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Emulsion Stability of Palladium Extraction Containing Cyanex 302 as a Mobile Carrier in Emulsion Liquid Membrane Process

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Emulsion Liquid Membrane (ELM) process is one of the alternative techniques to extract solutes from wastewater. It has been given considerable attention due to its advantages such as simultaneous extraction and recovery in a single step operation, non-equilibrium mass transfer, high fluxes, low energy consumption, reusability and high selectivity. The main concern in order to achieve high stability in the process is the size of internal droplets of primary emulsion. This study aims to investigate the affecting parameters such as concentration of surfactant, emulsification speed and emulsification time. ELM process containing bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) as a mobile carrier in kerosene and acidic thiourea as stripping agent was used. The stability results showed that 2.8 µm of droplet diameter was formed at favorable condition of 2 % w/v surfactant concentration, 12,000 rpm of emulsification within 3 min of emulsification time. At this condition, 84 % of Palladium was extracted.

1. Introduction

Palladium is normally used to plate semiconductor components in order to improve the component's electrical contact. As the metal are rare and very low concentrations in wastewater, the development of effective extraction and recovery processes is seriously required for palladium. Recovery of palladium from electroplating waste is attractive due to its high market value together with various applications in the industry. Because of the special electric conductivity and limited accessibility properties of palladium, recovering this metal from the electroplating waste solutions is economically interesting.

There are many techniques which have been commercially recognised to extract palladium from wastewater. For instance, ion exchange is one of the simple ways to separate palladium (Hubicki and Wolowicz, 2009). A disadvantage to this form of treatment is that this method involves high operating costs for the ion exchange unit due to resin costs. Solvent extraction has become an effective technique in the recovery and separation of palladium (Costa et al., 2016). Various problems have been associated with solvent extraction systems such as the corresponding hydrodynamics related problems, third phase problems, and compatibility issues with the diluent. A feasibility study was carried out on Indian almond leaf biomass (*Terminalia catappa L.*) by biosorption to remove palladium and platinum ions from water solution (Ramakul et al., 2012). Since biosorption frequently employs dead biomass, it can eliminate the problem of toxicity environments and the need of nutrient requirement (Volesky, 1990).

In order to realise the recovery, it is vital that an efficient recovery process is developed for the palladium. As an alternative, emulsion liquid membrane is one of the configurations in liquid membrane technology which was chosen in this present work due to several advantages over other methods, including single stage operation of both extraction and stripping, less energy requirement (Sulaiman et al., 2014), ease of functioning, less chemical consumption, low cost factor (Noah et al., 2016) and large interfacial area (Othman et al., 2016). As the concentration of palladium is very low in wastewater, the development of effective extraction and recovery

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processes is seriously required for palladium. This process can treat palladium even at very low concentrations and the extracted metal will be concentrated more than 10 times of the external phase in recovery phase (Ramazani et al., 2007). ELMs allow a highly selective transport and efficient enrichment of palladium ions through a very thin liquid membrane. ELM has been intensively investigated and demonstrated as an effective alternative technology for separation and purification process for precious metal extraction such as silver (Othman et al., 2006a), gold (Kargari et al., 2006) and palladium (Kakoi et al., 1996).

One of the disadvantages of ELM systems is their tendency to undergo swelling and internal phase leakage (breakage). When the membrane leakage, rupture or breakdown occurs, the previously extracted solutes as well as the stripping reagent are released back into the feed stream and this will have significant effect on the extraction efficiency of the ELM system (Tang et al., 2010). The instability of ELM is normally due to the globule rupture and osmotic swelling. Globule rupture is caused by the excessive interfacial shear between the continuous and membrane phase; the liquid membrane become thinner and easier to break. Osmotic swelling occurs when water diffuses from the external phase into the internal phase. In practical process, an emulsion swelling of about 10 % is considered acceptable while membrane leakage at the rate of about 0.1 % is allowable (Perera and Stevens, 2008). This research was conducted to investigate the effect of palladium extraction and membrane stability performance in ELM process.

2. Extraction mechanism of palladium

In the ELM process, both the extraction and stripping steps occur simultaneously. The mechanism for the extraction of palladium using ELM process is shown in Figure 1. In this mechanism the carrier, Cyanex 302 chemically reacts with the cationic palladium in kerosene to form complexes of Pd-Cyanex 302 at the membrane-external as illustrated by Eq(1). After that, the Pd-Cyanex 302 complexes diffuse through the membrane phase from the membrane-external interphase to the membrane-internal interphase. The Pd-Cyanex 302 complexes at the membrane-internal interphase undergo the stripping process by reacting with acidic thiourea from the internal phase as shown in Eq(2). The Pd-thiourea complexes released to the internal phase and the carriers diffuse back to the membrane-external interphase to react with other Pds.

$$\mathrm{Pd^{2+}}_{\mathrm{(aq)}} + \mathrm{(RH)_{2\,(org)}} \rightarrow \mathrm{PdR_{2\,(org)}} + 2(\mathrm{H^+})_{\mathrm{(aq)}} \tag{1}$$

Where, $(RH)_2$ represents the Cyanex 302in the liquid membrane phase and Pd^{2+} is palladium in liquid phase.

$$\mathrm{PdR_{2\,(org)}} + 2[\mathrm{CS(NH_2)_2H}]^{+}{}_{\mathrm{aq}} \rightarrow \mathrm{Pd[(CS(NH_2)_2)_2]^{2+}}{}_{\mathrm{(aq)}} + \mathrm{(RH)_{2\,(org)}} \tag{2}$$

Where, $[CS(NH_2)_2H]^+$ is thiourea in H_2SO_4 in aqueous phase (protonated thiourea under an acidic condition)

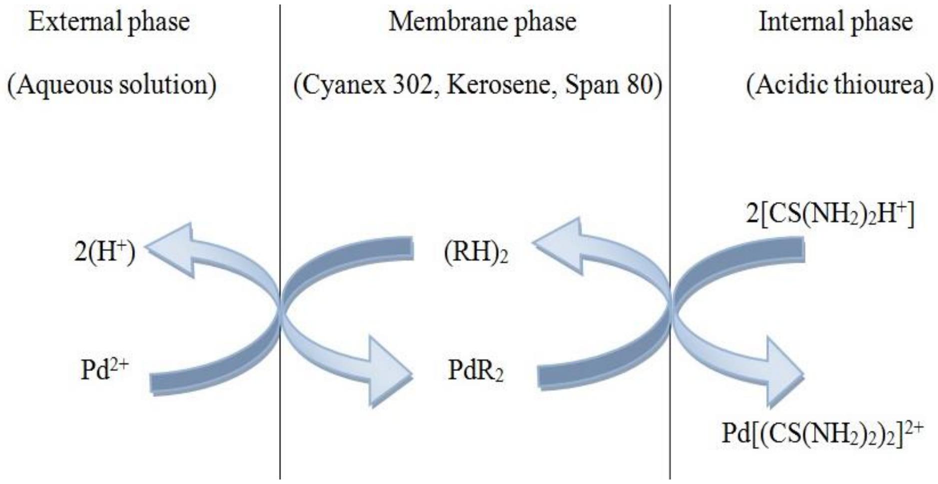

Figure 1: Schematic transport mechanism of palladium by ELM from the aqueous solution using Cyanex 302 as carrier (Noah et al., 2016)

3. Experimental

3.1 Reagents and solutions

There are four components in ELM system namely carrier, surfactant, stripping agent and diluent. All four components are manufactured for laboratory grade and were used as received. Cyanex 302 as a carrier for palladium was obtained from Sigma. Kerosene and Span 80 as a diluent and surfactant were purchased from Fluka Chemika. Thiourea and Sulfuric acid was purchased from Merck (M) Sdn. Bhd. The apparatus used including Homogeniser 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.

3.2 Experimental Procedures

The organic solution was prepared by dissolving an appropriate concentration of the carrier (Cyanex 302) and the surfactant (Span 80) in a diluent (kerosene). The internal aqueous phase was a Thiourea in H_2SO_4 solution. An equal volume of 5mL portions of organic phase and aqueous phase were stirred continuously at 12,000 rpm for about 5 min using a motor driven emulsifier to obtain stable water in oil emulsion. The emulsion must be freshly prepared before each experiment of extraction study. The prepared emulsion then dispersed into external phase containing palladium in the agitated vessel and stirred at 250 rpm for a few min. The aqueous phase was filtered in order to remove entrainment and the raffinate phases are analysed 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 waste was listed in Table 1. The liquid membrane component for this study such type of diluents and stripping agent and its concentration for palladium extraction is taken from previous studies (Othman et al*.,* 2014). All experiments were performed at a room temperature (26 ± 1 °C).

Table 1: Experimental conditions used for the preparations of ELMs

Solvent	Kerosene
Carrier	0.10 M Cyanex 302
Surfactant	1 – 7 % w/v Span 80
Stripping agent	1.0 M Thiourea in 1.0 M H2SO4
Extraction time	5 min
Emulsifying time	1 – 10 min
Treat ratio	1 : 3
Homogeniser speed	8,000 - 13,500 rpm
Agitation speed	250 rpm
pH of internal phase	3.46
Temperature	± 26 ºC

The percentage of palladium extraction and swelling or breakage was determined by using Eq(3) and (4):

$$\text{Extraction (\%)} = \frac{[\text{Pd}]_\text{i} - [\text{Pd}]_{[\text{f}]}}{[\text{Pd}]_\text{i}} \text{ x } 100\ \% \tag{3}$$

$$\text{Swelling/Breakage (\%)} = \frac{\text{V}_\text{f} - \text{V}_\text{i}}{\text{V}_\text{i}} \text{ x } 100\% \tag{4}$$

where, $[\text{Pd}]_\text{i}$is the initial concentration of Pd ion in aqueous before extraction, $[\text{Pd}]_\text{f}$ represents the final concentration of Pd ion in aqueous after extraction, V_i is the initial volume of emulsion before extraction, and V_f is the final volume of emulsion after extraction.

Image of emulsion droplet was measured using a microscope with camera and directly connected to Video Structure Image Analyser software at the computer. One drop of emulsion was carefully placed on a glass slide and by using the microscope with a camera, a few photos were captured. The photo was analysed and an average diameter of emulsion droplets was examined using the software.

4. Results and Discussion

4.1 Effect of Surfactant Concentration

The stability of ELM and permeation rate of palladium is strongly influenced by the concentration of surfactant. The emulsion stability is influenced by problems in the formation of emulsion droplets and viscosity of liquid membrane. Table 2 illustrates the influence of surfactant concentration on the palladium extraction, viscosity of liquid membrane and average sizes of droplets. The concentrations were varied from 1 to 7 % w/v. It was observed that palladium extraction had increased from 47 % to 84 % when the surfactant concentration was increased from 1 % to 2 %. Also, the size of droplet decreased from 5.6 to 3.0 µm as the concentration of the surfactant increased from 1 % to 2 %. This is because when increasing the span 80 concentration, the surface tension of the membrane phase will decrease, resulting in formation of smaller emulsion droplets. The mass transfer area and contact area will increase between the donor and the internal phase, hence increasing the removal efficiency. This finding is in line with Praipruke et al. (2012) and Noah et al. (2014) who reported that significant increases in the extraction rate due to a low surface tension of the membrane phase, resulting in small sized emulsion droplets, allow a faster mass transfer for palladium extraction.

Further increases to 7 % w/v of span 80 concentration resulted in a decrease of extraction efficiency for palladium from 84 % to 76 %. It is because the high surfactant concentration can hinder mass transfer of the solute by increasing the interfacial viscosity and interfering with the carrier reactions at the interphase. Table 2 shows that the concentration of Span 80 apparently affects the viscosity of the liquid membrane. The same conditions were attempted by Yang et al. (2005) who demonstrated that the increased of surfactant concentration will lead to higher emulsion viscosity. This condition will lead to decreasing extraction performance.

Table 2: Effect of surfactant concentration on the size of droplet (Experimental conditions: Homogeniser speed = 12,000 rpm; emulsifying time = 5 min)

Span 80 concentration (% w/v)	% extraction	Average size of droplet, (µm)	Liquid membrane viscosity (cP)
1	47	5.61	2.4
2	84	3.00	2.8
3	82	2.77	3.0
5	79	2.72	3.2
7	76	2.67	3.4

4.2 Effect of Emulsifying time

Another factor that influences the stability of ELM process is its emulsifying time. The effect of emulsifying time on palladium extraction, and average size of droplet is exhibited in Table 3.

Table 3: Effect of emulsifying time on the size of droplet (Experimental conditions: homogeniser speed = 12,000 rpm; [Span 80] = 2 % w/v

Emulsifying time (min)	% extraction	Average size of droplet, (µm)
1	68	5.6
3	75	2.5
5	64	2.8
7	64	2.7
10	60	2.7

Increasing the emulsifying time from 1 to 3 min tend to increase the palladium extraction from 68 % to 75 %. Increases in emulsifying time up to certain limits will affect the performance of internal phase dispersion as droplets in the membrane phase will increase and the size of the emulsion droplets becomes smaller, creating a larger surface area for mass transfer of palladium from the external phase into internal phase. More palladium will be extracted. It shows an agreement with Chiha et al. (2006) who showed that increases in emulsifying time will increase the percentage of extraction. It is also supported by average size of the resulting emulsion droplet as shown in Table 3. As illustrated in Table 3, the size of droplets decreases from 5.6 to 2.5 µm with increases in emulsifying time from 1 to 3 min. Further increases up to 5 min result in decreases of the palladium extraction percentage from 75 % to 64 % and increases in the size of emulsion droplet from 2.5 to 2.8 µm. It could be explained that by increasing emulsifying time beyond certain limits, internal phase droplets will coalesce and become larger droplets as seen in Table 3. Further increase up to 10 min result in slightly decreases of the palladium extraction percentage. This is because the droplets had coalesced, resulting in decreases of the mass transfer area. The palladium extraction rate will decrease.

4.3 Effect of Homogeniser Speed

Homogeniser speed influences the stability of emulsion and consequently, the extraction efficiency. An efficient homogeniser speed gives a uniform dispersion of the internal phase droplets into the membrane phase and it can provide emulsion globules with thinner membrane layers. Table 4 presents the effects of homogeniser speed on the percentages of palladium extraction and average size of emulsion droplet. The results show that at 8,000 rpm homogeniser speed, the palladium extraction efficiency is around 70 %. This indicates that slow mixing offers less interaction between the emulsion and palladium solutions treated, hence reducing the efficiency of ELM system. There was an augment of palladium extraction when the homogeniser speed was increased to 12,000 rpm. This is due to the decrease in size of internal droplet that occurs with the increase of homogeniser speed. It can be seen from Table 4 that the size of emulsion droplets decreased from 5.5 to 2.8 µm when the homogeniser speed was increased from 8,000 to 12,000 rpm. The smaller the emulsion droplets, the more number of emulsions are produced in certain volumes, and the surface area had definitely increased. The extraction performance also increases. This is in agreement with Gasser et al. (2008) who indicated that high homogeniser speeds are desired to obtain the smallest size of emulsion droplets. A larger interfacial area can also be obtained with an optimal homogeniser speed. Othman et al. (2006b) also stated that the size of emulsion droplets depends on the homogeniser speed. The removals of solute percentages increase with increases in homogeniser speeds.

Further increases up to 13,500 rpm had resulted in no significant effects on the palladium extraction which had stayed at 85 %. This indicates that 12,000 rpm homogeniser speed is enough for extraction of palladium. This is in line with Fouad (2008) who stated that increases in the speed of agitation above a critical value did not increase the extraction efficiency. As seen in Table 4, by increasing the homogeniser speed, the emulsion droplets become smaller, hence it will take much more time to coalesce. The emulsion becomes more stable. This is consistent with Malik et al. (2012) who indicated increases in homogeniser speed will lead to a large number of small droplets, which leads to higher stability. As the homogeniser speed increases from 12,000 to 13,500 rpm, the size of emulsion droplets remains stable around 2.7 µm.

Table 4: Effect of emulsifying speed on the size of droplet (Experimental conditions: [Span 80] = 2 % w/v; Emulsifying time = 5 min)

Emulsifying speed (x1,000 rpm)	% extraction	Average size of droplet, (µm)
8	70	5.6
10	77	3.0
12	85	2.8
13.5	85	2.7

5. Conclusions

The stability of emulsion in ELM process of palladium extraction was studied. Several parameters affecting the emulsion size such as surfactant concentration, emulsification speed and time were investigated. Based on the results obtained it can be concluded that, 2.8 µm size of emulsion droplet diameter was suitable and provide most stable condition for extraction of palladium. This stable emulsion formed at favourable conditions of 2 % w/v surfactant concentration, 12,000 rpm of emulsification speed and 3 min of emulsification time. At this condition, 84 % of Palladium was extracted.

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