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Highly selective transport of palladium from electroplating wastewater using emulsion liquid membrane process

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ABSTRACT

A new liquid membrane formulation containing phosphinic acid groups as a carrier was developed for the selective extraction of palladium (Pd) from electroplating wastewater using emulsion liquid membrane (ELM) process. The important parameters that affect the membrane stability and the recovery of Pd were investigated, such as extraction time, concentrations of carrier and stripping agents, pH of feed phase, and treat ratio. Furthermore, at the optimum condition, the performance of Pd extraction was evaluated using real matrices solution. All experiments were carried out using batch extraction process and the recovery stage at high voltage demulsifier was employed. The results showed that the favorable conditions obtained for the extraction and the recovery processes were at 0.2 M of Cyanex 302, 1.0 M thiourea in 1.0 M H_2SO_4 of stripping agent, 1:3 treat ratio, pH 3 of feed phase, and 5 mins of extraction time. At these conditions, the maximum extraction and recovery of the Pd was 97% and 40%, respectively. Moreover, the result from the real matrices showed that almost 100% of Pd was extracted selectively over chromium at these conditions.

1. Introduction

Recovery of electroplating wastewaters is an important subject not only from the view of waste treatment but also from the recovery of valuable metals that is Pd. Exposure of Pd can cause acute toxicity or hypersensitivity with respiratory symptoms, urticaria and less frequently, contact dermatitis. The epidemiological studies have demonstrated that the Pd ions are one of the most frequent reacting sensitizers, which affect the immune system that represents the most important health hazard to humans [1]. Pd with unique physical properties has been used in diverse industrial applications such as jewelry, semiconductors and connectors. These applications take benefit of Pd's lower cost and its material properties that are superior to gold. Due to its economic value and its limited natural resources, Pd recovery from the secondary resources is significant. According to the invention [2], the amount of Pd used in Pd exchange bath is 0.150–0.25 g/L [2]. Out of the total amount of precious metals used in electroplating, 4% goes as waste in the sludge spent wash and the electroplating solution [3]. Hence, it can be concluded that the Pd composition in the electroplating wastewater is in the range of 6–10 ppm.

In order to separate the Pd from aqueous solutions, various studies have been recently focused on conventional methods. For example, an ion exchange is one of the simple ways to separate Pd [4]. A disadvantage of this treatment is the method involves high operating costs for the ion exchange unit due to the resin costs. Biosorption is another efficient low cost process of Pd ions recovery from aqueous solutions. Since the biosorption frequently employs dead biomass, it can eliminate the problem of toxicity environments and the need of nutrient requirement [5]. Solvent extraction has become an effective technique in the recovery and separation of Pd [6,7]. However, various problems have been associated with the solvent extraction systems, such as the corresponding hydrodynamics related problems, third phase problems, and compatibility issues with the diluent.

In 1968, emulsion liquid membranes (ELMs) were first applied to the separation of hydrocarbons [8]. Recently, the ELM technology has become a promising method to recover precious metals, even in a very low concentration from the industrial wastes [9,10]. Since the ELM process combines the extraction and recovery process, this method does not need the second treatment like electrowinning that needs cementation or chemical precipitation process [11,12]. Due to its high surface area to volume ratio compared to solid membranes, it has high solute transfer flux and selectivity as well as low contacting equipment volume and cost [11,13], and it is chosen as the suitable method to extract and recover Pd

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Table 1
Experimental conditions used for the preparations of ELMs.

Solvent	Kerosene
Homogenizer speed (HS)	12,000 rpm
Emulsifying time	3 mins
Agitation speed (AS)	200 rpm
Surfactant	2% (w/v) Span 80
Carrier	0.001–0.7 M Cyanex 302
Stripping agent (SA)	0.3, 0.5, 1.0, and 1.5 M Thiourea in 0.3, 0.5, 1.0 and 1.5 M H_2SO_4
Treat ratio (TR)	1:3, 1:5, 1:7, 1:10
pH feed phase	1, 3, 5, 7
Extraction time	1, 3,5, 7, 10 mins

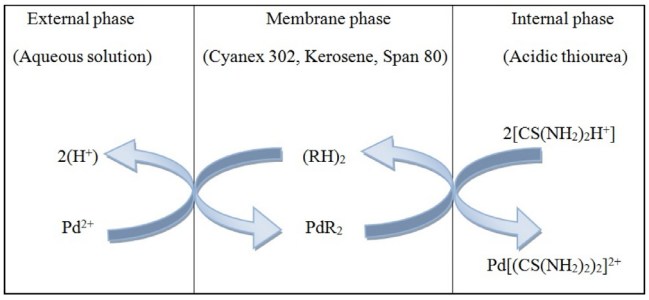

Fig. 1. Schematic transport mechanism of Pd by ELM from the aqueous solution using Cyanex 302 as carrier.

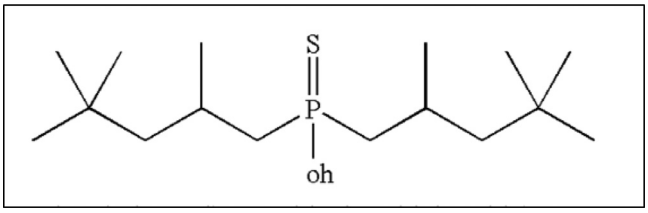

Fig. 2. Structure of Cyanex 302.

from the electroplating wastewater. ELM has been intensively investigated and demonstrated as an effective alternative technology for the separation and purification process for precious metal extraction such as silver [14], gold [15] and Pd [16]. Hence, in this research, the ELM process was utilized for the recovery of Pd from the electroplating wastewater. The ranges of parameters used in the ELM extraction of Pd from the simulated liquid waste are listed in Table 1. The liquid membrane components such as type of diluents and stripping agent and its concentration for the Pd extraction are taken from the previous studies [17].

2. Extraction mechanism of palladium

The transport mechanism of Pd by the ELM process using Cyanex 302 as a carrier is shown in Fig. 1. In this mechanism, the selected carrier, Cyanex 302 (Fig. 2) chemically reacts with the cationic Pd in kerosene to form complexes of Pd–Cyanex 302 at the membrane-external interphase as represented by Eq. (1).

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

After that, the Pd–Cyanex 302 complexes diffuse through the membrane phase from the membrane-external interphase to the membrane-internal interphase. Then, the Pd–Cyanex 302 complexes at the membrane-internal interphase undergo the stripping process by reacting with the 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

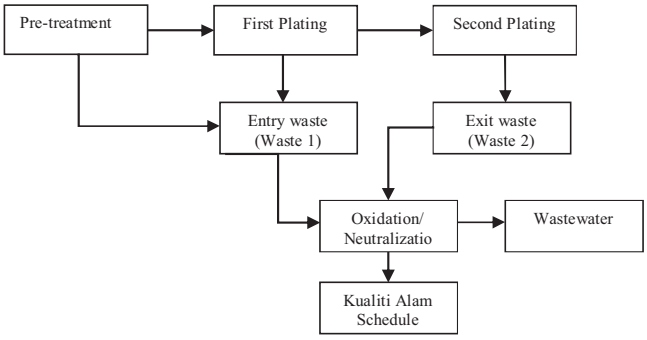

Fig. 3. Electroplating wastewater process flow diagrams.

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

3. Materials and methods

3.1. Materials

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. The Cyanex 302 (85% purity) as a carrier for Pd was obtained from Sigma. The kerosene (99% purity) and span 80 (99% purity) as a diluent and surfactant respectively were purchased from Fluka Chemika. The thiourea (99% purity) and sulfuric acid (99% purity) were purchased from Merck (M) Sdn. Bhd. An aqueous solution of Pd was prepared using palladium (II) nitrate ($Pd(NO_3)_2$) obtained from Merck (M) Sdn. Bhd. The water used in this research was distilled water.

3.2. Electroplating waste sample and characterization process

The real electroplating wastewater sample was obtained from the Electroplating Company at Masai, Johor. Ion chromatography (IC) model LC20 with electric chemical detector model ED40 was used to measure anion contents in the sample. Contents of metals in the electroplating wastewaters were measured using an atomic absorption spectrometer (AAS) (PerkinElmer, model: Analyst 400). A Cyber scan 100 pH meter model was used to measure the pH measurements. A hydrometer was used to measure the densities (ρ) of the samples. A programmable Rheometer Brookfield Model DV-III was used to determine the kinematic viscosity, ν [14].

3.3. Palladium in simulated electroplating wastewater

The palladium (II) nitrate was dissolved into real electroplating wastewater in the concentration range of 1–15 ppm. Then, the initial pH of the feed phase was measured. The pH for each sample was adjusted in the range of 3.0–3.5. In this preparation, two types of waste solutions were considered in the electroplating process, which were Waste 1 and Waste 2 for entry and exit effluents, respectively, as shown in Fig. 3.

3.4. Water in oil (W/O) emulsion preparation

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 stripping phase