

High Performance of Hollow Fiber Supported Liquid Membrane to Separate Silver Ions from Medicinal Wastewater

Thidarat Wongsawa, Ura Pancharoen, Anchaleeporn Waritswat Lothongkum

Abstract—The separation of silver ions from medicinal wastewater via hollow fiber supported liquid membrane (HFSLM) was examined to promote the performance of this technique. The wastewater consisting of 30mg/L silver ions and 120mg/L ferric ions was used as the feed solution. LIX84I dissolving in kerosene and sodium thiosulfate pentahydrate solution were used as the liquid membrane and stripping solution, respectively. In order to access the highest performance of HFSLM, the optimum condition was investigated via several influential variables. Final concentration of silver ions in feed solution was obtained 0.2mg/L which was lower than the discharge limit of Thailand's mandatory.

Keywords—Hollow fiber, Liquid membrane, Separation, Silver ions.

I. INTRODUCTION

CONVENTIONAL techniques such as precipitation, ion exchange and electrodialysis were used for separation of the target species from industrial wastewaters before their discharge to the environment. However, these techniques achieved limited success, especially when the wastewaters consist of target species at a very dilute concentration ($\leq 100\text{mg/L}$). In general, the treatment process should include several processes: preliminary treatment, primary treatment, and secondary treatment. One single technique is unable to solve all problems or cover all aspects [1]. As an alternative technique for the separation of target species at a dilute concentration, hollow fiber supported liquid membrane (HFSLM) is of interest to many researchers. This is due to its outstanding ability in separating the dilute target species in order to meet the mandatory discharge limit [2]-[5]. This technique has specific characteristics for the simultaneous extraction and stripping processes in one single stage, high selectivity and low solvent use. Other advantages of HFSLM over conventional techniques are lower energy consumption, lower capital and operating costs as well as higher fluxes [6].

The presence of silver ions in the environment is of great concern. Silver ions are toxic and nonbiodegradable. A dilute concentration of silver ions (1-5mg/L) can kill aquatic

microorganisms, insects, trout, and flounder [7]. The major sources of silver ions in the environment are found in wastewater from the manufacturing of silverware, electronics, and jewelry as well as in the wastewater from photographic-imaging industry, particularly from medicinal processes [8], [9]. In the Government Pharmaceutical Organization (GPO) of Thailand, 100L per mouth of wastewater is generated from the quantitative analysis of active medicinal ingredients and consisting of 30mg/L silver ions and 120mg/L ferric ions. In the case of ferric ions, separation was achieved through chemical precipitation but in the case of silver ions nothing happened. Thus, a challenging technique to separate silver ions from this wastewater to meet the discharge limit of Thailand's mandatory (1mg/L) is essential [10].

In this work, the separation of silver ions from medicinal wastewater of GPO via HFSLM was examined. LIX84I was selected as the extractant due to a greater transmembrane flux and dissolved with kerosene to use as the liquid membrane [11]. For the stripping solution, sodium thiosulfate pentahydrate solution was used. The optimum condition for the separation of silver ions was investigated by studying many variables such as pH of feed and stripping solutions, concentration of extractant and stripping solution, flow rates of feed and stripping solutions, separation time and the presence of ferric ions on silver ion separation.

II. TRANSPORT MECHANISMS

The transport mechanisms of silver ion separation in hollow fiber supported liquid membrane are presented schematically in Fig. 1. The liquid membrane is trapped in hydrophobic microporous hollow fibers. The feed and stripping solutions are fed counter currently into tube and shell sides of hollow fibers, respectively. Extraction at the feed-liquid membrane interface takes place when the extractant (HR) reacts with silver ion (Ag^+) in the feed solution to form the complex species ($\text{AgR}(\text{HR})$) and hydrogen ion (H^+) as shown in (1). Continuously, the complex species diffuses across the liquid membrane to the liquid membrane-stripping interface by its concentration gradient between two interfaces. Thereafter, the stripping occurs as shown in (2) where the complex species reacts with hydrogen ion and then releases silver ion into the stripping solution. Finally, silver and hydrogen ions are counter transported across the liquid membrane. Thus, the transport mechanisms depend decidedly on the strong

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chemical interactions and highly specific selectivity of the extractant.

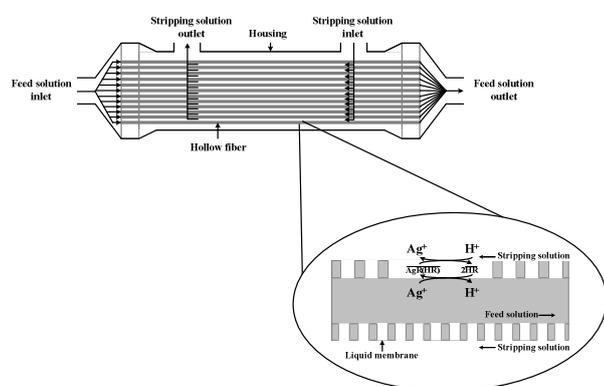
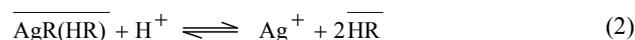
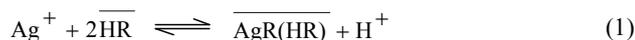


Fig. 1 Transport mechanisms of silver ions in HFSLM

III. EXPERIMENTAL

A. Chemicals

Medicinal wastewater of GPO consisting of 30mg/L silver ions and 120mg/L ferric ions was used as feed solution. The initial pH and other properties of the wastewater are listed in Table I. Ferric ions were precipitated by a phosphoric acid solution of 0.35 mg/L for the protection of its interference in silver ion separation. LIX84I (Henkel Thai Ltd., Bangkok) dissolved in kerosene was used as the liquid membrane. The chemical structure of LIX84I is shown in Fig. 2. Sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, BrightChem Sdn. Bhd., Selangor, Malaysia) dissolved in distilled water was used as the stripping solution. The initial pH of stripping solution was approximately 6. Nitric acid solution (BrightChem Sdn. Bhd., Selangor, Malaysia) was used to adjust the pH of feed and stripping solutions. Aqueous solutions were prepared using Milli-Q deionized water (Millipore, USA). All chemicals were of analytical grades and were used as received without any further purification.

TABLE I
PROPERTIES OF MEDICINAL WASTEWATER

Properties	Values
pH	6
Ag(I) (mg/L)	30
Fe(III) (mg/L)	120
TSS (mg/L)	730
BOD (mg/L)	1740
COD (mg/L)	3210
Viscosity (Pa.s)	0.001
Density (g/mL)	1.002

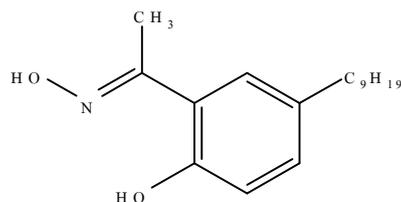


Fig. 2 Chemical structure of LIX84I

B. Apparatus

A laboratory scale hollow fiber supported liquid membrane (Liqui-Cel®Extra-flow: 2.5in. × 8in., Hoechst Celanese, Bridgewater, NJ) was used in the experiment and its properties are listed in Table II. Both pH of feed and stripping solutions were measured by a BP3001 pH meter (TransInstruments, Singapore). The concentration of silver ions in the above solutions was analyzed by an atomic absorption spectrometer (AAS, ModelAA280FS, Varian, Walnut Creek CA).

TABLE II
PROPERTIES OF HOLLOW FIBER SUPPORTED LIQUID MEMBRANE

Properties	Descriptions
Material	Polypropylene
Module diameter	6.3 cm
Module length	20.3 cm
Number of hollow fibers	35,000
Inside diameter of a hollow fiber	240 μm
Outside diameter of a hollow fiber	300 μm
Effective length of a hollow fiber	15 cm
Effective surface area of a hollow fiber	$1.4 \times 10^4 \text{ cm}^2$
Area per unit volume	$29.3 \text{ cm}^2/\text{cm}^3$
Pore size	0.03 μm
Porosity	25%
Tortuosity	2.6

C. Procedures

A hollow fiber supported liquid membrane was operated as shown in Fig. 3. Liquid membrane of 500mL was simultaneously pumped into the tube and shell sides of the hollow fibers for 40min to embed entirely in the micropores of hollow fibers. 500mL of each feed and stripping solutions were fed countercurrent circulating mode into the tube and shell sides of the hollow fibers, respectively. The influential variables such as pH of feed solution (values of 2-4), pH of stripping solution (values of 1-3), concentration of extractant (values of 0.01 M-0.20 M), concentration of stripping solution (values of 0.1 M-2.0 M), flow rates of feed and stripping solutions (values of 200 mL/min-1,000 mL/min), separation time and the presence of ferric ions on silver ion separation were investigated. The final feed and stripping solutions of each study were kept at 30min except for the study of separation time which was noted every 2min. The samples were analyzed by AAS to determine the concentration of the silver ions.

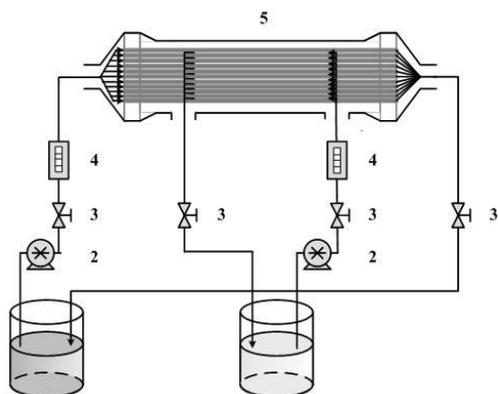


Fig. 3 Schematic diagram of HFSLM with countercurrent circulating flows of feed and stripping solutions: 1) feed reservoir 2) gear pumps 3) gate valves 4) flow meters 5) HFSLM 6) stripping reservoir

IV. RESULTS AND DISCUSSION

A. Influences of pH of Feed and Stripping Solutions

Taking into account the transport mechanisms of silver ions, one driving force is the concentration gradient of hydrogen ions in both feed and stripping solutions. Thus, the pH of feed and stripping solutions was adjusted for its acidity to enable a good driving force of hydrogen ions. In Fig. 4, the concentration of silver ions in the feed solution decreased rapidly within the range of pH 2-3.5. However, when pH was higher than 3.5 due to the equilibrium reaction at the feed-liquid membrane interface, the concentration of silver ions was quite constant. Furthermore, the concentration of silver ions in the stripping solution was pretty constant with pH in the range of 1-2. Then, when pH was higher than 2, it decreased due to less driving force. However, we do not take into consideration of the pH of stripping solution lower than 2 in order to prevent the corrosion of hollow fibers from the strong acid. Hence, the optimum pH of feed and stripping solutions is seen to be 3.5 and 2, respectively.

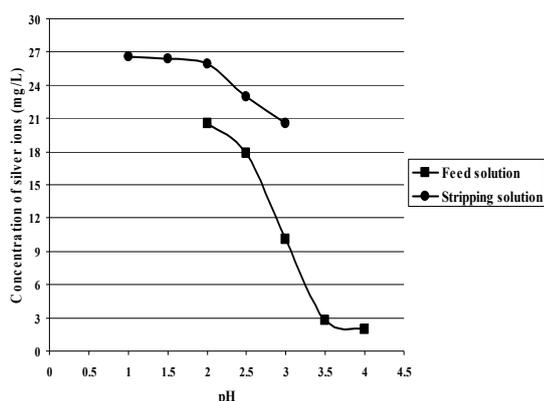


Fig. 4 Concentration of silver ions against pH of feed and stripping solutions (0.1 M extractant concentration, 0.5M stripping concentration, and 200mL/min feed and stripping flow rates)

B. Influence of Extractant Concentration

The influence of extractant concentration is shown in Fig. 5. In general, the rate of reaction increases with the extractant concentration. We observed that the concentration of silver ions in the feed solution decreased when the extractant concentration was increased to 0.1 M. Then, in contrast, when the extractant concentration was higher than 0.1 M, the concentration of silver ions increased. This was due to an increase of liquid membrane viscosity which obstructed the transport of the complex species. It was noticed that the extraction amount of silver ions had a direct effect on the stripping amount of silver ions. Thus, the concentration of silver ions in the stripping solution reached its maximum at the extractant concentration of 0.1 M. Hence, we selected the extractant concentration of 0.1 M for further study.

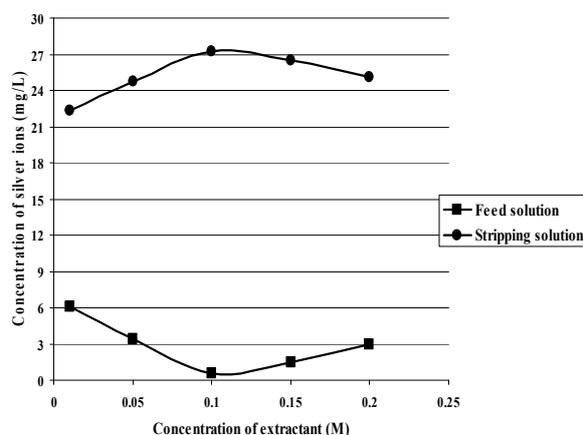


Fig. 5 Concentration of silver ions against concentration of extractant (pH of feed solution 3.5, pH of stripping solution 2, 0.5 M stripping concentration and 200 mL/min feed and stripping flow rates)

C. Influence of Stripping Concentration

The influence of stripping concentration is shown in Fig. 6. As can be seen, the concentration of silver ions in the feed solution decreased rapidly to 0.5M of the stripping concentration. Then, it was rather constant at a value higher than 0.5M. This resulted in an increase of silver ion concentration in the stripping solution to 0.5M which remained pretty constant. This was because the amount of silver ions in the stripping solution depended on the amount of complex species that reacted with the stripping solution. However, the excess concentration of stripping solution has no benefit. Thus, the optimum condition of stripping concentration is 0.5M.

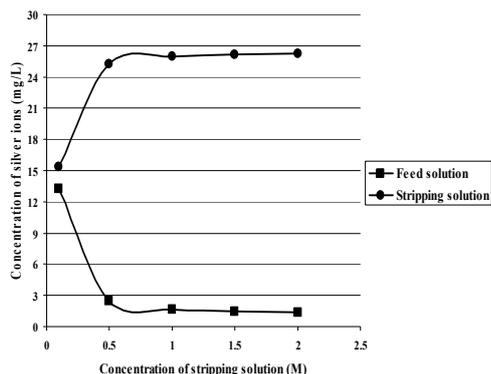


Fig. 6 Concentration of silver ions against concentration of stripping solution (pH of feed solution 3.5, pH of stripping solution 2, 0.1 M extractant concentration and 200mL/min feed and stripping flow rates)

D. Influences of Feed and Stripping Flow Rates

Fig. 7 shows the concentration of silver ions against flow rates of both feed and stripping solutions. The concentration of silver ions in the feed solution increased rapidly when flow rate increased higher than 200mL/min. On the other hand, the concentration of silver ions in the stripping solution decreased rapidly. This was due to the high flow rates of feed and stripping solutions which resulted in less contact time for the extraction and stripping reactions of silver ions at both feed-liquid membrane and liquid membrane-stripping interfaces. However, the slow chemical reactions of precious metal extraction and stripping require the long contact time [12]. This indicated that high flow rates were not appropriate conditions for our investigation. For flow rates lower than 200 mL/min, Altin et al. reported that their effects yielded low separation of silver ions in a flat sheet supported liquid membrane [8]. Thus, it was noticed that the optimum condition for flow rates of both feed and stripping solutions was 200mL/min.

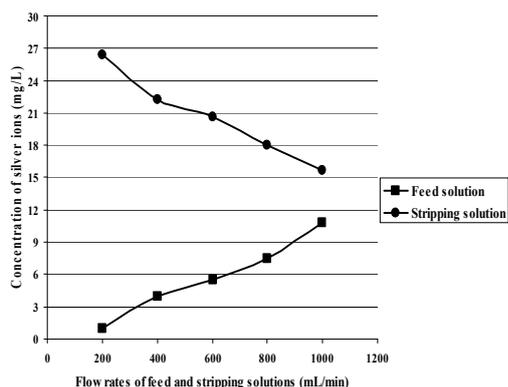


Fig. 7 Concentration of silver ions against flow rates of feed and stripping solutions (pH of feed solution 3.5, pH of stripping solution 2, 0.1M extractant concentration and 0.5M of stripping concentration)

E. Influence of Separation Time

The separation time of silver ions is shown in Fig. 8. From Fig. 8, we observed that the separation time after 26min resulted in the lowest concentration of silver ions in the feed solution of approximately 0.2mg/L. This concentration is lower than the discharge limit of Thailand's mandatory. In addition, the separation time after 26min also resulted in the highest concentration of silver ions in stripping solution. Thus, we select the separation time at 26min to be the optimum condition.

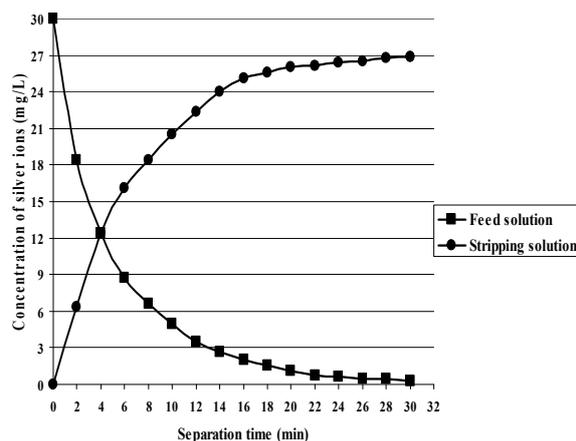


Fig. 8 Concentration of silver ions against separation time (pH of feed solution 3.5, pH of stripping solution 2, 0.1M extractant concentration, 0.5M of stripping concentration and 200mL/min feed and stripping flow rates)

F. Influence of Ferric Ion Presence on Silver Ion Separation

The influence of ferric ions on the separation of silver ions is shown in Fig. 9. The results were studied by using the wastewater containing 120mg/L of ferric ions and wastewater without ferric ions. The concentrations of silver ions in both cases were about equaled. This indicated that ferric ions have no effect on the separation of silver ions.

Results can be described by focusing on the extraction reaction between the ions and extractant as well as the chemical structure of the extractant. It is noted that silver ions can react with the extractant faster than ferric ions. This is because silver ions require one electron to share with the extractant forming eight electrons in its valence shell while ferric ions require three electrons. This corresponds to the octet rule. In addition, the chemical structure of extractant used in this work consists of acetophenone oxime which contains nitrogen coordination sites having a great affinity for silver ions [13].

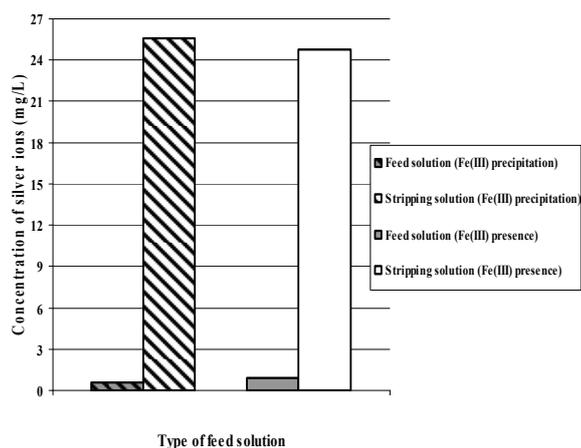


Fig. 9 Concentration of silver ions against type of feed solution (pH of feed solution 3.5, pH of stripping solution 2, 0.1M extractant concentration, 0.5 M of stripping concentration and 200mL/min feed and stripping flow rates)

V. CONCLUSION

Hollow fiber supported liquid membrane can successfully separate silver ions at a very dilute concentration from medicinal wastewater. An extractant can select the silver ions by its specific chemical property. The optimum conditions for silver ion separation were found to be pH of feed solution 3.5, pH of stripping solution 2, concentration of extractant 0.1 M, concentration of stripping solution 0.5 M, flow rates of feed and stripping solutions 200mL/min and separation time of 26 min. The final concentration of silver ions was lower than the discharge limit of Thailand's mandatory.

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