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Extraction of palladium from aqueous wastewaters using Alamine 300 as extractant

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ABSTRACT

In this paper, extraction of palladium from chloride media by Alamine 300 (tri-n-octyl amine) as an effective carrier (extractant) and toluene as diluent has been investigated. This carrier acted effectively even at low carrier concentration (0.004 M) and the extraction percentage after 20 min reached nearly 100%. The effect of different parameters such as pH, carrier concentration, feed concentration, and temperature has been evaluated in detail. The results revealed that although the extraction process was slightly exothermic, the temperature was not very effective. An increase of the carrier concentration and feed concentration had a direct and reverse effect on the extraction percentage, respectively.

Keywords: Solvent extraction; Palladium; Alamine 300; Extractant; Wastewater

1. Introduction

Platinum group metals (PGMs) are a group of precious metals consisting of six elements: ruthenium, rhodium, palladium, platinum, osmium, and iridium. Palladium is a heavy metal, and its extraction from various industrial solid wastes is important from an economical and environmental point of view. All palladium compounds are toxic and cancerous. Due to the characteristics such as resistance to corrosion and oxidation, high melting point, high electrical conductivity, and catalytic activity, palladium becomes very useful for different industries [1]. Palladium is very worthy (740 $/oz, March 2013) and has wide applications in the manufacturing of catalysts in oil refineries and petrochemical industries, jewelry, electrical and surgery equipment. Sometimes this metal exists in liquid streams of industrial effluents and wastewaters discharging. Despite its limited availability, the demand for palladium is continuously increasing (Table 1). Therefore, the recycling of palladium from secondary resources or from post-consumer scraps is emerging.

An important way to obtain noble metals like palladium is to reclaim them from sources such as used catalysts, electronic scraps, anodic mud in metallurgical plants, etc. Pyrometallurgy of noble metals is notorious for its tedious production cycle and serious

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Table 1
Palladium supply and demand: 2000–2011 [2]

	Supply (ton)											
	Year											
Country	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
South Africa	1,860	2,010	2,160	2,320	2,480	2,605	2,775	2,765	2,430	2,530	2,530	2,635
Russia	5,200	4,340	1,930	2,950	4,800	4,620	3,920	4,540	3,660	3,560	2,850	2,850
North America	635	850	990	935	1,035	910	985	990	910	750	665	865
Other	105	120	170	245	265	270	270	285	310	335	1,360	645
Total	7,800	7,320	5,250	6,450	8,580	8,405	7,950	8,580	7,310	7,175	7,405	6,995
Application	Demand (ton)											
Auto-catalyst	5,640	5,090	3,050	3,450	3,790	3,865	4,015	4,545	4,460	3,895	5,200	5,510
Recovery	230	280	370	410	530	625	805	1,015	1,115	950	1,370	1,530
Chemical	255	250	255	265	310	415	440	375	355	345	855	620
Dental	820	725	785	825	850	815	620	630	625	605	760	780
Electronics	2,160	670	760	900	920	970	1,205	1,240	1,100	1,000	1,815	1,320
Jewellery	255	240	270	260	930	1,430	995	715	855	920	1,150	1,200
Investment	0	0	0	30	200	220	50	260	420	635	800	830
Other	60	65	90	110	90	265	85	85	75	70	200	200
Total	8,960	6,760	4,840	5,430	7,355	7,355	6,605	6,835	6,775	6,520	9,410	8,930

environmental pollutions. In addition, conventional pyrometallurgical processes are very energy and time consuming, so energy-saving hydrometallurgical processes are preferred [3,4].

Wastewaters in petrochemical industries are currently treated by pretreatment of oil/water separation followed by an activated sludge process [5]. The conventional hydrometallurgical method for the separation of Pd from other PGMs is chemical precipitation. The precipitation process has several problems such as high chemical consumption, slow kinetics, and solid–liquid separation. The chemical precipitation process increases environmental pollution due to the use of toxic chemicals. Since aqueous chemistry for the extraction and separation of PGMs is extremely complicated, feasible hydrometallurgical techniques need to be developed to replace the conventional chemical precipitation methods [6–9].

Solvent extraction and liquid membranes are the most versatile methods used for the removal, separation, and concentration of metallic species from aqueous media [10–18]. In these processes, the organic and aqueous phases are kept in contact and the metal ions are transferred from aqueous to organic phase. The solvent extraction technique has also been used commercially in the separation of palladium, using various carriers such as dicyclohexyl-18-crown-6 ether [19,20], dibenzo-18-crown-6 [21], sulfoxide compounds [22–24], amide groups [25–27], thiosemicarbazone derivatives [28], etc. (Table 2).

Tri-n-octyl amine (Alamine 300) is a tertiary amine which is a basic extractant. The molecular structure of

Table 2
A history of palladium extraction with different extractants

Extractant	Diluent	Feed phase	[HCl] (M)	T (°C)	t (min)	Stripping phase	E (%)	Ref.
DC18C6	Chloroform	HCl	1	25	4	Ammonia	~100	[10]
LIX 84I	Dodecane	HCl	0.1	30	120	HCl	97	[29]
Cyanamides	Toluene	HCl	0.01	25	1,440	–	98	[30]
Ketones	Nitrobenzene	HNO_3	2	25	120	Thiourea	99	[31]
Alamine 300	Kerosene	HCl	0.5	25	30	Sodium thiosulfate	99.3	[1]
Alamine 336	Toluene	HCl	1	25	30	Thiourea, HCl	>99	[32]
Cyanex 471X	Kerosene	HNO_3	2	25	10	Thiosulfate	93	[33]
CyphosIL 104	Toluene	HCl	0.1	20	20	NH_4OH	96	[34]

this extractant has been shown in Fig. 1 and its properties have been presented in Table 3.

Swain et al. [1] extracted 97.8% of palladium from the mixture of palladium and platinum using Alamine 300 salt in kerosene. This result was obtained under these conditions: aqueous solution containing 0.0005 M Pt and Pd, 0.005 M carrier concentration, and 30 min contact time. Sun and Lee [32] separated more than 99% of palladium from spent catalysts by Alamine 336 dissolved in toluene.

As the solutions of Alamine 300 in toluene are harmful due to the presence of toluene, the extraction processes are usually performed in closed extraction and stripping vessels (mixer and settlers) so that the vaporization of toluene into the environment becomes negligible. On the other hand, the solubility of toluene in water is also very low (0.47 g/L) which reveals that the amount of the dissolved toluene in the aqueous phase is low and this can be treated by commonly practiced wastewater treatment technologies. Moreover, toluene is much less toxic than benzene and it becomes a proper substitute for benzene in many chemical products such as paints, lacquers, rubbers, and adhesives. Also, it is a main constituent of octane boosters in gasoline. Then it could be concluded that toluene is a good choice for the diluent in liquid–liquid extraction processes.

The present work examines the efficiency of separating palladium from a chloride solution using Alamine 300 salt as a carrier diluted in toluene. The effect of pertinent parameters including pH, carrier concentration, feed concentration, and temperature on palladium extraction has been investigated to obtain the optimum separation conditions.

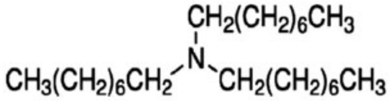

Fig. 1. The chemical structure of Alamine 300 [35].

Table 3
Some properties of Alamine 300 [35]

Chemical name	Tri-n-octylamine
Chemical formula	$C_{24}H_{51}N$
CAS no.	1116-76-3
Molecular weight (g/mol)	353.67
Boiling temperature (℃)	365–367
Density (kg/m^3)	810 at 20℃
Color	Colorless liquid

2. Experimental

2.1. Reagents

A palladium foil with purity of 99.9% was used for preparation of the stock solution. A stock solution of 0.01 M palladium (II) chloride was prepared by dissolving 1gr palladium in aqua regia solution followed by evaporation and then diluted to 1,000 ml with dilute HCl solution. The feed solution for each solvent extraction experiment was prepared by diluting the stock solution to the desired concentration with deionized water. Tri-n-octyl amine (Alamine 300) and toluene were supplied from Merck Co. and used without further purification. Sodium hydroxide, nitric acid, and hydrochloric acid, all of reagent grade, were supplied from Merck Co. The solutions of organic phase were prepared by diluting Alamine 300 salt in toluene to a predetermined volume ratio.

2.2. Apparatus

An inductively coupled plasma optical emission spectrometer (ICP-OES), model Varian 735-ES, was used for determination of Pd^{2+} concentration in the aqueous solutions. For separation of the organic phase from aqueous phase, a Denley centrifuge, model BS400, was used with 6,000 rpm maximum speed. A Denley shaker was used for the extraction experiments and a precise digital pH meter (Metrohm-780) was used for pH measurement of the aqueous solutions. The adjustment of the pH of the aqueous feed solutions was performed by diluting of the stock solution by distilled water to nearly the desired volume and then the final volume adjustment was done by the addition of dilute hydrochloric acid solution and distilled water until the desired value of volume and pH were achieved. Temperature was adjusted by a water bath equipped with an Autonics PID temperature controller.

2.3. Solvent extraction procedure

The aqueous feed (15 ml) containing palladium chloride was contacted with an equal volume of Alamine 300 salt in the toluene organic phase. After vigorous shaking of the mixture for 20 min, the two phases were decanted quickly and then the aqueous part was centrifuged at 2,300 rpm for 5 min and was analyzed for palladium assay. Then the extraction percentage ($E\%$) was calculated as follows:

$$E\ (\%) = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

3. Results and discussion

3.1. Effect of feed concentration

To evaluate the effect of feed concentration, experiments were performed at different feed concentrations of 50, 100, 200, and 300 ppm. Fig. 2 shows the effect of the palladium concentration in the aqueous phase on the extraction of palladium using 0.01 M Alamine 300 salt at an initial pH of 0. As it was expected, the extraction percentage decreased with an increase of the aqueous phase concentration. This result shows that at these conditions, the carrier is not able to extract more palladium ions, so extraction percentage is decreased with an increase of the feed concentration. The next experiments were carried out at other pH values as well as lower carrier concentrations to obtain optimal conditions.

3.2. Effect of feed pH

The extraction of palladium from the solutions at different initial pH was studied using Alamine 300 salt as carrier. The effect of pH on the extraction of palladium from chloride solution has been shown in Fig. 3. To determine the optimum pH of the feed solution, different feed solutions with pH values of 0, 1, 2, 3, and 4 were prepared. At constant carrier concentration, the extraction efficiency was enhanced with an increase of pH, reached a maximum value at pH = 2 and then decreased slowly. Alamine 300 (R_3N) was first pretreated by HCl to form Alamine 300 chloride salt (R_3NHCl) and was then diluted with toluene. According to Eqs. (2) and (3), at low pH values and consequently high HCl concentrations, there would be a competition between the formation of $[R_3NH_2Cl_2]_{org.}$ and $[R_3NH^+Cl^-]_{org.}$. In the presence of excess HCl, the formation of $[R_3NH_2Cl_2]_{org.}$ is facilitated over $[R_3NH^+Cl^-]_{org.}$. According to Eq. (5), only $[R_3NH^+Cl^-]_{org.}$ is active and reacts with $[PdCl_4^{2-}]$ anion and is extracted as $[(R_3NH^+)_2(PdCl_4^{2-})]$ complex [1]. This may be the contributing cause for the decrease of the palladium extraction by a decrease in pH of the feed. By increasing pH of the feed, the extraction process is improved but at higher pH values and consequently low HCl concentrations, according to Eq. (4), the formation of the $[PdCl_4^{2-}]$ anion is reduced and consequently, the extraction percentage is decreased. The best result was obtained at pH = 2 and the extraction percentage reached nearly 100% at 0.004 M carrier concentration.

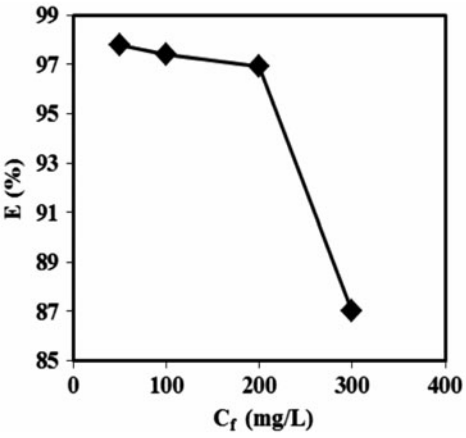

Fig. 2. The effect of feed concentration on the extraction percent (carrier concentration = 0.01 M, pH = 0, contact time = 20 min, and temperature = 23°C).

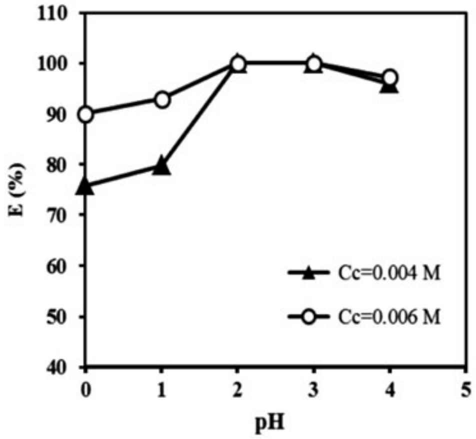

Fig. 3. The effect of pH on the extraction percent ([Pd] =100 ppm, contact time = 20 min, temperature = 23°C).

$$[R_3N]_{org} + [HCl]_{aq} \rightleftharpoons [R_3NH^+Cl^-]_{org} \quad (2)$$

$$[R_3NH^+Cl^-]_{org} + [HCl]_{aq} \rightleftharpoons [R_3NH_2Cl_2]_{org} \quad (3)$$

$$[PdCl_2]_{aq} + 2[HCl]_{aq} \rightleftharpoons [PdCl_4^{2-}]_{aq} + 2[H^+]_{aq} \quad (4)$$

$$[PdCl_4^{2-}] + 2[R_3NH^+Cl^-]_{org} \rightleftharpoons [(R_3NH^+)_2(PdCl_4^{2-})]_{org} + 2[Cl^-]_{aq} \quad (5)$$

3.3. Effect of carrier concentration

The extraction behavior of palladium was studied at Alamine 300 salt concentration range of 0–0.012 M, at a pH of 1 and 2. Fig. 4 shows the effect of the Alamine 300 salt concentration on the extraction of palladium from chloride solution containing palladium of 100 ppm. Based on Fig. 4, the extraction of

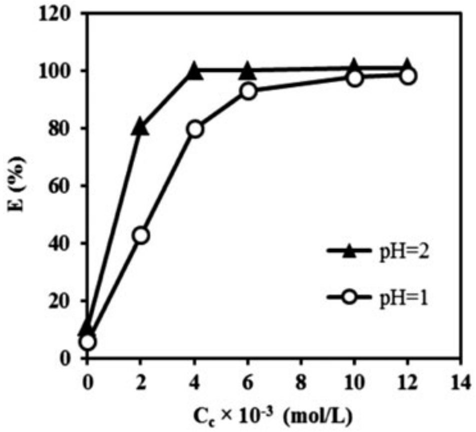

Fig. 4. The effect of carrier concentration on the extraction percent ([Pd]=100 ppm, contact time = 20 min, temperature = 23˚C).

palladium was increased sharply from 9 to 100% as the carrier concentration increased from 0 to 0.004 M. Therefore, the carrier concentration has a significant effect on the extraction efficiency. At an Alamine 300 salt concentration of 0.004 M and pH 2, the extraction percentage was very high and nearly all of the palladium was extracted at this concentration.

3.4. Effect of temperature

Extraction percentage was studied at different temperatures (20, 23, 30, 40, and 50˚C) when the other parameters were constant. Results indicated that extraction efficiency is decreased by increasing the temperature (Fig. 5). Hence, the palladium extraction by Alamine 300 salt is an exothermic process. The smooth slope of the diagram shows that the temperature is not an effective parameter in this process. The activation energy of extraction was obtained as 1,124 J/mol from Fig. 6 and Eq. (6).

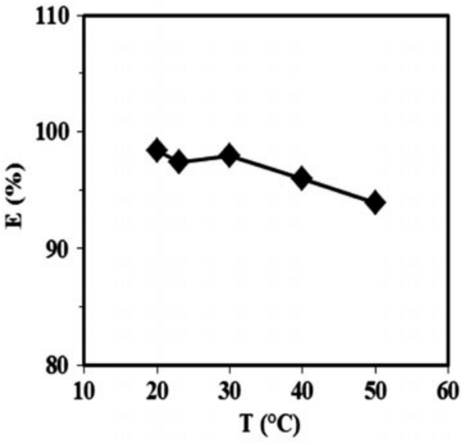

Fig. 5. The effect of temperature on the extraction percent ([Pd]=100 ppm, carrier concentration = 0.01 M, pH = 0, contact time = 20 min).

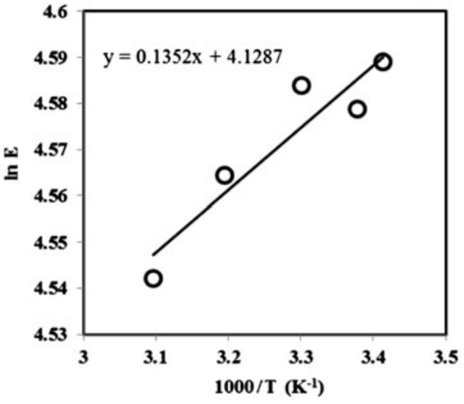

Fig. 6. Diagram of ln E vs. 1/T ([Pd]=100 ppm, carrier concentration = 0.01 M, pH = 0, contact time = 20 min).

$$\ln E = \ln E_0 - \frac{\Delta E}{R}\frac{1}{T} \tag{6}$$

4. Conclusion

The separation of palladium is very important from an economical and environmental point of view. In this work, palladium extraction was performed by Alamine 300 salt dissolved in toluene. The effect of pertinent parameters such as pH, feed concentration, carrier concentration, and temperature on the extraction percentage was studied. The temperature variation had no significant effect on the extraction percentage. The palladium extraction was a slightly exothermic process. The results showed that the extraction percentage was enhanced by increasing the carrier concentration. In addition, the pH of feed solution must have a defined value. The best result was obtained at pH = 2 and the extraction percentage reached nearly 100% in 0.004 M carrier concentration. The extraction efficiency was decreased by increasing feed concentration, which is an evident result. Solvent extraction has some advantages in comparison with other separation methods. Adsorption systems have limited adsorption capacity and adsorbents are saturated after a few times. Adsorption and chemical precipitation processes are time consuming while solvent extraction is a fast process. Recently, membrane contactors have been developed for metal ion separation from aqueous solutions. These processes are simple, easy to scale up, and environmentally friendly. Liquid membranes are based on the solvent extraction process. Therefore, the conditions of this investigation can be used for liquid membrane systems.

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