

## Liquid-Liquid Extraction of Palladium from Simulated Liquid Waste using Phosphinic Acid as a Carrier

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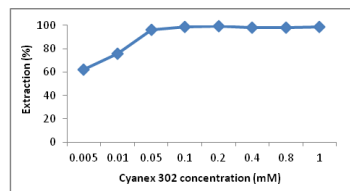
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### Graphical abstract



### Abstract

Nowadays, extraction and recovery of metals from industrial wastewater has become a major concern owing to the toxicity of heavy metals and economic value of precious metals such as gold, palladium and silver. In this research, the extraction of palladium from simulated aqueous solution using liquid-liquid extraction was studied. The organic phase containing bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) as a carrier was used. Several parameters such as concentration of carrier, type of diluents and stripping agent type and its concentration were investigated. The results showed that at the favourable condition of 0.1 mM Cyanex 302 in kerosene as a diluent, and 2.0 M of thiourea in 1.0 M sulphuric acid as a stripping agent, almost 100% of palladium was extracted from the liquid waste solution and 90% was recovered in the receiving phase.

**Keywords:** Solvent extraction; phosphinic acid; palladium; extraction; wastewater

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### 1.0 INTRODUCTION

Recently, the development of an efficient method for the recovery of palladium metals from industrial wastes has come under serious concern due to the palladium are known to possess unique physical and chemical properties that are suitable for manufacturing industrial materials such as catalysts, electrical and corrosion-resistant alloys. Therefore, it is essential to develop an effective and inexpensive recovery process for palladium. There are a large number of separation processes applicable to recover palladium from industrial wastewater which are biosorbent [1], ion exchange [2], membrane separations [3], precipitation [4] and adsorption [5] but these methods have some limitation.

The solvent extraction process has already been industrially applied to the recovery of precious metals [6]. It has been widely used as a process for separation, purification, and recovery of rare metals, due to its simplicity of equipment and operation. Solvent extraction also identified as liquid-liquid extraction, is a technique to separate compounds based on their relative solubility in two different immiscible liquids, usually water and an organic solvent by shaking mechanically equivalent volumes of aqueous and organic solution at room temperature until it achieve equilibrium. However because metal salts are usually not soluble in organic solvents, the process requires the introduction of an extractant that will combine with the metal ion to form an organic soluble species.

The advantage of solvent extraction includes high throughput, ease of automatic operation and of scale up, and high purification.

The biggest disadvantage of solvent extraction compared with the liquid membrane process is that it must always be in equilibrium conditions [7]. Extraction of palladium wastewater by the solvent extraction process is governed by several parameters. The choice of carrier, diluents and stripping agents is vital for the success of solvent extraction process. Organophosphorus acid compounds have been widely used as an extractant in recent years in solvent extraction of many metal ions on a commercial scale [8]. Among these, bis(2,4,4-trimethylpentyl) monothiophosphinic acid has been widely studied as an extractant for titanium separation [9], copper separation [10] and silver extraction [7, 11]. Cyanex 302 is the sulfur substitution of organophosphorous extracting reagent. This reagent should therefore be beneficial for the extraction of metal ions [12]. The significantly lower electronegativity of sulfur renders it more polarizable than oxygen. Electrons are more readily shared in a metal-sulfur bond than in a metal-oxygen bond, introducing a greater degree of covalency and increasing the strength of the bond [11].

In the present study, liquid-liquid extraction of palladium from simulated liquid waste solution using Cyanex 302 as a carrier was studied. This is the preliminary study for screening the suitable carrier, diluents and stripping agent used in liquid membrane process. To the best of our knowledge, no studies have been reported on the recovery of palladium using Cyanex 302 as a carrier in emulsion liquid membrane (ELM) process. Liquid membrane process is a new separation process as a modification of solvent extraction. The simultaneous extraction and stripping operation is

very attractive, because it can transport the solute of interest from a low concentration solution to a high concentration solution with suitable carrier in one step process [7]. Therefore, this is an important part in liquid membrane formulation which is based on solvent extraction.

## 2.0 EXPERIMENTAL

### 2.1 Materials and Apparatus

All the chemicals are analytical grade reagents and used without purification. The following reagents were used: Palladium stock solution, bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) as a carrier and Thiourea were obtained from Sigma Aldrich. Kerosene, chloroform, and toluene were purchased from Fluka. Palm oil was purchased from Buruh. Hydrochloric acid, sodium hydroxide and sulphuric acid were procured from Merck. The equipment required to measure palladium concentration was Atomic Absorption Spectrometry (AAS). For agitation of solutions a mechanical shaker was used (IKA-KS 130 Basic, Germany). The 10 ppm aqueous palladium solution was prepared and used as simulated aqueous waste solution.

### 2.2 Liquid-Liquid Extraction

The experiments on the rate of forward extraction were carried out by mixing an equal volume (10 mL) of organic solvent (Cyanex 302 in diluent) with an aqueous palladium (Pd) solution (10 ppm) at 320 rpm for a period of 18 hours using a mechanical shaker. The solution was then carefully poured into a separating funnel and leave for phase separation for about 15 min. Sample of aqueous solution at the bottom of the separating funnel was taken for concentration measurement of palladium using Atomic Absorption Spectroscopy (AAS). The same procedures were repeated for the study of other parameters such as carrier concentrations, types of the diluents and stripping agent.

The general equation of extraction and stripping as state in Equations (1) and (2),

$$\text{Extraction (\%)} = \frac{[Pd]_{i(aq)} - [Pd]_{f(aq)}}{[Pd]_{i(aq)}} \times 100 \quad (1)$$

$$\text{Stripping (\%)} = \frac{[Pd]_{fs(aq)}}{[Pd]_{i(org)}} \times 100, \quad (2)$$

where,

$[Pd]_{i(aq)}$  is the initial Pd concentration in aqueous phase (ppm),  
 $[Pd]_{f(aq)}$  is the Pd concentration in aqueous phase after extraction (ppm),  
 $[Pd]_{fs(aq)}$  is the Pd concentration in aqueous phase after stripping (ppm),  
 $[Pd]_{i(org)}$  is the Pd concentration in the organic phase after extraction process (ppm).

### 2.3 Stripping Process

Stripping process is the reverse extraction step. Therefore, organic phase (palladium loaded organic phase) is taken from the extraction process from Section 2.2. An equal volume of the palladium loaded organic phase and the aqueous strippant (stripping solution) were mixed together at 320 rpm for a period of 18 hours using mechanical shaker. The mixture was then carefully poured into a separating funnel and was left for phase separation for 15 min. The aqueous strippant was taken for palladium concentration

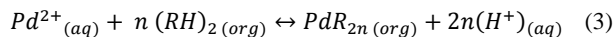
measurements. The stripping procedures are repeated for other stripping agent and concentrations.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Mechanism of Chemical Equilibrium

#### 3.1.1 Extraction Process

During the forward extraction process, the cationic Palladium reacts with Cyanex 302 in organic solvents to form complex. The mechanism can be represent by following sets of reaction [13],



where,

$(RH)_2$  is Cyanex 302 in organic phase,  
 $PdR_{2n}$  is Pd-Cyanex 302 complex in organic phase,  
 $n$  is the number of mole of Cyanex 302.

The amount of palladium extraction is determined by analysis of the aqueous phase after extraction process. The distribution ratio of the palladium between an aqueous and organic phase is known as the distribution coefficient,  $D$  and is defined as:

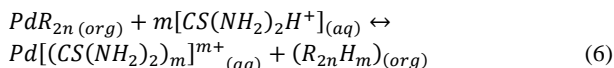
$$D = \frac{\text{Concentration of pd in organic phase after extraction process}}{\text{Concentration of pd in aqueous phase after extraction process}} \quad (4)$$

The relationship between the distribution ratio,  $D$  and the extraction constant,  $k_{eq}$  can be described as [14]:

$$\log D = n \log [(RH)_2] + \log \left[ \frac{k_{eq}}{[H^+]^{2n}} \right] \quad (5)$$

#### 3.1.2 Stripping Process

From Equation 3, continually with stripping process, the Pd-Cyanex 302 complex in organic solvents then undergo stripping process by reacting with thiourea in  $H_2SO_4$  and releases the Pd molecule to the strip phase. The mechanism can be represent by following sets of reaction [7],



where,

$CS(NH_2)_2H^+$  is thiourea in  $H_2SO_4$  in aqueous phase,  
 $m$  is the number of mole of thiourea in  $H_2SO_4$ .

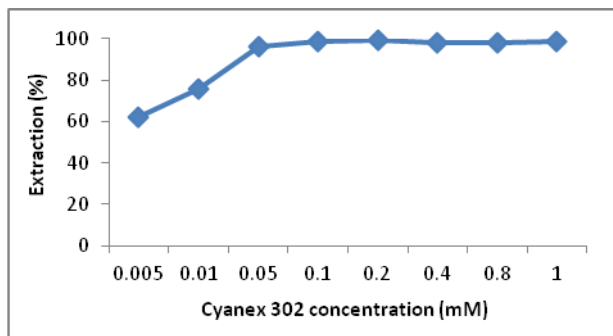
The relationship between the distribution ratio,  $D$  and the stripping constant  $k_{eq}$  can be described as [14]:

$$\log D = -m \log [CS(NH_2)_2H^+] + \log \left[ \frac{(R_{2n}H_m)}{k_{eq}} \right] \quad (7)$$

### 3.2 Effect of Cyanex 302 Concentration on the Extraction of Palladium

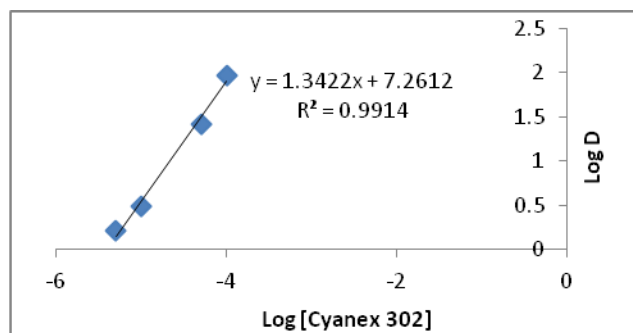
Figure 1 shows the effect of Cyanex 302 concentration on the extraction performance of palladium. It could be seen that the extraction percentage increased as the carrier concentration increased from  $5 \times 10^{-3}$  mM to 1 mM. The maximum extraction was obtained at 0.1 mM when almost 100% of Pd was extracted. Beyond 0.1 mM, the extraction percentage started to get plateau. It

indicates that the saturation capacity of the organic phase for the complex Pd-Cyanex 302 have reached at 0.1 mM Cyanex 302 concentration. There was no significant effect with further increment of carrier concentration which only indicates the excess of 'free carrier'. This result strongly supported by Sarkar and Dhadke [15] who indicated that sulfur substituted phosphinic acids like Cyanex 302 are known to be useful as carrier for the extraction studies of transition metals. Thus 0.1 mM Cyanex 302 was chosen as a preferable carrier concentration.



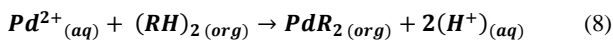
**Figure 1** Effect of carrier concentration in palladium extraction (Experiment condition: [Pd] =10ppm, Agitation speed=320rpm, Duration=18hrs, T=26°C, Diluents=kerosene, Treat ratio= 1:1)

Based on Equation 5 and the result in Figure 1, the nature of the extracted solute was evaluated by plotting a graph of log D versus log [Cyanex 302] as shown in Figure 2.



**Figure 2** Stoichiometric plot for the equilibrium extraction of palladium using Cyanex 302 as a carrier

The slope of the line was used in order to determine the molar ratio of palladium to Cyanex 302. From the result, it gives a straight line with the slope,  $n$  (Equation 3) of 1.34 which is nearly equal to 1.0. Hence, the molar ratio of palladium to Cyanex 302 was found to be 1:1. Therefore, it indicates that one mole of palladium requires one mole of Cyanex 302 for the reaction of extraction to occur as shown in Equation 8 where  $(RH)_2$  represents the carrier in the organic phase which is Cyanex 302 and  $Pd^{2+}$  is palladium in aqueous phase.

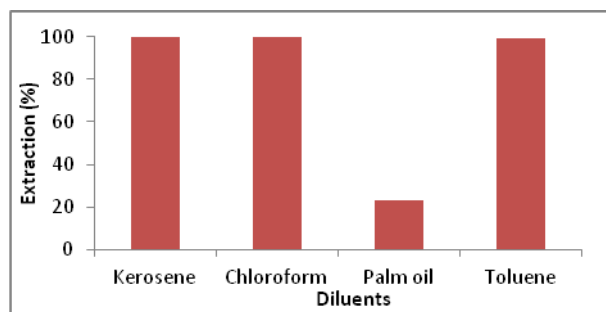


### 3.3 Effect of Diluents on Palladium Extraction

Different types of diluents which have been used in the palladium extraction are kerosene, chloroform, toluene and palm oil. Palm oil was studied as the alternative and renewable organic diluent, as it

is non-toxic and readily available. Liquid membrane can be modified to "green liquid membrane" by using environmentally friendly diluent. In addition, palm oil has been found to work well for extraction of phenol using supported liquid membranes (SLM) [16]. The effect of diluents towards the extraction efficiency of palladium is shown in Figure 3. The results revealed that the extraction were high with kerosene, toluene, and chloroform where almost 100% Pd was extracted. This result indicate that the aliphatic diluents such as kerosene and n-dodecane are generally more preferred than aromatic diluents such as toluene and benzene because of its low solubility in water [17]. The solubility of kerosene is negligible in water while solubility of toluene in water is 0.53 g/l and it also has high volatility in ambient temperature. While, chloroform was not preferred as diluent because it is more toxic and carcinogenic. Moreover, it has been replaced by other solvents in most industrial degreasers and paint removers [18]. Kerosene also has a high flash point, thus decreasing losses due to volatility as well as fire hazards. The graph showed that there was very minimal extraction found with palm oil. So, the extraction of palladium was considered weak in palm oil because of less solubility of Cyanex 302 in this organic diluents. Palm oil has a high viscosity of 106 mPa.s at room temperature [19] that decrease the mass transport of the solute due to higher resistance to diffusivity. The viscosity of kerosene, chloroform, and toluene are 2.2, 0.38 and 0.68 mPa.s respectively, is much lower compared to palm oil [8]. A lower viscosity of the diluent benefits the solvent extraction process due to the decreased mass transport resistance.

For further study, the performance of palm oil can be modified by adding a modifier to prevent third phase formation and improve its properties such as increasing the solubility of an extractant, changing interfacial parameters or reducing adsorption losses. Generally, a modifier is an alcohol with an aliphatic chain with at least eight carbon atoms that modifies the polarity of the solvent, promoting the breakage of the stable emulsion, and its content solubilization [20]. Other than that, the addition of amine group such as Aliquat 336 also can be used as a catalyst to enhance extraction rates [21]. Therefore, kerosene was chosen as the best diluent in this study which provides high in dielectric constant and flash point, low viscosity and density, cheap and readily available [22].

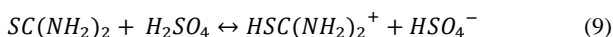


**Figure 3** Effect of diluent on extraction of palladium (Experimental conditions: [Pd] =10ppm, [Cyanex 302] = 0.1 mM; agitation speed=320rpm, duration= 18hrs, T= 26°C, Treat ratio= 1:1)

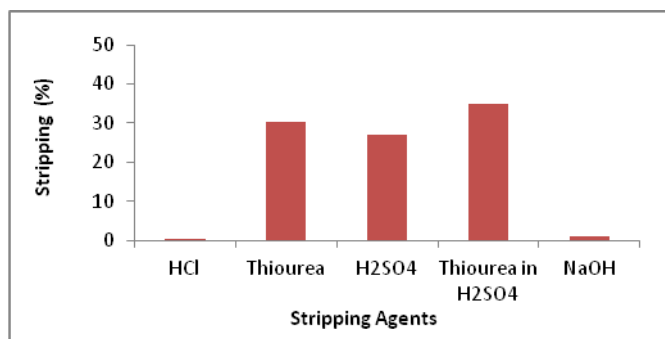
### 3.4 Effect of Stripping Agent Type

Different types of stripping agent have been used in backward extraction and the rates of stripping performance of palladium are reported in Figure 4. Result shows that acidic thiourea (thiourea in  $H_2SO_4$ ) has the highest percentage of Pd extraction. This can be attributed that in acidic medium (Equation 9), thiourea is protonated and the proton will be bonded to the sulfide atom

favouring the bonding of the metal ions to nitrogen atoms [7]. This reaction shows an agreement with Akretche *et al.* [23] who indicated that thiourea has an ability to extract precious metal in acidic medium. Thus, acidic thiourea was found to be the most promising stripping agent [24].



Thiourea and sulphuric acid itself also showed good stripping performance with 30% and 27% of palladium stripped respectively. It means that thiourea is capable of forming the coordinate bonds through both sulphur and nitrogen atoms even though the extremely low basicity of the ligand plays against the formation of nitrogen-metal bonds. In contrast, hydrochloric acid was the weaker stripping agent in this study due to the precipitation of palladium chloride (PdCl<sub>2</sub>) which occurred at the stripping phase. Similar observation was observed with sodium hydroxide which also shows the lowest stripping rate due to the precipitation of palladium hydroxide (Pd(OH)<sub>2</sub>) that insoluble in aqueous phase. Thus, thiourea in H<sub>2</sub>SO<sub>4</sub> is used as a stripping agent.



**Figure 4** Effect of stripping agent types on the stripping of palladium (Experimental conditions: Stripping agents concentration=1.0 M, agitation speed=320rpm, duration= 18hrs, T= 26°C, Treat ratio= 1:1)

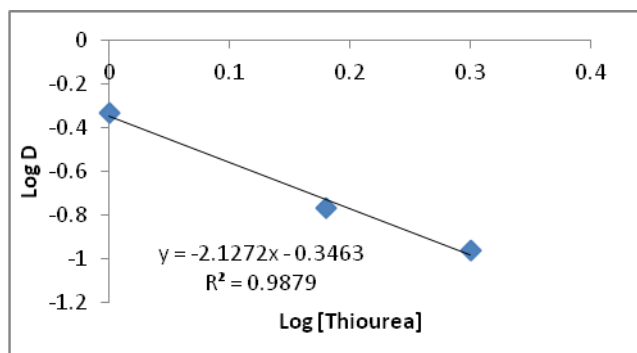
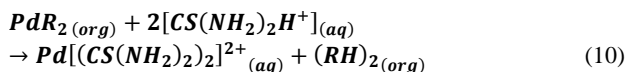
### 3.5 Effect of Stripping Agents Concentration

Table 1 present the effect of stripping agent concentration on the stripping efficiency of palladium. The results show that even though thiourea functions well as a stripping agent in the acidic solution, there seem to be a limitation on the extent of acidity of the solution. If the acidity of the solution is high, more thiourea is needed to ensure that the acidic thiourea acts as an excellent stripping agent for Cyanex 302 [7]. Meanwhile, at the fixed concentration of 1.0 M H<sub>2</sub>SO<sub>4</sub>, there is an increment of Pd stripping percentage as the thiourea concentration increased from 1.0 M up to 2.0 M.

**Table 1** Effect of stripping agent concentration on stripping of Palladium (Experimental conditions: agitation speed=320rpm, duration= 18hrs, T= 26°C, Treat ratio= 1:1)

Stripping Agent (Acidic Thiourea)		Stripping (%)
1.0 M Thiourea	1.0 M H <sub>2</sub> SO <sub>4</sub>	68.14
	1.5 M H <sub>2</sub> SO <sub>4</sub>	32.86
	2.0 M H <sub>2</sub> SO <sub>4</sub>	42.08
1.0 M H <sub>2</sub> SO <sub>4</sub>	1.0 M Thiourea	68.14
	1.5 M Thiourea	85.79
	2.0 M Thiourea	90.14

Based on Equation 7 and the result in Table 1, by assuming that all the thiourea in H<sub>2</sub>SO<sub>4</sub> that existed in the system reacted with Pd-Cyanex 302 complex, the nature of log D versus log [Thiourea] was evaluated by plotting a graph of log D versus log [Thiourea] as shown in Figure 5. From the result, it gives a straight line with the slope, m (Equation 7) of 2.1272 which is nearly equal to 2.0. Hence, Pd-Cyanex 302 complex to thiourea in H<sub>2</sub>SO<sub>4</sub> molar ratio was found to be 1:2. Therefore, it indicates that one mole of Pd-Cyanex 302 complex require two mole of thiourea for stripping reaction to occur. The stripping reaction of palladium-Cyanex 302 complex is shown in Equation 10.



**Figure 5** Stoichiometric plot for the equilibrium stripping of palladium using thiourea in H<sub>2</sub>SO<sub>4</sub> as stripping agent

## 4.0 CONCLUSION

The findings of this study can be concluded as the following:

- Phosphinic acid (Cyanex 302) provided good extraction performance as a carrier where almost 100% palladium was extracted, 90% get stripped at the favourable condition of kerosene as diluents, 0.1 mM Cyanex 302 and 2.0 M thiourea in 1.0 M sulphuric acid as stripping solution.
- The slope analysis studies of log D versus log [Cyanex 302] and log D versus log [Thiourea] indicates that one mole of Palladium requires one mole of Cyanex 302 for the reaction of extraction to occur and one mole of Pd-Cyanex 302 complex requires two mole of thiourea in H<sub>2</sub>SO<sub>4</sub> for stripping reaction to occurs.

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