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Solvent extraction of palladium(II) from oxalate medium by 2-dodecylaminopyridine

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Abstract: A Novel approach was designed to extract palladium(II) from oxalate solution via solvent extraction method. The performances of palladium(II) with 2-dodecylaminopyridine(2-DDAP) under optimized conditions were investigated. The results indicate that palladium(II) extraction became quantitative at pH 3 but decreased with increase in concentration of oxalate above 0.04M in aqueous phase. The extraction of palladium reached 99.45% with 7×10^{-4} M, 2-DDAP in xylene. The transfer speed of palladium(II) from aqueous phase to organic phase was fast, and extraction equilibrium established within just 60 seconds. The selective separation of palladium(II) from precious metals was carried out by proposed extractant and stripping conditions.

Keywords: Solvent extraction, palladium(II), 2-DDAP, oxalate.

INTRODUCTION

Solvent extraction is generally used in hydrometallurgy for the separation of PGMs from laboratory scale to large scale operations. Separation of PGMs is extremely difficult task on account of their occurrence in the nature as well as due to their similar structure and chemical behavior[1]. These elements have paramount significance in technology, mainly these are used as metallic catalysts in automobiles to reduce air pollution[2] and applicable for surgical appliances, electronic devices and hydrogen storage materials[3,4,5,6]. It is very difficult to

fulfill the present demand of these elements just based on natural resources, hence secondary resources should be tackled to meet the present requirement. The existing forms of PGMs and availability of metal species is highly depending on the acidic, basic and chloride concentration in aqueous solution[7,8,9]. As the aqueous chemistry of one metal may resembles that of some others in mixture, selective recovery of any desired metal from such complex mixture is difficult[10].

Several analytical methods have been reported for separation and purification of PGMs such

as precipitation[11-13], adsorption[14-17], solid phase extraction[18,19] and solvent extraction[20-26]. Solvent extraction of palladium is already well established as efficient alternative to traditional techniques. Different extractant have been developed and employed as extractants for PGMs especially for palladium(II) for both commercial and analytical purpose[27-46]. However, all of traditional solvent extraction systems used excess amount of extractant in different organic solvents, which may cause some of the environmental and health problems. Furthermore, most of the solvent extraction systems were conducted under the strong acidic condition [22,28,30-38,40,41,43,44] and resulted in severe corrosion of the equipments used for extraction purpose. Hence, it is inevitable to improve the separation factors and extraction efficiency by way of introducing newer extractants and by changing the solvent systems. Several methods are available in the literature, however, each method is associated some limitations, hence to overcome these, a effort has been made to use new extractant which has enhanced basic character which is in favour of formation of stronger ion-pair complex thereby increasing efficiency of extraction. The superiority of the proposed method is shown by comparison with reported methods in **Table 1**.

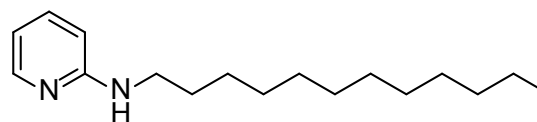
In the present work, extraction of palladium(II) and its separation from PGMs using 2-DDAP from oxalate media was investigated. The experiments which were carried out indicated that efficient extraction of palladium(II) and its separation from PGMs could be understood by controlling the extractant and oxalate concentration. This is the first example of optimization of equilibrium conditions, including pH of aqueous phase, weak organic acid salt concentration in aqueous phase, concentration of 2-DDAP, diluents and equilibrium time. We have also studied the stripping of palladium(II) from organic

phase which confirms the selectivity towards palladium(II). The novelty of present work lies in the fact that the use of 2-DDAP as extractant and oxalate ions in aqueous phase not only enhanced the extraction efficiency but also increased the selectivity in the presence of other PGMs in comparison to existing methods.

EXPERIMENTAL

1. Materials

A Shimadzu UV-Visible Spectrophotometer (UV 1800) with 1 cm² quartz cell was used for absorbance measurements and pH optimization was carried out by Elico digital pH meter Model LI -120 (± 0.01). All the chemicals used were of AnalaR grade and purchased from commercial suppliers, AlfaAesar (Thermo Fisher Scientific, Hyderabad, India) and Spectrochem (Spectrochem Pvt. Ltd., Mumbai, India). These are used as such without further purification. The stock solutions were prepared by dissolving appropriate amount of PdCl₂·xH₂O and other metal salts in deionized distilled water. A series of working solutions were prepared by diluting the stock solution. An extractant, 2-dodecylaminopyridine (2-DDAP) was synthesized by reported method[47] and characterized by spectral techniques. Doubly distilled water was invariably used throughout the experiments. The structure of the extractant 2-dodecylaminopyridine (2-DDAP) is shown as;



2. Solvent extraction procedure

Extraction of palladium(II) was carried out in a typical experimental procedure with 100 μg mL⁻¹ of palladium(II) in 0.01M to 0.1M weak organic acid salts as aqueous phase (25 mL) and

Table 1

Comparative summary of earlier and proposed solvent extraction methods for palladium(II).

Entry	Extractant	Solvent	Medium	Equilibrium time	Stripping agent	Determination method	Ref.
1	2-octylaminopyridine	Xylene	Salicylate	5 min.	Ammonia(3-10M)	Spectrophotometry	27
2	mono-TODGTA, di-TODGTA	Kerosene	HNO ₃	60 min.	0.01 mol/L TU in 0.1 mol/L HNO ₃	ICP-AES	28
3	MPHTA, MCHTA	Toluene	Chloride	30 min.	0.1M TU in 1 M HCl	ICP-AES	29
4	DMDOHEMA	n-Hepatne	HNO ₃	5 min.	0.1 M TU	ICP-AES	30
5	AAI	Toluene+n-octanol	HCl	5 min.	5% TU in 0.1M HCL	Spectrophotometry	31
6	DMDCHTDGA	1,2-dichloroethane	HCl	30 min.	0.1M TU in 1 M HCl	AAS	32
7	DMDBMA	1,2-dichloroethane	HCl	30 min.	0.1M TU in 1 M HCl	ICP-AES	33
8	Hexakis [(dimethylthiocarbamoyl)oxy]thiacalix[6]arene and Tetrakis[(dimethylthiocarbamoyl)oxy]thiacalix[4]arene	Chloroform	HCl	24 hrs	1 M TU	ICP-AES	34
9	Ph ₃ P, Ph ₃ PO, Ph ₃ PS.	Benzene	HCl	30 min.	1M thiosulphate	Spectrophotometry	35
10	Synthetic sulphoxide MSO	Kerosene	HCl	5 min.	NH ₄ Cl +NH ₃	AAS	36
11	Cyphos IL 104	Kerosene	HCl	5 min.	0.5 M NH ₄ OH	ICP-AES	37
12	DMDPHTDMA	1,2-dichloroethane	HCl	10 min.	4M HCl+ 0.05 M NaClO ₃	AAS/ICP-OES	38
13	Alamine 300 (TOA)	Kerosene	Chloride	30 min.	0.5m HCL+ 0.1M TU	ICP-AES	39
14	TBP	Kerosene	HCl	5 min.	1M TU in 0.1 M HCl	ICP-OES/ AAS	40
15	*2-DDAP	Xylene	oxalate	60 sec.	4% NH ₄ Cl + 1M ammonia	Spectrophotometry	PM

*PM= present method, TU= Thiourea.

TOA: *Tri-n*-octylamine (Alamine 300); TBP : *Tri-n*-butylphosphate; mono-TODGTA:2-(2-dioctylamino)-2-thioxoethoxy)-*N,N*-dioctylacetamide,*di*-TODGTA:2,2'-oxybis(*N,N*-dioctylethanethioamide); MPHTA : *N*-methyl-*N*-phenyl-octanthioamide; MCHTA : *N*-methyl-*N*-cyclohexyl-octanthioamide; DMDOHEMA : *N,N'*-dimethyl,*N,N'* dioctylhexylethoxymalonamide ; AAI :1-[2-(alkanoylamino)ethyl]-2-alkyl-2-imidazolines; DMDCHTDGA: *N,N'*-dimethyl-*N,N'*-dicyclohexylthiodiglycolamide; DMDBMA : *N,N'*-dimethyl-*N,N'*-dibutylmalonamide; Ph₃P : Triphenylphosphine, Ph₃PO : triphenylphosphine oxide; Ph₃PS : triphenylphosphine sulphide; Cyphos IL 104 : Trihexyl(tetradecyl)phosphoniumbis-2,4,4 trimethylpentylphosphinate; DMDPHTDMA: *N,N'*-dimethyl-*N,N'*-diphenyltetradecylmalonamide

$1 \times 10^{-4} \text{M}$ to $1 \times 10^{-3} \text{M}$ of 2-DDAP as extractant in the presence of appropriate organic solvents (10 mL). The two phases were equilibrated by mechanical shaker for a period, 20 seconds to 180 seconds at ambient temperature. After equilibration, the two phases were separated by glass separatory funnel. The extracted palladium(II) in organic phase was stripped using different stripping agents and determined by UV Visible spectrophotometry [48]. Distribution ratio (D) was calculated as the ratio of palladium concentration in organic phase $[\text{Pd}]_o$ to aqueous phase $[\text{Pd}]_{aq}$ after extraction using equation

$$D = \frac{[\text{Pd}]_o}{[\text{Pd}]_{aq}} \quad (1)$$

The percentage extraction of palladium(II) was calculated by equation, where V_{aq} is volume of aqueous phase and V_o is volume of organic phase,

$$\% E = \frac{100 D}{D + V_{aq}/V_o} \quad (2)$$

RESULTS AND DISCUSSION

1. Effect of aqueous phase pH on extraction of palladium(II)

The extraction of palladium(II) from the aqueous phase is highly depends on the pH of aqueous phase. In these experiments, the following parameters were fixed: palladium(II) concentration, $100 \mu\text{g mL}^{-1}$ in 0.04M oxalate; 2-DDAP concentration, $7 \times 10^{-4} \text{M}$ in xylene; equilibrium time, 60 seconds. Therefore, percentage extraction of palladium(II) with 2-DDAP was determined at different pH in the range, 1-10. Fig.1 depicts the extraction of palladium(II) with 2-DDAP which starts at pH 1 and becomes quantitative in the pH range 2-4, the maximum percentage extraction was observed at pH 3. However, it decreased from

99.45% to 27.20% when pH has increased from 3 to 10. At lower pH than 3, hydrogen ion activity which inhibits ion pair formation ability of 2-DDAP with palladium(II). Whereas increasing the pH of aqueous phase more than 7 lead to the formation of palladium hydroxide [34] and therefore percentage extraction decreases. Hence basic condition is not favorable for the formation of ion pair complex of palladium(II) with 2-DDAP. Therefore all further extraction procedures were carried out at pH 3.

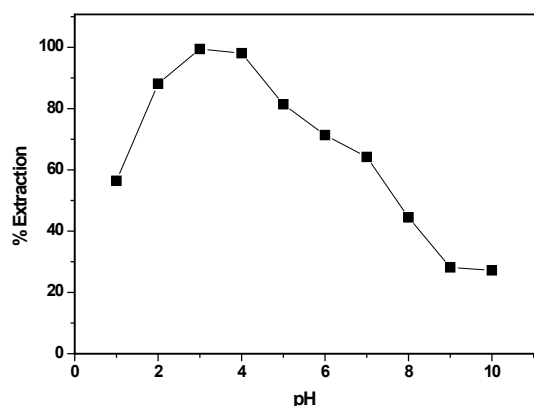


Fig.1. Effect of aqueous phase pH on extraction of palladium(II). Experimental conditions: Palladium(II) = $100 \mu\text{g mL}^{-1}$, sodium oxalate = 0.04 M, 2-DDAP = $7 \times 10^{-4} \text{M}$ in xylene, equilibrium time = 60 seconds, Strippant = 1 M NH_3 + 4% NH_4Cl

2. Effect of 2-DDAP concentration

In order to achieve higher extraction efficiencies of palladium(II) from oxalate solution, the concentration of 2-DDAP was scanned in the range $1 \times 10^{-4} \text{M}$ to $1 \times 10^{-3} \text{M}$. The extraction experiments were performed at fixed conditions: concentration of palladium(II), $100 \mu\text{g mL}^{-1}$ in 0.04M oxalate; aqueous phase pH 3; equilibrium time, 60 seconds; organic phase, xylene. The percentage extraction of palladium(II) increases with increasing concentration of 2-DDAP. Results of these experiments are presented in Fig.2. The extraction of palladium(II) remained

constant (99.45%) with increase in concentration of extractant(2-DDAP) from $7 \times 10^{-4} \text{M}$ to $1 \times 10^{-3} \text{M}$. The concentration of 2-DDAP was kept at $7 \times 10^{-4} \text{M}$ for further experiments.

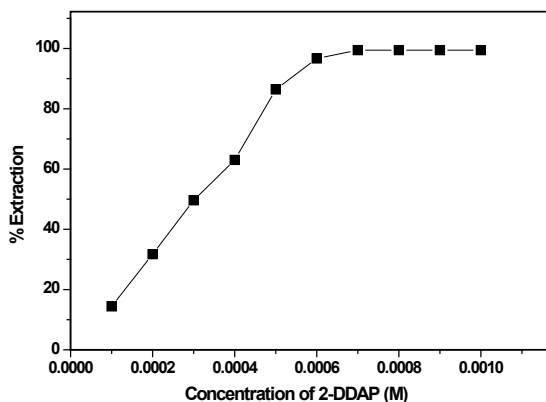


Fig.2. Effect of 2-DDAP concentration on extraction of palladium(II). Experimental conditions: palladium(II)= $100 \mu\text{g mL}^{-1}$, sodium oxalate = 0.04 M, pH = 3, equilibrium time = 60 seconds, Strippant = 1 M NH_3 + 4% NH_4Cl

3. Effect of organic solvents

To assess the efficient solvent as organic phase for extraction of palladium(II) with 2-DDAP, the experiments were performed at fixed conditions: palladium(II) concentration, $100 \mu\text{g mL}^{-1}$ in 0.04M oxalate; aqueous phase pH, 3; equilibrium time, 60 seconds; 2-DDAP concentration $7 \times 10^{-4} \text{M}$ in different solvent. Generally, solvent extraction is dependent on the polar nature of the organic solvent used during the experiments; therefore, selection of proper solvent is important for efficient extraction. We performed extraction of palladium(II) with $7 \times 10^{-4} \text{M}$ of 2-DDAP in different organic solvents. The results are presented in **Table 2**. It is seen that no proper relation between dielectric constant, polarity of organic solvents and extraction of palladium(II) is observed. The use of xylene as solvent resulted in higher percentage extraction

of palladium(II) even though the dielectric constant of xylene is not so high and can be used as best solvent. The extractant (2-DDAP) was not soluble in many organic solvents and cyclohexane, whereas anisole formed emulsions with palladium(II). From the studied solvents xylene, toluene, benzene were found to be suitable for the extraction of palladium(II). Results of the experiments clearly indicate that extraction is dependent on the solvent used for organic phase and pH of aqueous phase. For effective extraction of palladium(II) from PGMs, the solvent (organic phase) used should not be able to extract any other PGMs and other metals from the PGM solutions. Solvents, such as isoamyl alcohol and 2-ethyl-1,3-hexanediol were not suitable for the extraction of palladium(II) [49].

Table 2

Effect of organic solvents on percentage extraction and distribution ratio of palladium(II).

Solvent	Dielectric constant	Dipole moment	Density	% E	Distribution ratio (D)
Xylene	2.20	0.07	0.861	99.45	497
Toluene	2.38	0.31	0.867	91.12	26.02
Benzene	2.28	-	0.879	89.60	21.85
Anisole	4.33	1.38	0.990	E	E
Chloroform	4.81	1.15	1.489	51.12	2.62
Cyclohexane	1.88	-	0.779	NS	NS
n-butanol	17.51	1.66	0.81	41	1.73
dichloromethane	8.93	1.14	1.326	77.80	8.84
Ethylbenzene	2.41	-	0.867	81.64	11.17
1,2-dichloroethane	10.36	1.83	1.253	N	N
n-hexane	1.88	0.08	0.65	61.20	3.94

E, Emulsion; NS, Not soluble; N= No clear layer

Experimental conditions: palladium(II)= $100 \mu\text{g mL}^{-1}$, sodium oxalate = 0.04 M, pH = 3, 2-DDAP = $7 \times 10^{-4} \text{M}$, equilibrium time = 60 seconds, Strippant = 1 M NH_3 + 4% NH_4Cl

4. Effect of weak organic acid salt concentration

To achieve the highest extraction efficiency of palladium(II), extraction was carried out

from different aqueous phase media. In our study, extraction experiments of palladium(II) were carried out at fixed conditions: 2-DDAP concentration, $7 \times 10^{-4} \text{ M}$ in xylene; equilibrium time, 60 seconds; concentration of palladium(II), $100 \mu\text{g mL}^{-1}$; aqueous phase pH, 3. Extraction of palladium(II) was performed from different organic acid salt solutions such as sodium oxalate, sodium citrate, sodium malonate and sodium succinate in the concentration range from 0.01 M to 0.1 M. The results obtained are shown in Fig. 3, which clearly indicates that sodium oxalate exhibits as most excellent aqueous phase media for effective extraction of palladium(II) and percentage extraction increased from 62.30% to 99.45% with increase in concentration of oxalate in aqueous phase from 0.01 M to 0.04 M, however, percentage extraction decreased with further increase in concentration of oxalate (from 0.04 M to 0.1 M) in aqueous phase. This may be because of formation of very stable ion pair complex of 2-DDAP with oxalate, which prevent the exchange of palladium(II), thereby decreasing extraction [50]. Among the different organic acids used, oxalic acid is found to be more acidic character [51], hence it is easy to maintain pH of aqueous to 3 as compared to other organic acids. The comparative results of percentage extraction and distribution ratio of palladium(II) from different weak organic acid salt media are given in Table 3.

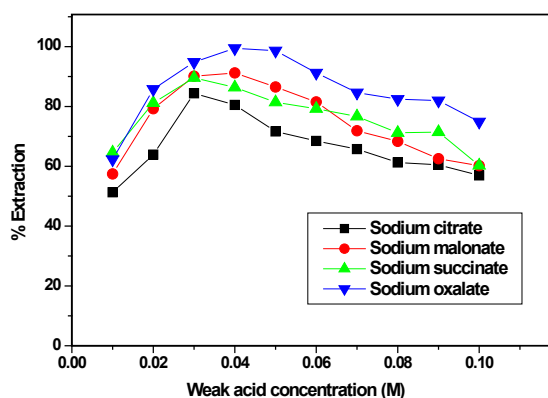


Fig. 3. Effect of weak organic acid concentration on percentage extraction of palladium(II). Experimental conditions: Palladium(II) = $100 \mu\text{g mL}^{-1}$, pH = 3, 2-DDAP = $7 \times 10^{-4} \text{ M}$ in xylene, equilibrium time = 60 seconds, Strippant = 1 M $\text{NH}_3 + 4\% \text{NH}_4\text{Cl}$

Table 3

Distribution ratio of palladium(II) with different aqueous phase.

Concentration (M)	Distribution Ratio (D)			
	Sodium succinate	Sodium malonate	Sodium citrate	Sodium oxalate
0.01	4.58	3.37	2.63	4.15
0.02	10.82	9.54	4.43	15.32
0.03	21.85	23.10	13.61	47.4
0.04	15.98	26.05	10.30	497
0.05	11	16.01	6.33	197.2
0.06	9.54	11.01	5.42	26.05
0.07	8.23	6.41	4.79	13.86
0.08	6.19	5.42	3.94	11.77
0.09	6.26	4.19	3.82	11.37
0.1	3.81	3.78	3.30	7.49

Experimental conditions: Palladium(II) = $100 \mu\text{g mL}^{-1}$, pH = 3, 2-DDAP = $7 \times 10^{-4} \text{ M}$ in xylene, equilibrium time = 60 seconds, Strippant = 1 M $\text{NH}_3 + 4\% \text{NH}_4\text{Cl}$

5. Effect of equilibration time

The effect of equilibrium time on the percentage extraction of palladium(II) with 2-DDAP was determined by varying the equilibrium time in the range from 20 seconds to 180 seconds. The experiments were carried out at fixed parameters: palladium(II) concentration, $100 \mu\text{g mL}^{-1}$ in 0.04 M oxalate; aqueous phase pH, 3; 2-DDAP concentration, $7 \times 10^{-4} \text{ M}$ in xylene. The aqueous phase and organic phase was equilibrated in the range between 20 seconds to 180 seconds. From the Fig. 4, it is observed that the percentage extraction of palladium(II) has increased from 44.30% and reached to 99.45% in 60 seconds, but it almost remained constant up to 180 seconds. It was

also confirmed that the no adverse effects of prolonged equilibration time on the extraction efficiency. Hence the equilibration time was kept constant to 60 seconds in further studies.

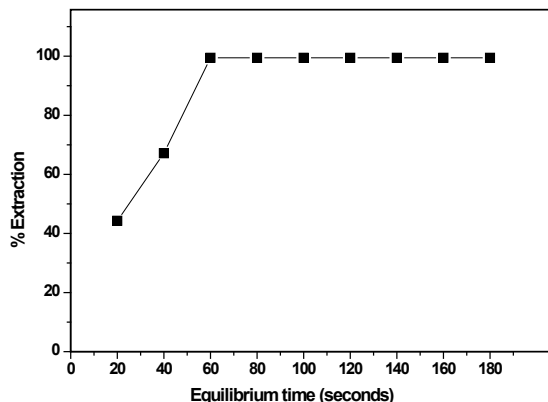


Fig.4. Effect of equilibrium time on percentage extraction of palladium(II). Experimental conditions: Palladium(II)= $100 \mu\text{g mL}^{-1}$, pH = 3, sodium oxalate = 0.04 M, 2-DDAP = 7×10^{-4} M in xylene, Strippant = 1 M NH_3 + 4% NH_4Cl

6. Stripping of palladium(II) from organic phase

To recover palladium(II) from loaded organic phase, highly efficient stripping process is required. In the following experiments, the organic phase was loaded with $99.45 \mu\text{g}$ of Pd(II) and stripping was carried out with two times 10 mL of stripping agent. When extraction of palladium(II) was carried out from acidic medium, then stripping is generally possible from basic medium in order to dissociate the ion pair complex of palladium(II) with extractant (2-DDAP). With that aim in mind sodium hydroxide and 1:1 ammonia solutions were tested for stripping of palladium(II). But it was observed that both solutions formed stable emulsion with organic phase. Therefore, it was decided to check the use of mixture of ammonia with ammonium chloride [36] and thiourea [40,49,52] for this purpose. The percentage stripping

data is shown in **Table 4**. The results obtained indicate that the thiourea shows incomplete (69.40%) stripping of palladium from loaded organic phase (2-DDAP). The mixture of 1M ammonia with ammonium chloride, shows that the percentage stripping increases with increasing concentration of ammonium chloride. **Fig.5** shows that 4% ammonium chloride in 1M ammonia was sufficient for complete stripping of palladium (II) from organic phase. On the basis of results obtained, 1 M NH_3 + 4% NH_4Cl was selected as the most effective stripping solution for palladium(II) from organic phase.

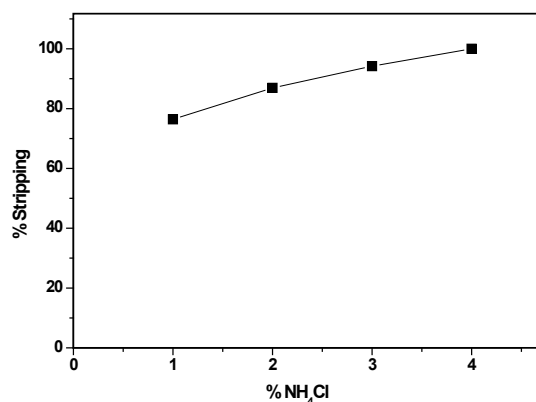


Fig.5. Effect of ammonium chloride concentration on percentage stripping of palladium(II). Experimental conditions: Palladium(II)= $100 \mu\text{g mL}^{-1}$, pH = 3, sodium oxalate = 0.04 M, 2-DDAP = 7×10^{-4} M in xylene, equilibrium time = 60 seconds.

Table 4

Percentage stripping of palladium(II) with different stripping agents.

Stripping agents	% Stripping
1 M NaOH	E
2 M NaOH	E
1:1 ammonia	E
0.1M thiourea in 1M HCl	63.42
0.5M thiourea in 1M HCl	67.80
1 M thiourea in 1 M HCl	69.40
1 M NH_3 + 1% NH_4Cl	76.4

1 M NH ₃ + 2% NH ₄ Cl	86.94
1 M NH ₃ + 3% NH ₄ Cl	94.20
1 M NH ₃ + 4% NH ₄ Cl	100

E = Emulsion formation

7. Selective separation of palladium(II) from precious metals

The separation of palladium(II) from commonly associated metals is challenging task in the solvent extraction experiments. Therefore, in order to investigate the utility of proposed method, it was successfully applied for selective separation of palladium(II) from binary mixture of metals such as Rh(III), Pt(IV), Au(III), Ru(III), Ir(III), and Os(VIII). The experiments were performed at following conditions: concentration of palladium(II) = 100 µg mL⁻¹ in 0.04 M oxalate at pH 3; 2-DDAP, 7×10⁻⁴ M in xylene; equilibrium time, 60 seconds. The proposed method selectively and efficiently separates the palladium(II) from the added metals by taking the advantages of their differences in extraction and stripping conditions. During these experiments palladium(II) was quantitatively extracted into organic phase and Rh(III), Pt(IV), Au(III), Ru(III), Ir(III), and Os(VIII) were remained in aqueous phase. Results of these experiments are presented in **Table 5**. It is observed from the results that other metals do not form ion pair complex with 2-DDAP under proposed conditions. The applicability of the proposed method is confirmed by successfully performing selective separation of palladium(II) from several precious metals such as Rh(III), Pt(IV), Au(III), Ru(III), Ir(III), and Os(VIII).

Table 5

Selective separation of palladium(II) from precious metals.

Amount of metal ions (µg)	Average ^a % recovery of Pd(II)
Pd(II) 100 + Rh(III) 100	99.45
Pd(II) 100 + Pt(IV) 100	99.40

Pd(II) 100 + Au(III) 100	99.40
Pd(II) 100 + Ru(III) 100	99.45
Pd(II) 100 + Os(VIII) 500	99.45
Pd(II) 100 + Ir(III) 500	99.45

a : average of six determinations

Experimental conditions: Palladium(II)= 100 µg mL⁻¹, pH = 3, 2-DDAP = 7×10⁻⁴ M in xylene, equilibrium time = 60 seconds, Strippant = 1 M NH₃ + 4% NH₄Cl

CONCLUSIONS

In this study, we have investigated a novel approach for selective and efficient extraction of palladium(II) from oxalate medium using 2-DDAP as efficient extractant. The 2-DDAP showed a remarkable high affinity and selectivity towards palladium(II) under the optimized conditions and expected to be the new benchmark for the separation of palladium(II) from PGMs. The extraction behavior of palladium(II) in the presence of Rh(III), Pt(IV), Au(III), Ru(III), Ir(III) and Os(VIII) has also been tested with 2-DDAP and percentage extraction in the case of palladium was found to be very high. The extent of stripping is also found to be very high (100%). The proposed method thus requires less amount of 2-DDAP (7×10⁻⁴M) and equilibrium time. The results obtained supports that 2-DDAP have excellent potential as extractant to recover palladium(II) from synthetic mixtures, automobile and catalytic waste materials.

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