Selective Extraction of Palladium from Simulated Liquid Waste Solution by Emulsion Liquid Membrane Process using D2EHPA as a Mobile Carrier

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Abstract
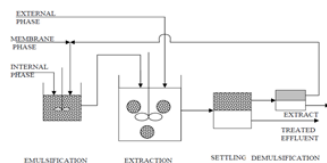
Liquid semiconductor waste has become a serious problem to the environment due to the toxicity of heavy metals in the wastewater. However the monetary value of precious metals such as gold, silver and palladium has become a great concern nowadays. Therefore this study is investigating the recovery of palladium by emulsion liquid membrane (ELM) process using di-(2-ethylhexyl) phosphoric acid (D2EHPA) as a carrier. The important parameters affecting the extraction of palladium such as concentrations of carrier and stripping agents, extraction time and treat ratio were investigate. This experiment was conducted using a mixer-settler in a batch system. The results showed that more than 90% of palladium was extracted using 0.05M D2EHPA, 0.1 M H_2SO_4 as a stripping agent, 5 minutes extraction time, and 1:3 treat ratio. However, the study on emulsion stability showed unstable results due to the leakage and swelling occurrence during the extraction process. As a conclusion, the research shows that ELM has the potential to extract palladium from simulated waste solution using D2EHPA as a mobile carrier.

Keywords: Emulsion liquid membrane; semiconductor waste; D2EHPA; palladium; extraction

◼1.0 INTRODUCTION

Precious metals such as gold, palladium and silver are well-known as valuable metals due to its special electric conductivity and very limited availability. As one of platinum group metals (PGMs), palladium has great value in modern industry due to its favorable physical and chemical properties, such as good corrosion resistance, good wear resistance, high melting point and extraordinary catalytic ability [1-2]. The strong release of palladium into the environment by several industries has meant that its recovery from wastewater has become a major topic of research in wastewater treatment. By going through the recovery process, palladium can be extracted and at the same time reduce environmental problems. Various methods are used to recover palladium from industrial semiconductor waste such as ion exchange [3], solvent extraction [4], chemical precipitation [5], ion exchange and adsorption [6] and liquid membrane process [7]. From this point of view, emulsion liquid membranes (ELMs) proved to be an effective and economical method with potential application for this goal.[3] In this process, both extraction and stripping steps were combined in one stage, which led to simultaneous purification and concentration of the solute [8].

Liquid membrane process consists of four steps which are emulsification, extraction, settling and emulsion breaking/demulsification. The metal extraction process using emulsion liquid membrane system schematically shown in Figure 1. A water-in-oil emulsion (W/O) is prepared in the first step (emulsification) by the creation of a dispersion of the stripping phase droplets within the organic phase containing carrier that is stabilised by the addition of a surfactant appropriate for the organic phase. The separation of the metal starts in the permeation step, when this (W/O) emulsion is dispersed in the feed phase containing the metal to be separated, giving water-in-oil-in-water (W/O/W) emulsion globules. The metal is extracted by chemical reaction with a suitable carrier also added to the organic phase, producing a metal complex soluble in the organic phase that permeates towards the stripping phase. After extraction of the metal, the complex-loaded (W/O) emulsion is separated from the feed phase (settling step) and sent to the splitting step (demulsification) to recover the metal-concentrated stripping phase and return the organic phase to the emulsification step.

Extraction of palladium from simulated wastes by the ELM process is governed by several parameters. The choice of carrier is vital for the success of ELM process and it works on liquid-liquid extraction study. There is research on type of diluent used where aliphatic diluents are more preferred compared aromatic diluent [9]. The type of surfactant used is also one of the factors for membrane stability where different surfactant has different

hydrophilic-lypophilic balance (HLB) according to solution condition [10]. To focus on the palladium metal extraction, there are several studies using ELM process; a novel bi-functional surfactant will acts as an emulsifier and carrier to stabilize the emulsion in low concentration [11]. Other than that, there is study of selective recovery of palladium from simulated industrial waste water by liquid surfactant membrane process, but the palladium was recovered from an acidic solution of high iron concentration where the di-2-ethyhexyl monothiophosphoric acid (MSP-8) acts as a carrier [12]. By using the PX100 at low concentration, high degree of recovery of palladium were obtained.
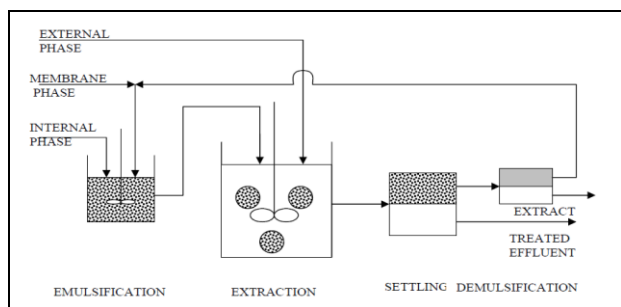

Figure 1 A schematic diagram of mixer-settler extraction using in Emulsion Liquid Membrane (ELM) system [13]

In this present study, the separation of palladium from simulated liquid waste solution containing low concentration of 10 ppm palladium was conducted by ELM using a bis(2-ethylhexyl)phosphate acid (D2EHPA) as a carrier, sorbitan monooleate (span 80) as a surfactant, and kerosene as a diluent in a batch process. In the batch mixer-settler operation, the optimum condition for the effective extraction of palladium and also the membrane stability were investigated. The main parameters influencing the extraction efficiency in the ELM system such as carrier and stripping agent concentration, extraction time and treat ratio are discussed in this paper.

■**2.0 EXPERIMENTAL**

2.1 Reagents and Solutions

There are four components in the ELM system namely carrier, surfactant, stripping agent and diluent. All four components are manufactured for laboratory grade and were used as received. D2EHPA as a carrier for palladium was obtained from Sigma. Kerosene and span 80 as a diluent and surfactant respectively were purchased from Fluka Chemika. Sulfuric acid was purchased from Merck (M) Sdn. Bhd. The apparatus used include Homogenizer Heidolph Silent Crusher M Emulsifier, Perkin Elmer Flame Atomic Absorption Spectrometer (AAS) for concentration measurement of palladium ion. The 10 ppm aqueous palladium solution was prepared and used as feed solution.

2.2 Experimental Procedures

The organic membrane solution was prepared by dissolving the carrier (D2EHPA) and the surfactant (Span 80) in a diluent (kerosene). The internal aqueous phase was a H_2SO_4 solution. An equal volume of 5 mL portions of organic phase and

aqueous phase were stirred continuously at 12000 rpm for about 5 minutes using a motor driven emulsifier to obtain stable water in oil emulsion. The stable white emulsion obtained was then cooled down to the room temperature. Importantly, the emulsion must be freshly prepared before extraction study experiment. The prepared emulsion then dispersed into the agitated vessel with the external solution (waste containing palladium) and stirred at 240 rpm for a few minutes. The aqueous phase was filtered in order to remove entrainment and the raffinate phases are analyzed by AAS. The volume of emulsion before and after extraction was measured for emulsion stability study. The range of parameter used in the ELM extraction of palladium from simulated liquid wastewater is listed in Table 1. The percentage of palladium extraction and swelling or breakage were determined by using Equation 1 and 2. Positive value in Equation 2 represents emulsion swelling while negative value represents emulsion breakage. All experiments were performed at room temperature (26±1°C).

Table 1 Experimental conditions used for the preparations of ELMs

Internal aqueous phase	V_{int}=5 mL
Organic phase	V_{org}=5 mL
Solvent	*Kerosene*
Carrier	*0.01-0.10 M D2EHPA*
Surfactant	*3% (w/v) Span 80*
Stripping agent	*0.01-1.5M H_2SO_4*
Extraction time	*3-15 minutes*
Treat ratio	*1:3 – 1:15*

$$Extraction\ (\%) = \frac{[Pd]_i - [Pd]_f}{[Pd]_i} \times 100\% \qquad (1)$$

$$Swelling/Breakage\ (\%) = \frac{V_f - V_i}{V_i} \times 100\% \qquad (2)$$

Where,

$[Pd]_i$: Initial concentration of palladium ion in aqueous before extraction

$[Pd]_f$: Final concentration of palladium ion in aqueous after extraction

V_i : Initial volume of emulsion before extraction

V_f : Final volume of emulsion after extraction

■**3.0 RESULTS AND DISCUSSION**

3.1 Effect of Extraction Time

Extraction time is the period of time the emulsion phase is in contact with the aqueous feed phase.[9] The experiments were run to investigate the effect of extraction time toward extraction and swelling percentage in order to select the optimal extraction time. Figure 2 shows the percentages of extraction and emulsion swelling at various extraction times. It was observed that increasing the extraction time from 3 to 15 minutes, no significant effect can be observed on the extraction percentage, where more than 90% of palladium was extracted. This means that 3 minutes of time is sufficient for the extraction process. However, emulsion stability was significantly affected by the extraction time in the process. It can be seen that higher swelling occurs within 3 minutes of the extraction time. This is due to the production of larger emulsion droplets, which leads to an increase in the permeation coefficient of water into the membrane phase. However, at 5 minutes of extraction time, the percentage of extraction is more than 96% and no swelling was observed. This shows that 5 minutes extraction time is the

optimum condition to perform ELM system. Further increase up to 15 minutes, caused the swelling percentage to gradually increase. This is due to the fact that by extending the extraction time, the emulsion promotes more entrainment of water into receiving phase of emulsion. This was in agreement with Chiha *et al.* (2006) who indicated that increasing extraction time will increase emulsion breakage [14]. Meanwhile, Kulkarni *et al.* (2000) also agreed that the longer extraction of time will cause the membrane to swell due to more water being transferred into the internal phase and break the emulsion where the solute was transferred from internal to external phase [15]. Thus, 5 minutes of extraction time was chosen for the next experiment.
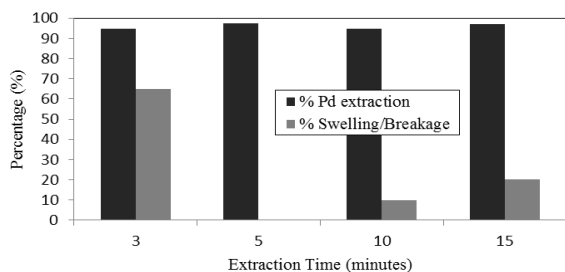

Figure 2 Percentages of extraction and swelling at various extraction time [Carrier] =0.1 M D2EHPA, [Stripping agents] =0.1 M H$_2$SO$_4$, Aqueous/Organic =5 mL/5 mL, Homogenizer speed =12000 rpm, Emulsion time =5 min, Stirrer speed =240 rpm, Treat ratio =1:3

3.2 Effect of Treat Ratio (Volume Ratio of Emulsion to External Phase)

Treat ratio is defined as the volume ratio of emulsion phase to the aqueous external phase. The effect of treat ratio on palladium extraction and emulsion swelling is exhibited in Figure 3. Decreasing the treat ratio from 1:3 to 1:15 tends to slightly reduce the extraction performance. This is due to the decrease in the capacity of the emulsion phase is in contact with external phase that reduce the extraction and stripping of the palladium ion into the internal phase. This is in line with Othman *et al.* (2006)[9] who reported that an increment in the volume of external phase will decrease the extraction efficiency. The results show that the swelling occurs at 1:3 treat ratio. This is due to the large amount of water molecules present in the external phase transport into the membrane phase by the surfactant molecules. Meanwhile, for treat ratio of 1:5 and 1:10, no swelling or breakage was observed, which indicates that some globules tend to swell and break at the same time. Therefore, there exists a trade-off between these two effects. Further increase of treat ratio up to 1:15, the emulsion breakage was observed. It seems possible that these results are due to shear or hydrodynamic effect of the process. Goyal *et al.* (2011) have discussed that an increase of the volume of external phase will increase the possibility of swelling and breakage of the emulsion [16].
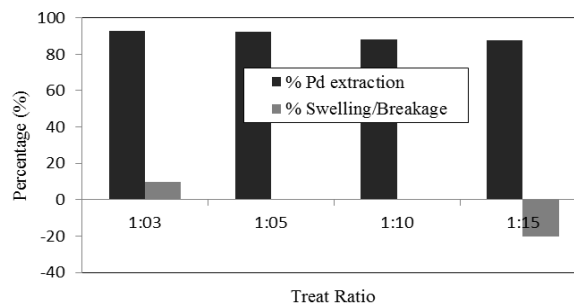

Figure 3 Percentages of extraction and swelling at various treat ratio [Carrier] =0.1 M D2EHPA, [Stripping agents]=0.1 M H$_2$SO$_4$, Aqueous/Organic =5 mL/5 mL, Homogenizer speed=12000 rpm, Emulsion time=5 min, Stirrer speed=240 rpm, Extraction time=5 min

3.3 Effect of Concentration Stripping Agents

Figure 4 presents the effect of stripping agent concentration on the percentages of palladium extraction and emulsion swelling. The concentrations were varied from 0.01 to 1.0 M. It can be seen that increasing the concentration of H$_2$SO$_4$, no significant effect can be observed on the extraction percentage where more than 90% was extracted. This indicates that 0.05 M of H$_2$SO$_4$ concentration is enough for extraction of palladium. However, further increase in H$_2$SO$_4$ concentration from 0.01 to 1.00 M tends to increase the emulsion swelling. This can be explained by the increase of hydrogen ion concentrations which gives a higher pH difference between the external phase and the internal phase. This condition might lead to a high osmotic pressure gradient between the internal and external phases. Therefore, more water molecules were transported from the external into internal phase. This finding is in agreement with Malik et al (2011) who indicate an increase of the stripping agent concentration gives a higher pH difference between both external and internal phase, which increases the osmotic pressure and cause membrane swelling [17]. The suitable concentration exists for H$_2$SO$_4$ as a stripping agent, and the optimum value was obtained at 0.1 M in which higher degree of palladium extraction and minimum percentage of swelling.
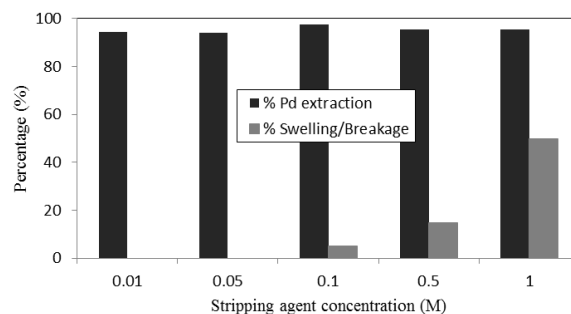

Figure 4 Percentages of extraction and swelling at different stripping agent concentration [Carrier] = 0.1 M D2EHPA, [Stripping agents]= H$_2$SO$_4$, Aqueous/Organic =5 mL/5 mL, Homogenizer speed=12000 rpm, Emulsion time=5 min, Stirrer speed=240 rpm, Extraction time=5 min, Treat ratio=1:3

3.4 Effect of Carrier Concentration

The effect of carrier concentration on the extraction of palladium is presented in Figure 5. The results show that more than 80% of palladium was extracted at 0.01 M. Further increasing the concentration up to 0.1 M provided no significant effect on the palladium extraction. This indicates that 0.01 M is enough for facilitated transport of palladium. However, 20% of emulsion swelling was observed at 0.01 M. This is might be due to the transportation of water into the internal phase by hydration of surfactant. At 0.05 M no swelling was observed. Further increasing the carrier concentration up to 0.1M significantly increased the emulsion swelling. This indicates that besides the solute molecules in the external phase reacting with the carriers at the interphase, at the same time these D2EHPA-Pd complexes also react with water molecules. Thus, water molecules in the external phase were carried by the carrier–solute complex into the internal phase. This is in line with Yuanli *et al.* (2001) who indicates that solubilization of water in the membrane phase is caused not only by surfactant but also by carrier–solute complexes [18]. Based on the emulsion phase, the most stable emulsion occurs at 0.05 M D2EHPA.
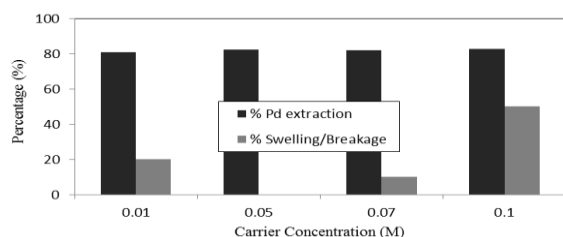

Figure 5 Percentages of extraction and swelling at different carrier concentration [Carrier] = D2EHPA, [Stripping agents]= 0.1 M H_2SO_4, Aqueous/Organic =5 mL/5 mL, Homogenizer speed=12000 rpm, Emulsion time=5 min, Stirrer speed=240 rpm, Extraction time=5 min, Treat ratio=1:3

■4.0 CONCLUSION

The extraction of palladium from a simulated liquid waste solution by emulsion liquid membrane was studied by investigating four parameters which are carrier and stripping agent concentration, treat ratio and extraction time. The highest extraction was obtained at conditions 0.05 M D2EHPA, 0.1 M H_2SO_4 as stripping agent, 5 minutes of extraction time and with a 1:3 treat ratio of the emulsion phase to the aqueous external phase solution. As a conclusion, the research shows high possibility of palladium extraction from simulated liquid waste using ELM process.

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