

Precious Metals Enrichment from Wastewater Solution Using Emulsion Liquid Membrane Process

N. Othman^{1,2}, N. F. M. Noah²

¹Centre of Lipids Engineering and Applied Research (CLEAR), Ibnu Sina Institute for Scientific and Industrial Research (Ibnu Sina ISIR), Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

²Department of Chemical Engineering, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

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ABSTRACT

Recovery of precious metals including palladium and silver from liquid waste solutions is vital, in order to sustain the resources and to conserve the environment from hazardous materials, particularly heavy metals. Many methods were studied for precious metal recovery, but constrained by several limitations. One of the promising methods for industrial wastes treatment and precious metals recovery is emulsion liquid membrane (ELM). This method able to selectively separate and concentrate the target metals through a very thin layer of liquid membrane with large surface area. In this study, an attempt was made to recover palladium and silver from liquid waste solution using bis (2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) as a mobile carrier. Several important parameters affecting the ELM recovery process such as extractant/carrier and stripping agent concentration, phase treatment ratio between emulsion and feed phase were studied. The results showed that at optimum process conditions of 0.03 M Cyanex 302 carrier concentration, 1.0 M of thiourea in 1.0 M of H₂SO₄ (1.0 M acidic thiourea) stripping agent concentration and 1:4 treat ratio, almost 100% of silver was extracted and recovered with 11 times of enrichment. Whilst for the palladium treatment, almost 100% of palladium was extracted and recovered with 3 times enrichment in the receiving phase at 0.2 M of Cyanex 302, 1.0 M acidic thiourea of stripping agent and 1:3 treat ratio. Therefore, it can be concluded that the ELM system is very promising and has high potential in removal and recovery of precious metals.

KEYWORDS: Emulsion Liquid Membrane, Metal Recovery, Silver, Palladium, Liquid Wastes Solution.

INTRODUCTION

There are various separation processes applicable to recover precious metals from industrial wastewater which are biosorbent, ion exchange, membrane separations, precipitation and adsorption but these methods have some limitation [1-5]. Emulsion liquid membrane (ELM) process is a recognized technique of removal and recovery for the metals from industrial wastewater and it also has been utilized in the separation of organic acids from aqueous waste [6]. Recently, it becomes a promising technique in treating industrial wastes because of its capability to separate and concentrate precious metals even in a very dilute solution like silver, gold, palladium and platinum from industrial waste. Recovering precious metals would be an attractive approach due to price of metals and stricter regulations concerning the environmental and economic aspects.

Compared to conventional solvent extraction process, it has been reported that ELM is an exceptional process and more economic from both operating costs and capital viewpoints [7]. Main benefits of ELM process are extraction and stripping occurred simultaneously in the one step process, which can remove the equilibrium limitations. It also provides high fluxes, high selectivity, and can reduce the amount of expensive carrier used. This process operation has previously been carried out in an industrial pilot plant in Austria and now has progressed to the point of practical/applied application [8]. Unfortunately, the application is very specific because it is process of a tailor-made system which implication that the operating conditions and liquid membrane formulation were not the same for each ELM systems. Besides that, emulsion stability was the main concern of Emulsion Liquid Membrane in its practical application. The water-in-oil (W/O) emulsion must sustain the stability during the extraction process and easily to be demulsified for the stripping and recovery process. Though there is large number of research on the various metals extraction via ELM, only in [9-11] were attempted to apply ELM for silver extraction and in [12-15] for palladium extraction respectively. Meanwhile, another key process for emulsion liquid membrane application is

demulsification, which is used for recovering the liquid membrane phase containing carrier, surfactant, organic diluent, and high value of solute ions in wastewater treatment processes. Several typical methods of demulsification are thermal breaking, sedimentation, centrifugation, electrostatic and freeze and thaw method. The most established method is a high voltage demulsifier which offered the most effective and simplest method and being used in this study.

The major parameter affecting the extraction efficiency in ELM systems is the types and concentration of carrier, stripping agent for the target metal ion, the level of agitation and the membrane phase viscosity. Besides, other influencing parameters on the extent and rate of extraction are the surfactant concentration used with membrane phase and treat ratio (the volume phase ratio of the emulsion to the aqueous feed).

This paper presents the high selectively extraction of palladium and silver from liquid waste using ELM process containing Cyanex 302 as a mobile carrier, which was conducted in a batch ELM extraction process. Various parameters influencing the transport of silver and palladium across the membrane such as concentrations of carrier and strip agent, and treat ratio was discussed and determined in this research.

METHODOLOGY

Materials and compounds

There are four main components that was used in the ELM system namely stripping agent, carrier/extractant, diluent, and surfactant. Cyanex 302 was used as a extractant/carrier was supplied by Sigma-Aldrich. This carrier was dissolved in kerosene as a diluent with span 80 as a surfactant that was supplied by Fluka. An acidic thiourea (thiourea with sulphuric acid) solution was prepared and used as a strip agent. Sulfuric acid was supplied by Sigma-Aldrich meanwhile thiourea was supplied by Fluka. All materials and compounds used were analytical grade and used as received.

Emulsion Liquid Membrane Extraction

During ELM process, it consists of four steps which are emulsification, extraction/permeation, settling and emulsion breaking/demulsification. Figure 1 shows the metal extraction process using ELM system. The water in oil (W/O) emulsion was prepared by emulsifying aqueous internal phase solution with metal's formulated organic phase. Same volume (5 ml) of formulated organic diluent and aqueous internal solutions were stirred continuously by using homogenizer (IKA, Turrax (8000-24000 rpm)) at formulated speed and emulsification times for each metals as stated in previous study [10, 15] to gain a white stable emulsion. The W/O emulsion have to freshly prepared each time before the permeation experiment to avoid any destruction occurred.

Then, emulsion liquid membrane extraction and recovery of metals were conducted by dispersing the white stable emulsion into feed/external solution of metals ions with a various treat ratio. The W/O/W (water-in-oil-in-water) emulsion was continuously agitated at 250 rpm using an agitator brand Cole-Parmer and model: 50006-00 for 5 minutes. After that, the W/O/W emulsion are quickly placed into a separation funnel and left for phase separation. After collecting the sample at the end of experiment, the samples was analysed using Atomic Absorption Spectroscopy (PerkinElmer, model: AAnalyst 400).

A batch high voltage demulsifier system was used for operation of demulsification/emulsion breaking process. This emulsion was demulsified until the organic and internal phases were visibly separated. The experimentations were conducted at a room temperature.

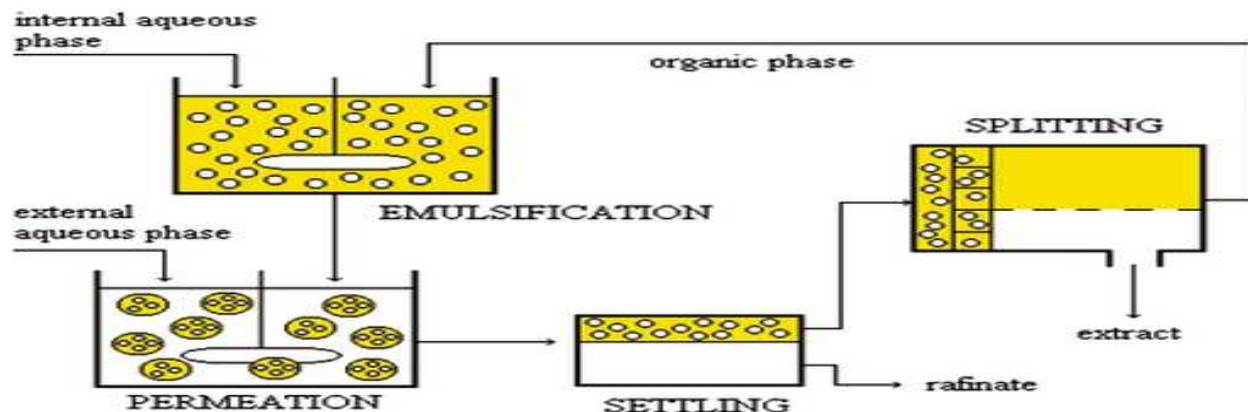


Figure 1: The emulsion liquid membrane process

The percentage of silver/palladium extraction, stripping and enrichment was calculated by using Equation (1)-(3):

$$\text{Extraction (\%)} = \frac{[M]_{\text{initial}} - [M]_{\text{final}}}{[M]_{\text{initial}}} \times 100\% \tag{1}$$

$$\text{Stripping (\%)} = \frac{[M]_{\text{int}}}{[M]_{\text{mem}} \times \text{TR}} \times 100\% \tag{2}$$

$$\text{Enrichment} = \frac{[M]_{\text{int}}}{[M]_{\text{initial}}} \tag{3}$$

where, $[M]_{\text{mem}}$ = Silver/palladium ion concentration in the membrane after the extraction process, $[M]_{\text{mem}} = [M]_{\text{initial}} - [M]_{\text{final}}$ where $[M]_{\text{int}}$ = Silver/palladium ion concentration in the internal aqueous phase after the extraction process, $[M]_{\text{initial}}$ = Silver/palladium ion initial concentration in the aqueous before extraction, $[M]_{\text{final}}$ = Silver/palladium ion final concentration in the aqueous after extraction and TR = Volume W/O emulsion to volume external phase ratio.

RESULTS AND DISCUSSION

Effect of Carrier (Cyanex 302) Concentration

The metals recovery process and permeation rate is strongly influenced by the concentration of cyanex 302 as a carrier. Table 1 presents the effect of Cyanex 302 concentration as a carrier on the extraction and stripping of silver ions from waste solution. The result shows that the extraction percentage of silver was increased when increase the concentration of carrier from 0.01 to 0.04 M. Apparently, with an increasing of carrier concentration, there is more Silver-Cyanex 302 complex can be formed and, hence, the percentage of chromium extracted from feed phase increase gradually. After that, there is no no significant effect on extraction performance when the Cyanex 302 concentration was increased up to 0.05 M. This is due to silver-Cyanex 302 complex that remains in the membrane phase has achieved its maximum percentage that not being strip into the internal phase. Besides, increasing the cyanex concentration over certain limit can affect the osmotic pressure become higher and swelling of the emulsion also increased. Therefore, only small amount of carrier is required in this system for the transporting of silver that should be acts as shuttle vehicle to transport silver ions from the feed phase into the stripping phase.

As can be seen, the percentage of silver strip increased to 100% by increasing concentration of carrier from 0.01 M to 0.03 M. However, the performance drop down to 42% when further increase to 0.05 M. This is due to silver-Cyanex 302 complex that remains in the membrane phase has achieved its maximum percentage that not being strip into the internal phase. The accumulation will increase the silver transport resistance that contribute to a reduction in the stripping percentage. Besides, liquid membrane viscosity will reduced with high concentration of Cyanex 302 that will affect the emulsion stability. This effect can be concluded by the remaining of silver in the feed phase. Thus, it is essential to find the optimum limit of carrier concentration which is having advantageous until a certain level. Otherwise in excess of the carrier concentration would destroy efficiency of the process. The finding shows that the strip and recovery process functions to strip silver from membrane phase into the stripping phase because the silver-Cyanex 302 complexes was not saturated with in the membrane phase.

Table 1: Effect of carrier (Cyanex 302) concentration on silver extraction and stripping (experimental conditions: [Stripping Agent] = 1.0 M acidic thiourea; treat ratio = 1:5, [Span 80] = 3% (w/v), feed phase = Real photographic wastes and agitation speed = 250 rpm)

[Cyanex 302] (M)	% E	% S	Enrichment
0.01	80	58	5
0.02	87	95	8
0.03	93	100	11
0.04	94	100	10
0.05	90	42	4

E= Extraction, S= Stripping

As for palladium, the effects of Cyanex 302 concentration on the extraction and stripping are showed in Table 2. In The ELM system, the right range concentration of carrier is always utilizes an important effect[16]. The results show that by increasing of the Cyanex 302 concentration up to 0.3 M, the palladium extraction percentage significantly increased, which is 95%. This showed that when higher the quantity of Cyanex as a carrier exists in the membrane organic phase, the higher percentage of palladium is react to be extracted. This discovery is in agreement with [17] who exposed that with an increase amount of carrier in the membrane phase, extraction percentages will

increase. Besides, when there is increment concentration of the carrier from 0.3 to 0.7 M, caused in reduction of the extraction percentage to 90%. Too high amount of carrier over certain limit can cause the easy carrier access into the membrane phase leads to accumulation of complexes occurring. Thus, 0.3M of cyanex 302 is sufficient for facilitated transport of palladium.

On the other hand, the results show that there is increment percentage of palladium stripping when increase the carrier concentration up to 0.2 M, which was around 64%. Meanwhile, due to rapidly accumulation of palladium-Cyanex 302 complexes in the membrane organic phase at the 0.3 M of Cyanex 302 concentration, the stripping performances decreased. Increasing the amount of carrier up to 0.7 M in the membrane phase will result in high viscosity of the membrane. Hence, the mass transport resistance was increased and the amount of palladium diffused into the internal phase was decreased. Therefore, the stripping percentage of palladium was declined.

Table 2: Effect of carrier (Cyanex 302) concentration on palladium extraction and stripping in ELM system (experimental conditions: mixing time = 5 min; emulsifying time = 3 min; treat ratio = 1:3; [Stripping Agent] = 1.0 M acidic thiourea; agitation speed = 250 rpm; homogenizer speed = 12000 rpmpH of feed phase = 3.46 and [span 80] = 2% w/v)

[Cyanex 302] (M)	% E	% S	Enrichment
0.1	86	49	2
0.2	91	64	4
0.3	95	57	3
0.5	94	33	2
0.7	90	19	1

E = Extraction, S = Stripping

Effect of Thiourea Concentration

Table 3 presents the concentration of the thiourea effect on silver extraction and stripping performance. Equation 4 shows the reaction of the silver-loaded Cyanex 302 complex with acidic thiourea.



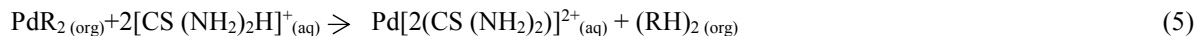
Therefore, when using excess thiourea in the solution, it will disturb the stripping process because it solubility in the organic solution. The permeation thiourea from internal to external phase will form a stable complex with silver in the external phase, which is not transported by the carrier. On the other hand, the extraction performance was increased when increasing thiourea acidic concentration up to 1.0 M. But, there is constant percentage of extraction was observed at 1.5 M of thiourea acidic concentration. This indicates that the excess of thiourea. However, at 0.5 M thiourea the extraction decreased due to not enough an acidic thiourea as stripping agent to react with the metal complexes. It is important in finding the optimum concentration of thiourea and acid solution in the first extraction process. Stripping agent solution strongly influenced the extraction performance. If the strip agent not performs well, the complexes of silver-Cyanex302 will not release into the internal phase. Therefore, the accumulations of silver- Cyanex 302 complexes occur in the membrane phase.

Table 3: Effect of Thiourea concentration on silver extraction and stripping (experimental conditions: [H₂SO₄] = 1.0 M H₂SO₄; [Span 80] = 3% (w/v), treat ratio = 1:5, feed phase = Real photographic wastes, agitation speed = 250 rpm and [Cyanex 302] = 0.03 M)

[Thiourea] (M)	% E	% S	Enrichment
0.25	25	34	1
0.50	54	78	4
1.00	93	100	16
1.50	93	100	24

E = Extraction, S = Stripping

Table 4 indicate the thiourea acidic concentration effects on the palladium extraction and stripping performance. The stripping reaction of palladium-cyanex 302 complex with thioureaacidic is as below:



The results show that when increase the thiourea concentration up to 0.5 M the percentage extraction increased from 86% to 96%, and the additional of thiourea concentration up to 1.5 M give constant percentage of palladium

extraction at around 96%. By increasing the amount of thiourea acidic concentration in the stripping phase, extraction percentage will increase. This is due to the increasing in the size of palladium ion strip.

Meanwhile, although the extraction performance had increased, the results show that the stripping of Pd decreased from 50 to 45% when the concentration of the thiourea was increased from up to 0.5 M. This is owing to the concentrations of the thiourea strip the palladium-Cyanex 302 complexes from the membrane-internal interphase into the stripping phase. There is increment of stripping percentage up to 58% when increase the concentration of the thiourea up to 1.0 M. This indicates that the amount of the thiourea concentration to strip the palladium-Cyanex 302 complexes from the membrane-internal interphase into the stripping phase was increased. Further increases the concentration of the thiourea at 1.5 M, there is decrement on the stripping percentage to 49%. This indicates that there is an excess of thiourea ions in the internal phase. Thus, a 1.0 M H₂SO₄ concentration only needs 1.0 M thiourea concentration to make sure that the acidic thiourea can perform as an excellent stripping agent for Palladium in the ELM process.

Table 4: Effect of stripping agent (Thiourea) concentration on palladium extraction and stripping in Emulsion Liquid Membrane system (experimental conditions: mixing time = 5 min; emulsifying time = 3 min; [H₂SO₄] = 1.0 M; treat ratio = 1:3; agitation speed = 250 rpm; pH of feed phase = 3.46; homogenizer speed = 12000 rpm; [Cyanex 302] = 0.1 Mand [span 80] = 2% w/v)

[Thiourea] (M)	% E	% S	Enrichment
0.3	87	51	3
0.50	96	46	3
1.00	96	58	3
1.50	95	49	3

E = Extraction, S = Stripping

Effect of Treat Ratio (TR)

One of the important roles in ELM extraction performance is treat ratio. It was defined as the volume ratio of W/O emulsion phase to the external feed phase. The treat ratio effect on the extraction of silver was exhibited in Table 5. As present in Table 5, the increasing values of treat ratio from 1:3 to 1:4, the silver extraction was increased due to the increase of water-in-oil-in-water emulsion was formed. Thus, making the surface area for mass transfer increased owing to a larger amount of emulsion globules. Consequently, a higher degree of extraction and stripping was obtained. It is desired to use less amount of emulsion (at the lower treat ratio) to extract silver because it will result in high concentration of silver in the internal phase.

At treat ratio of 1:4, the extraction of silver was decreased due to inadequate amount of droplet (less mass transfer area) to react with the silver. This in agreement with [10] also claimed that it is plausible that there is no sufficient free internal reagent, thiourea acidic to strip the silver ion from complex silver-Cyanex in organic membrane phase. Consequently, there is accumulation of silver-Cyanex 302 complex in the organic membrane phase and the amount of free carrier to diffuse back to react with remaining silver was decrease. The recovery efficiency decrease due to the increasing of internal feed phase volume because of the increasing osmotic pressure difference could also bring the rupture of ELM. Also, water transportation by span 80 as a surfactant still carries on.

Table 5: Effect of treat ratio on silver extraction and stripping (experimental conditions: [Stripping Agent] = 1.0 M acidic thiourea; [Span 80] = 3% (w/v), feed phase = Real photographic wastes, [Cyanex 302] = 0.03 Mand agitation speed = 250 rpm)

Treat Ratio Emulsion : Feed	% E	% S	Enrichment
1 : 3	99	100	11
1 : 4	90	100	11
1 : 5	94	100	9
1 : 6	56	100	8
1 : 7	43	100	8

E = Extraction, S = Stripping

Table 6 exhibited the treat ratio effects on the palladium percentage extraction. The results present that ELM possessed its great ability to extract and strip palladium ions from the feed phase when the lower treat ratio was applied which is 1:3. This is due to the fact that when treat ratio was decrease from 1:3 to 1:10, it tends to decrease possible active site on the emulsion phase available in contact with palladium for permeation process. This is in agreement with [10] who reported that increments in the volume of external feed phase will lower the permeation

rate and decrease the extraction efficiency. On the other hand, when treat ratio was decrease from 1:3 to 1:7, stripping percentage performance was decreases from 58% to 19%. This indicates that, too larger volume of external phase making the emulsion fails to disperse well in order to treat the palladium ions. Hence, the interfacial areas between membrane and internal phases reduce, results the decrement of the palladium extraction and stripping. Previous researcher had agreed that alarge volume of external phase to emulsion will reduce the recovery percentage [18-20]. There is no significant effect on the stripping percentage when increasing of the volume of external phase up to 1:10. It shows that the internal droplets was saturated in the peripheral region of the emulsion.

Table 6: Effect of treat ratio on palladium extraction and stripping (experimental conditions: mixing time = 5 min; emulsifying time = 3 min; [Stripping Agent] = 1.0 M acidic thiourea; agitation speed = 250 rpm; pH of feed phase = 3.46; homogenizer speed = 12000 rpm; [Cyanex 302] = 0.1 M and [span 80] = 2% w/v)

Treat Ratio Emulsion : Feed	% E	% S	Enrichment
1 : 3	96	58	3
1 : 5	94	25	1
1 : 7	82	19	1
1 : 10	81	21	1

E = Extraction, S = Stripping

CONCLUSION

The extraction and recovery of palladium and silver from wastewater using ELM was investigated with respect to various affecting parameters. The higher extraction of palladium from aqueous waste solutions can be achieved at 1.0 M acidic thioureaas the stripping agent, 0.2M of Cyanex 302 as a carrier and 1:3 of treat ratio. While, the higher extraction of silver from wastewater solutions can be achieved at 0.03M of Cyanex 302 as a carrier, 1.0 M acidic thioureaas the strip agent and 1:4 of treat ratio. It was found that the extraction and recovery performance was very encouraging which almost 100% of silver and palladium was extracted and recovered simultaneously in the internal phase. This can be concluded that this formulation is very promising for extracting precious metals of silver and palladium.

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