Number of fiber	-	35,000
Effective length	-	1.5 (dm)
Inner diameter	-	0.0024 (dm)
Outer diameter	-	0.0030 (dm)
Effective surface area	-	140 (dm^2)
Pore size	-	3.7×10^{-7} (dm)
Membrane porosity	-	25%
Tortuosity		2.6

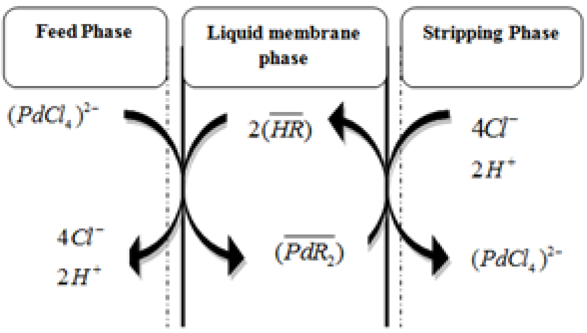

Fig. 3. Transport of palladium ions in the HFSLM system.

C. Transport of palladium ions via the liquid membrane phase

The organic extractant dissolved in solvent solution is trapped in the hydrophobic microporous of hollow fiber as the liquid membrane. The extraction of palladium ions through the hollow fiber supported liquid membrane containing LIX84-I dissolved in kerosene and hydrochloric acid was used as a stripping solution is generally fed counter-currently in the tube and shell of a hollow fiber module, respectively. The transport of palladium ions across liquid membrane phase is presented in Fig. 3. The extraction at the feed liquid membrane interface (subscript $_{fi}$) takes place when the organic extractant ($\overline{HR}$) reacts with palladium ions in feed phase to form complex species ($\overline{PdR_2}$) in Eq. (1). Next, the complex species diffuses across the liquid membrane phase to the liquid membrane-stripping interface (subscript $_{si}$) since the concentration gradient between the two interfaces. Later, the stripping reaction Eq. (2) occurs and so palladium ions are released into the stripping phase. Finally, palladium, chloride and hydrogen ions are counter-transported across the liquid membrane phase [4].

$$PdCl_4^{2-} + 2\overline{HR} \xleftarrow{k_{extraction}}\!\!\rightarrow \overline{PdR_2} + 4Cl^- + 2H^+ \quad (1)$$

$$\overline{PdR_2} + 4Cl^- + 2H^+ \xleftarrow{k_{stripping}}\!\!\rightarrow PdCl_4^{2-} + 2\overline{HR} \quad (2)$$

In this work, the extraction of palladium ions was only investigated. The over bar denotes the species in the liquid membrane phase. The rate of extraction is described by Eq.(3).

$$r_{Pd^{2+}} = k_{ex}(C^j_{Pd^{2+},f})^m(x,t) \quad (3)$$

where x is the longitudinal axis of the hollow fiber, t is the extraction time, k_{ex} is the reaction rate constant of extraction, $C^j_{Pd^{2+},f}$ is the concentration of palladium ions in the feed phase as a function of longitudinal axis of the hollow fiber and time, and m is the reaction orders of the extraction.

Using Taylor series to linearize the reaction rate of extraction in Eq. (4), following equation is obtained:

$$r_{C^j_{z,f}} = \alpha C^j_{z,f} + \beta \quad (4)$$

when

$$\alpha = -mk_{ex}(C^j_{0,f})^{m-1} \quad (5)$$

$$\beta = (m-1)k_{ex}(C^j_{0,f})^m \quad (6)$$

where $C^j_{0,f}$ is the concentration of palladium ions in feed phase at z = 0, and represents an individual value of each sequence of the space time j.

D. Modeling of palladium-ion extraction for the recycling mode operation

For the recycling mode, both feed and stripping solutions are recycled, as shown in Fig. 4, [5].

The laminar transport of palladium ions in feed phase corresponds to the axial convection and diffusion. The concentrations of palladium ions along the hollow fibers depending on the longitudinal axis of the hollow fiber and the extraction time corresponding to the accumulation of palladium ions in the feed phase. The fluid-flow model in feed phase is made according to the following assumptions [6]:

1. The physical properties in the feed phase such as pressure and volume are constant.
2. Based on the facilitated coupled counter-transport, the palladium ions are transported across the feed-liquid membrane interface into the liquid membrane phase by the reaction flux.
3. Since the inside diameter of hollow fibers is very small, the concentration of palladium ions in the radial direction is constant. This means that the diffusion fluxes of palladium ions in the feed phase exist only in the axial direction.

4. Only complex species, not palladium ions, are transported across the liquid membrane phase.
5. The forward reaction is dominant.

The transports of palladium ions through the small segments in the feed phase and the cross-sectional areas of the hollow fiber is show in Fig. 5.

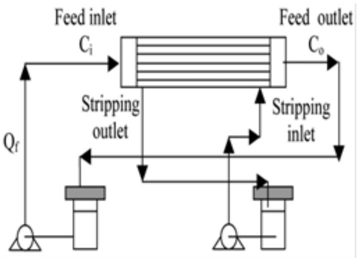

Fig. 4. Schematic diagram of a single HFSLM with counter-current circulating flow patterns of feed and stripping solutions [5]

The mass conversation of palladium ions in each small segment (Δx) is considered by Eqs. (7) and (8):

[Rate of mass transport into the system by convection]
- [Rate of mass transport out of the system by convection]
+ [Rate of mass transport through the system by diffusion]
- [Rate of mass extracted by extraction reaction]
= [Rate of mass accumulation within the system]

$$qC_{z-1,f}^{j} - qC_{z,f}^{j} + \frac{A_{c,f}D_f}{\Delta x}\left(C_{z,f}^{j} - C_{z-1,f}^{j}\right) - \Delta x A_{c,f}\left\langle r_{C_{z,f}^{j}}\right\rangle \quad (7)$$

$$= \frac{\Delta x A_{c,f}}{\Delta t}\left(C_{z,f}^{j} - C_{z,f}^{j-1}\right) \quad (8)$$

where q is the volumetric flow rate of feed solution, z is the number of small segments in feed phase, $A_{c,f}$ is inside cross-sectional area of the hollow fibers, j and $j-1$ are the sequence of space time j and $j-1$, $C_{z,f}^{j}$ is the concentration of palladium ions as a function of z and j, $\left\langle r_{C_{z,f}^{j}}\right\rangle$ is the average rate of extraction as a function of palladium ion concentration at segment z and sequence j, Δt is the space time for the feed solution and D_f is the diffusion coefficient of palladium ions in feed phase as calculated by the Wilke-Chang equation in [7], as shown in Eq. (9):

$$D_f = \frac{7.4\times10^{-8}\left(\phi M_w\right)^{0.5} T}{\eta_w \upsilon_{Pd^{2+}}^{0.6}} \quad (9)$$

where ϕ is the association factor of water (ϕ = 2.6), M_w is the molecular weight of water, T is the temperature of feed phase in Kelvin, η_w is the viscosity of water, and $\upsilon_{Pd^{2+}}$ is the molar volume of palladium ions at normal boiling point.

E. Validity of the mathematical model

In order to validate the proposed models for the extraction of palladium ions in the hollow fiber module, two indicators are used as follow. The final feed solution was collected to analyze the amount of palladium ions by AAS. The percentage of extraction was calculated by Eq. (10) and the average percentage of deviation was calculated by Eq. (11).

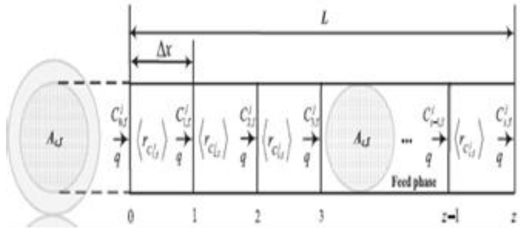

Fig. 5. Transport of palladium ions through small segment in feed phase [6]

TABLE II. **PARAMETER VALUES IN FEED PHASE USED FOR THE CALCULATION OF THE SYSTEM**

Properties	**Descriptions**	
	Variables (unit)	***Values***
Number of small segment	z	35,000
Space time for the feed solution	Δt (min)	0.5
Small segment	Δx (dm)	4.29x10^{-5}
Volumetric flow rate	q (dm^3/min)	0.1
Length of a hollow fibers	L (dm)	1.5
Diffusion coefficient of palladium ions	D_f (dm^2/min)	2.46x10^{-5}
Inside cross-sectional area of hollow fiber	$A_{c,f}$ (dm^2)	0.16
Concentration of palladium ions as a function of z and j	C_0^j (mg/dm^3)	300

$$\%Extraction = \frac{C_{0,f}^{j} - C_{z,f}^{j}}{C_{0,f}^{j}} \times 100 \quad (10)$$

$$\%Deviation = \frac{\Sigma_1^i \left(\frac{C_{Expt}^{j} - C_{Theo}^{j}}{C_{Expt}^{j}}\right)}{i} \times 100 \quad (11)$$

III. RESULTS AND DISCUSSION

A. Experimental operation conditions for HFSLM

The properties of the flexible printed circuit board wastewater is shown in Table. 2. It includes of 300 mg/dm^3 of palladium ions in feed solution. It found that LIX84-I of extractant and flow rate of 0.1 dm^3/min are the most selective extractant. The percentage of extraction of palladium ions was 96.08%.

B. Influence of extractant concentration

The influence of the concentration of LIX84-I was showed in Fig. 6. Normally, the reaction rate increases with the concentration of the extractant. From Fig. 4, when the concentration of LIX84-I increases the percentage of palladium ions increase and the optimum concentration of extractant is 0.06 M.

C. Influence of flow rate in feed solution

Flow rate of feed solution was demonstrated in Fig. 7. The percentage of extraction decreased from the flow rate of 0.15 dm^3/min. The maximum extraction of 0.1 dm^3/min was the percentage of extraction of palladium ions was 96.08%.

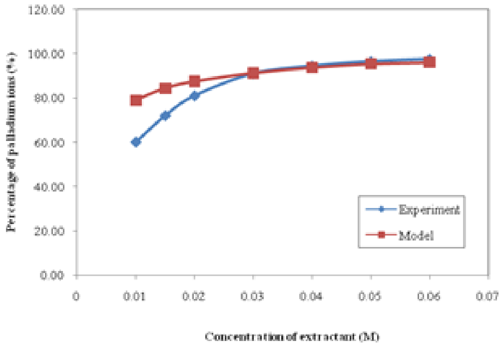

Fig.6. Extraction of palladium ions against concentration of the extraction (flow rate of feed solution of 0.1 dm^3/min)

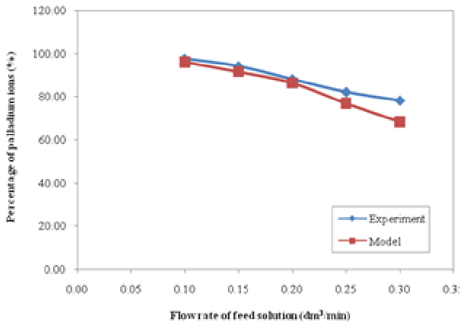

Fig.7. Extraction of palladium ions against flow rate of feed solution (0.06 M LIX84-I)

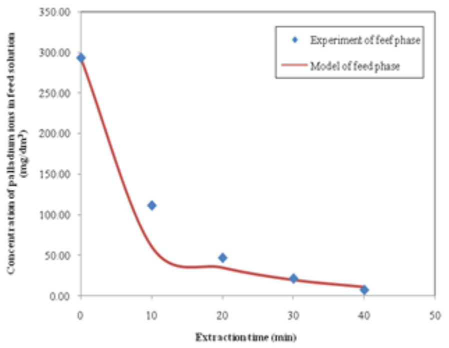

Fig. 8. Stability of HFSLM for extraction of palladium ions and the validation of fluid-flow model at the optimum condition (concentration of LIX84-I in feed solution of 0.06 M and flow rate of feed solution at 0.1 dm3/min)

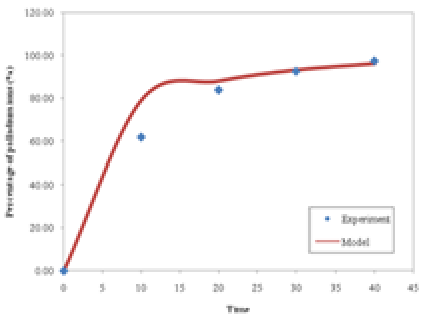

Fig. 9. Percentage of palladium ions against time of the extraction (flow rate of feed solution of 0.1 dm^3/min and 0.06 M LIX84-I as extractant)

D. Stability of HFSLM operation and validation of the fluid-flow model

The stability of the hollow fiber supported liquid membrane operation of extraction in a single hollow fiber module for 40 minute. From Fig. 8, the extraction result showed that proposed fluid-flow model have high accuracy as the calculated values was in line with the experimental result at the deviation of about 4.69% and percentage of palladium ion in feed solution of about 96.08 % as shown in Fig.9.

IV. CONCLUSION

In this work, mathematical models for the extraction process of palladium ions have been developed. This process uses LIX84-I dissolved in kerosene and hydrochloric acid as the feed solution through a hollow fiber supported liquid membrane. The models based on the principle of material balances and validated against the experiment data can provide good prediction of the final concentration of the extraction with an average percentage deviation of 4.69%. The simulation results show that the highest palladium ions extraction of about 96.08% is achieved under the feed solution of 0.06 M and the volumetric flow rate of 0.1 dm^3/min.

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