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2-Dodecylaminopyridine assisted solvent extraction system for selective separation of rhodium (III) ion-pair complex from synthetic mixtures

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Abstract

A Novel approach was designed to extract rhodium(III) from salt of citric acid solution via solvent extraction method. The performances of rhodium(III) extraction with new extractant 2-dodecylaminopyridine (2-DDAP) were investigated. The results indicate that rhodium(III) extraction increased with increasing the pH of aqueous phase and became quantitative at pH 9 but decreased with increase of the concentration of citric acid solution above 0.06 M in aqueous phase. The transfer speed of rhodium(III) from aqueous phase to organic phase was fast, and the extraction equilibrium was established within 60 seconds. The extraction of rhodium(III) reached 99.43% with 5×10^{-4} M, extractant in xylene. Stripping behavior of rhodium(III) was studied with different strippants at various concentrations and stripping reached 100% by the use of 1M of hydrochloric acid solution. The selective and efficient separation of rhodium(III) from Pd(II) and Ru(III) was also carried out by proposed extraction and stripping conditions.

1. Introduction

The natural abundance of platinum group metals is very limited. The technological importance of these metals always created demands. The demands of these metals has increased because of their number of applications such as in automobile industry, electronic devices, laboratory vessels, thermocouple wires, fuel cells, jewellery making, pharmaceutical and petroleum industry. According to recent survey 58% palladium and 85% rhodium are used in the catalytic converter industry [1,2]. During the fuel burning process and automobile exhaust, release of gaseous components such are NOx, COx and hydrocarbons, which are dangerous to human health and the environment. Emissions of these components are reduced by the catalysts consisting of PGMs such as platinum, palladium and rhodium. Separation of PGMs is one of the most difficult processes in hydrometallurgy due to their similar chemical behavior [3]. A gap between demand and abundance of natural resources may be reduced by recycling of catalytic waste, spent material containing platinum group metals [4]. According to literature survey, the existing forms of platinum group metals and availability of metal species is highly dependent on the acidic, basic and chloride concentration in the aqueous solution [5]. Natural resources of these metals are limited and their demand in industry is ever increasing, therefore it is necessary to find an effective separation process to recover PGMs with excellent purity and efficiency from the secondary resources. For these purposes, efficient recovery of trace amounts of valuable metals, using highly selective processes that have no affinity for other base metals is required. As the aqueous chemistry of individual metal ion may resembles that of others in mixture, selective recovery of any particular metal from such complex mixture is difficult [6].
Many studies have been reported on the separation of rhodium(III), palladium(II), platinum(IV) and gold(III) from chloride solutions [7,8]. Several analytical methods such as ion exchange [9,10], sorption [11], precipitation [12], extraction chromatography [13] etc. has been reported for the separation of PGMs. The solvent extraction technique is one of the most versatile methods used for the selective separation of PGMs from mixed metal aqueous media. Recently, solvent extraction has become a suitable method for the extraction of PGMs from low concentrated sources, because it offers a number of advantages such as high selectivity and

purity. Many different extractants have been proposed for the extraction of rhodium(III), including ionic liquids [14,15], Nano particles [16], *N*-n-hexyl-bis-(N-methyl-*N*-n-octylethylamide)amine (HBMOEAA) [17], Phosphonic acids [18], Tri-n-octylamine (TOA), di-n-hexyl sulfide(DHS), Thiodiglycolamide (TDGA) [19], extraction of Rh(III) by *N*-n-octylaniline from malonate media [20], extraction of Rh(III) from bromide media in the presence of $SnCl_2$ by Cyanex 471 and Cyanex 926 [21], *N*-*N*'-dimethyl-*N,N'*-diphenyltetradecylmalonamide(DMDPHTDMA) [22], Tributylphosphate [23], Alkylaniline hydrochloride petroleum sulphide [24,25], Alamine 304-1, Alamine 308, Alamine 336 [26], Cyanex 925 [27], Cyanex 923 [28], Silica based (poly) amine [29] and Cetylpyridiniumchloride [30]. Two or more kinds of extractants (synergistic effect) has been widely studied in both fundamental [31,32] and practical aspects [33]. Though, number of extractants were used for the separation of rhodium(III) but few of them gave efficient results [34]. In some extraction procedures, rhodium(III) was partially extracted from chloride solution, required long time for extraction and difficult for stripping [35,36]. Therefore, the rhodium(III) chloro complex is not easily extracted which is due to its charge and labile character towards aquation. Hence, it is necessary to develop extraction procedure in weak organic acid media which gave better separation of metals due to enhanced stability of metal organic acid complexes.

In the present work, rhodium(III) and its selective separation from palladium(II) and ruthenium(III) was carried out directly and effectively using new extractant 2-DDAP from sodium citrate media. The effects of various parameters like pH, extractant concentration, organic acid concentration, stripping agents, diluents on the distribution ratio have been studied. The novelty of the present method is that the proposed extractant, has better selectivity and efficiency as compared to reported methods, and also reduced amounts of reagent and strippant are sufficient to extract the rhodium(III). In addition to this, the observed extraction parameters indicates that the present methodology may have potential application for selective and efficient separation of rhodium(III) from other PGMs.

2. Experimental

2.1 Apparatus and chemicals

A Shimadzu UV-Visible Spectrophotometer (UV 1800) with 1 cm^2 quartz cell was used for the determination of extracted metal and pH optimization was carried out by a Systronics Digital pH meter model No. 802 with combined glass electrode. All the chemicals used were of AnalaR grade and purchased from commercial suppliers Alfa Aesar (Thermo Fisher Scientific, Hyderabad, India) and Spectrochem (Spectrochem Pvt. Ltd., Mumbai, India). These are used as such without further purification. The stock solutions of metals were prepared by dissolving necessary amount of $PdCl_{2.}xH_2O$, $RhCl_3.4H_2O$ and $RuCl_3.xH_2O$ in minimum quantity of dil. hydrochloric acid and diluted to required dilution using deionized water and standardized by known methods [37,38]. A series of concentration of working solutions were prepared by diluting the above stock solution. An extractant 2-dodecylaminopyridine (2-DDAP) was synthesized by reported method [39] and characterized by spectral techniques. The organic phase was prepared by dissolving 2-DDAP in xylene. Doubly distilled water was invariably used throughout the experiment. The structure of the extractant 2-dodecylaminopyridine (2-DDAP) is shown as;

2.2 Liquid-liquid extraction procedure

An aliquot of 100 µg of rhodium (III) has been mixed with sodium salt of citric acid to make its concentration in the range 0.01 to 0.1 M, in total volume of 25 mL of the solution. The pH of the aqueous phase was adjusted by dilute hydrochloric acid and sodium hydroxide solution. The solution was then transferred to 125 mL separating funnel and shaken with 10 mL of 2-DDAP ($1×10^{-4}$ M to $1×10^{-3}$ M) in xylene for appropriate time to attain the equilibrium. After separating the two phases, the aqueous phase was discarded and organic phase was stripped with two 10 mL portions of 1 M hydrochloric acid solution. The stripped portion was evaporated to moist dryness and extracted metal was leached with dilute hydrochloric acid solution and transferred in to 50 ml volumetric flask, 10 ml of 20 % potassium iodide was added, the solution was mixed well and heated for 15 min. in boiling water bath. To the cooled solution, 10 ml of 10 % stannous chloride solution was added and diluted with distilled water containing 1 M hydrochloric acid in final concentration. The unstoppered flask was kept in boiling water bath for 2 min. The solution was then cooled and the absorbance of reddish brown solution was measured at λmax 460 nm against a reagent blank [40]. The concentration of rhodium (III) was computed from the calibration curve. Distribution ratio (D) was calculated as the ratio of rhodium(III) concentration in organic phase $[Rh]_o$ to aqueous phase $[Rh]_{aq}$ after extraction using equation

$$D = \frac{[\mathrm{Rh\,(III)}]\mathrm{org}}{[\mathrm{Rh\,(III)}]\mathrm{aq}} \qquad (1)$$

Where $[Rh(III)]_{org}$ is concentration of Rh(III) in organic phase, $[Rh(III)]_{aq}$ is concentration of Rh(III) in aqueous phase. From the D values percentage of extraction was calculated by following equation, where V_{org} is volume of organic phase and V_{aq} is volume of aqueous phase.

$$\%\,E = \frac{100\,D}{D + {}^{\mathrm{Vaq}}/_{\mathrm{Vorg}}} \qquad (2)$$

In the extraction experiments 2-DDAP displays very good extractability for rhodium (III), and extraction mechanism discussed here for understanding the nature of ion pair complex of rhodium (III) in citric acid media with 2-DDAP. The mechanism of ion pair complex was initiated through protonation of 2-DDAP to form cationic species, while anionic species was formed by combining citric acid with rhodium (III) and both of these formed the ion pair complex as given, [20].

$$[\text{2-DDAPH}]^{+}_{org} + [\text{Rh(citrate)}]^{-}_{aq} \rightarrow [\text{2-DDAPH}^{+} : \text{Rh(citrate)}^{-}]_{org}$$

The subscripts org and aq denote the species in organic and aqueous phases, respectively.

3. Results and discussion

3.1 Effect of pH on rhodium(III) extraction

The role of aqueous phase pH on the extraction of rhodium(III) was investigated in the pH range 1-10. The pH of aqueous phase was maintained by dilute hydrochloric acid and sodium hydroxide solution. The results are shown as **Figure 1**.

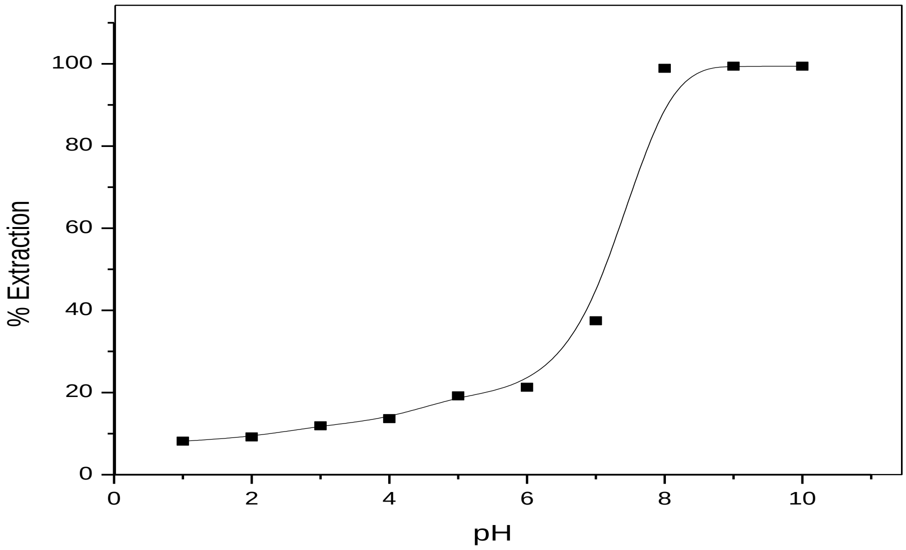

Figure 1. Effect of aqueous phase pH on extraction of rhodium(III), Experimental conditions: rhodium= 100 µg, citric acid = 0.05 M, 2-DDAP = 5×10^{-4} M in xylene, phase contact time = 60 seconds, Strippant = 1 M hydrochloric acid solution

It can be seen from figure 1, that the extraction of rhodium(III) slightly increased from 8.16% to 37.45% with increasing pH from 1 to 7, but it increased suddenly when pH has increased from 7 to 10. The corresponding change in extraction (98.9% to 99.43%) of rhodium(III) was observed due to establishment of equilibrium in the pH range 8-10. It is evident that extraction efficiency increases with an increase in equilibrium pH. The further experiments for quantitative extraction were carried out at pH 9 of aqueous phase. Extraction of rhodium(III) is negligible in acidic pH, as the acidic condition is not favourable for the formation of ion pair of complex. The extraction of rhodium(III) complex with citrate and 2-DDAP becomes quantitative in the pH range 8-10. In this pH range ion pair complex of rhodium(III) with 2-DDAP is stable which enhance the selective and efficient extraction of rhodium.

3.2 Effect of 2-DDAP concentration

The effect of concentration of 2-DDAP was scanned in the range of 1×10^{-4} M to 1×10^{-3} M for the extraction of 100 µg rhodium(III) from 0.05 M citric acid solution. **Figure 2**, shows that the extraction of rhodium(III) increases from 29.6% to 99.43% with increasing 2-DDAP concentration from 1×10^{-4} M to 5×10^{-4} M using xylene as diluting solvent. The extraction of rhodium(III) was almost remained constant (99.43%) by further increasing 2-DDAP concentration from 1×10^{-4} M to 1×10^{-3} M. In order to effective extraction of rhodium(III), the concentration of 2-DDAP in the following experiments was fixed at 5×10^{-4} M.

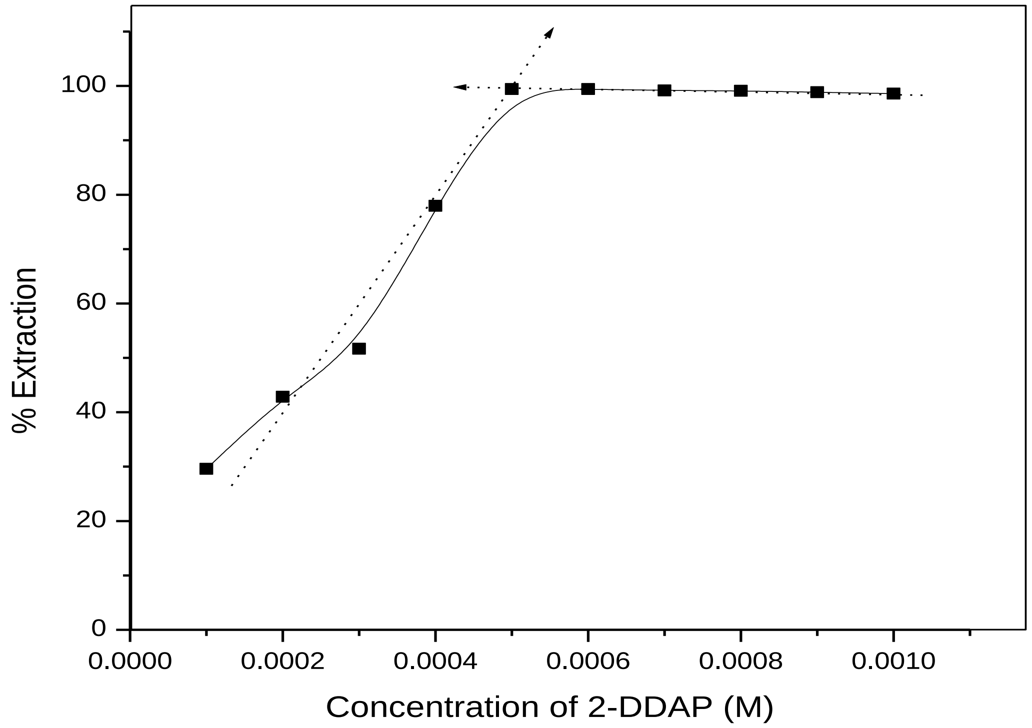

Figure 2. Effect of 2-DDAP concentration on extraction of rhodium(III). Experimental conditions: Rhodium(III)= 100 µg, citric acid = 0.05 M, pH = 9.0, phase contact time = 60 seconds, Strippant = 1 M hydrochloric acid solution

3.3 Effect of weak organic acid concentration

The dependence of extraction efficiency of rhodium(III) metal ion was studied in the presence of weak organic acid. Aqueous phase of experiments were prepared by sodium salt of malonic, succinic, oxalic and citric acid in the range of 0.01 M to 0.1 M concentration. The results obtained are shown in **Figure 3,** which clearly indicates that citric acid exhibited the most excellent aqueous media because of more basic in nature than malonic, succinic and oxalic acid for the extraction of rhodium(III). It is also shown that the extraction of rhodium(III) increases from 61.9% to 99.43% with increasing the concentration of citric acid from 0.01 M to 0.06 M. But extraction efficiency decreased (from 99.43% to 78.10%) when concentration increased from 0.06 M to 0.1 M. This is because of the formation of stable ion pairs of 2-DDAP) with citrate which prevent exchange of complex ions, thereby decreasing extraction. Comparison of the distribution ratio (D) of rhodium(III) from the various acid solutions (aqueous phase) by 2-DDAP is shown in **Table 1**.

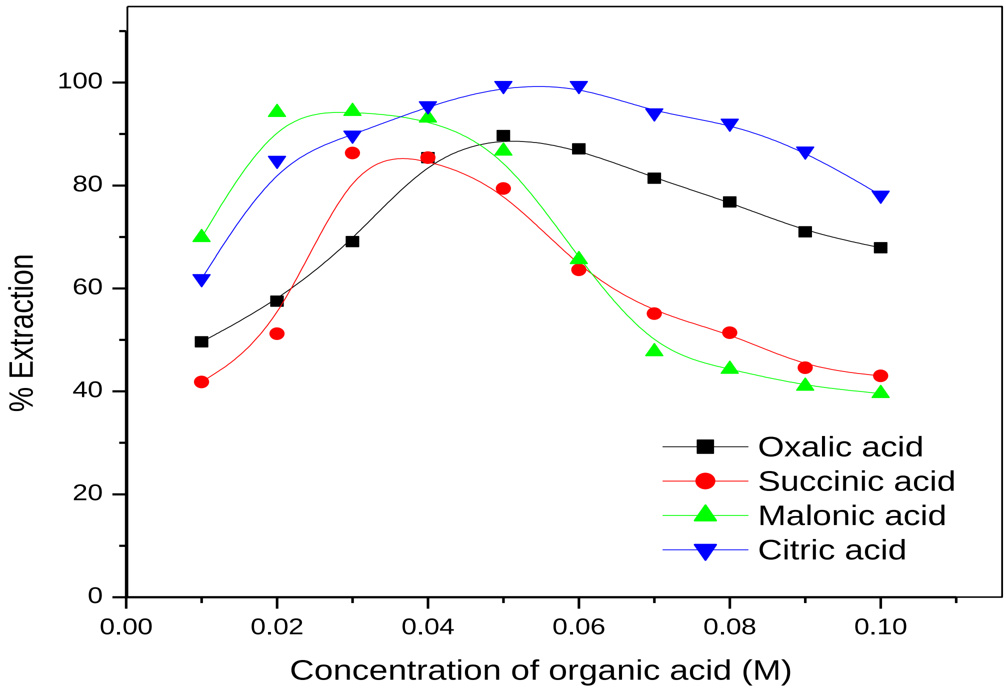

Figure 3. Effect of weak organic acid concentration on percentage extraction of rhodium (III). Experimental conditions: Rhodium(III)= 100 µg, pH = 9.0, 2-DDAP = 5×10^{-4} M in xylene, phase contact time = 60 seconds, Strippant = 1 M hydrochloric acid solution

Table 1. Distribution ratio of rhodium(III) from various media (Aqueous phase)

Concentration(M)	**Distribution Ratio (D)**			
	Malonic acid	**Succinic acid**	**Oxalic acid**	**Citric acid**
0.01	5.82	1.80	2.46	4.07
0.02	40.95	2.50	3.38	14.15
0.03	42.90	15.98	5.61	22.45
0.04	34.48	14.72	14.72	53.00
0.05	16.35	9.68	21.87	451.95
0.06	4.78	4.38	17.07	451.95
0.07	2.28	3.07	11	40.91
0.08	1.99	2.64	8.34	29.7
0.09	1.73	2.00	6.03	16.35
0.10	1.64	1.88	5.30	8.97

3.4 Effect of various organic solvents

The extraction system containing identical amount of rhodium(III), 100 µg in 0.05 M citric acid media at pH 9 was prepared and extracted with 2-DDAP (5×10^{-4} M) in number of diluents. It was investigated that solution of 2-DDAP in toluene, benzene, xylene provide quantitative extraction of rhodium(III). Xylene solvent among the other diluents shows highest distribution ratio. The extractant solutions (2-DDAP) were also prepared in different solvents such as n-hexane, isobutylmethylketone, n-butanol and have shown less distribution ratios. Therefore, xylene is preferred for further extraction studies as it is nonpolar solvent with minimum toxicity as compared to benzene and toluene and offers better phase separation. Polar solvents consist of uneven distribution of charges or electron density which inhibits ion pair formation of extracted species. It is evident that nonpolar solvent has no repulsive forces therefore extraction of rhodium(III) is found to be more efficient and the results obtained are presented in **Table 2**.

Table 2. Effect of solvents/diluents on Distribution ratio and percentage extraction of Rh(III).

Solvent	**% Extraction**	**Distribution ratio (D)**
Xylene	99.43	451.95
Toluene	93.54	37.41
Benzene	91.80	28.68
n-Butanol	51.70	2.69
Isobutylmethylketone	47.60	2.27
n-Hexane	44.30	1.99
Chloroform	43.80	1.95

3.5 Stripping of rhodium(III) loaded in organic phase

In order to recover the metal from loaded organic phase, stripping studies are crucial in solvent extraction experiments [41]. Different stripping agents like HCl, HNO_3, and H_2SO_4 in the concentration range 0.2 M to 1 M (two 10 mL portion) were employed for stripping of Rh(III) from the loaded 5×10^{-4} M 2-DDAP containing 99.43 µg of Rh(III). The results are shown in **Figure 4**, it was observed that the percentage stripping increases with increase in concentration of stripping agent. Percentage of stripping with 1 M HNO_3 and 1 M $H_2SO_4$was found to be 94% and 93.1% respectively. It was investigated that 100% stripping of rhodium(III) with 1 M HCl and can be selected as best stripping agent from our studies. The stripping process is reverse of extraction. When extraction of metal is carried out from basic medium, then stripping is generally possible from acidic medium in order to dissociate ion pair complex. In the present method, concentration of stripping agent was less as compared to reported method [19].

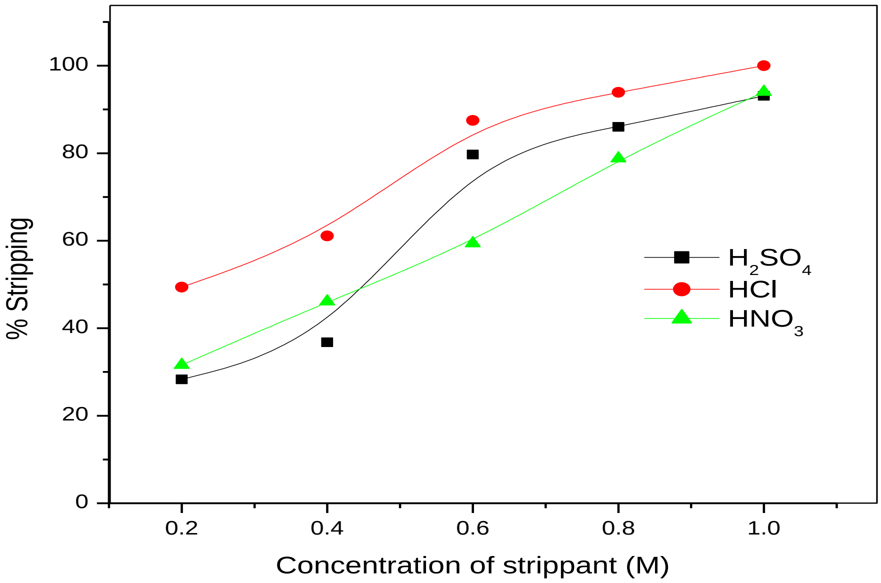

Figure 4. Effect of stripping agent on percentage stripping from loaded organic phase of rhodium(III), Condition: Two portions of 10 mL of strippant.

3.6 Effect of equilibration time

The dependence of equilibrium time for extraction was studied in the range 20 seconds to 180 seconds. **Figure 5** shows the percentage of extraction of 100 µg rhodium(III) in 0.05 M citric acid solution of pH 9 with 2-DDAP (5×10^{-4} M) as a function of equilibration time. The results indicate that the extraction of rhodium(III) increased from 44.2% to 99.43% as equilibrium time varied from 20 seconds to 180 seconds, but it almost remained constant when the equilibrium time exceeded 60 seconds. The results proved that rhodium(III) could be extracted fast by 2-DDAP extractant. But to ensure complete extraction of rhodium(III), 60 seconds time period is sufficient. In order to extract efficiently and selectively rhodium(III), the equilibrium times in further experiments were fixed at 60 seconds. It was also confirmed that the no adverse effect of prolonged equilibration time was observed on extraction equilibrium.

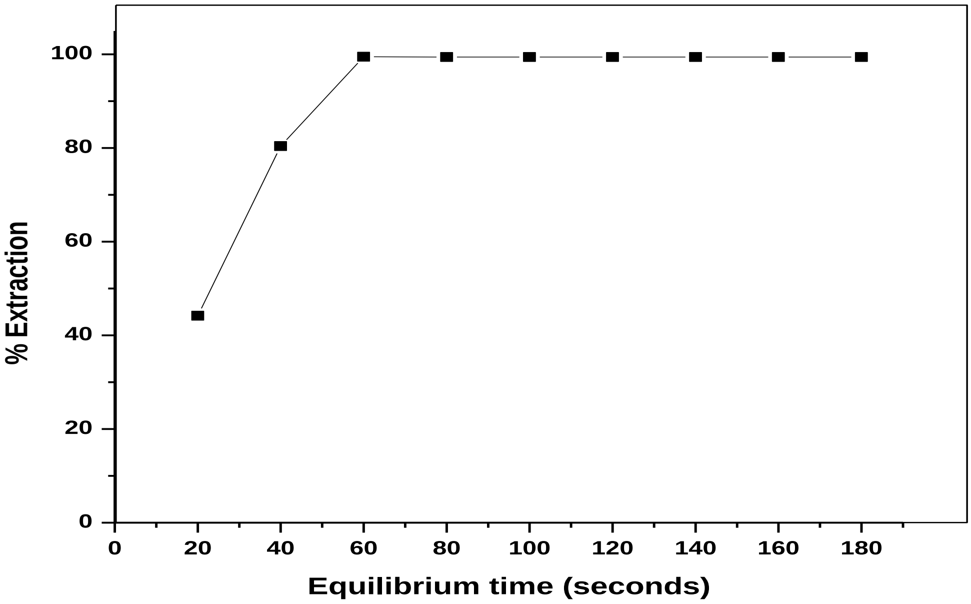

Figure 5. Effect of equilibrium time on percentage extraction of rhodium(III). Experimental conditions: Rhodium(III)= 100 µg, pH = 9, citric acid = 0.05 M, 2-DDAP = 5×10^{-4} M in xylene, Strippant = 1 M hydrochloric acid solution

3.7 Effect of phase ratio(A/O)

For the study of effect of phase ratio (aqueous to organic), 100 µg rhodium(III) was extracted in the range of 10 mL to 100 mL aqueous phase having 0.05 M citrate solution at pH 9 with 10 mL of 5×10^{-4} M extractant (2-DDAP) and equilibrium time was 60 seconds. The rhodium(III) was stripped with 1 M, two 10 mL portion of hydrochloric acid solution and estimated by present method. It was observed that the percent extraction is efficient when aqueous to organic volume ratio was 1:1 to 5:1 and while it decreased when ratio was changed from 5:1 to 10:1. Hence, the recommended aqueous : organic volume ratio is 2.5:1 for quantitative and effective extraction.

3.8 Effect of foreign ions

In order to investigate the tolerance limit of foreign ions, standard solutions of different metal ions were prepared. Rhodium(III) was extracted in the presence of different concentrations of foreign ions. The extraction of rhodium(III) was carried out by proposed reagent and procedure. Initially the extraction of rhodium(III) with large amount of foreign ion shows large deviation from extractability of 2-DDAP, this deviation from the results may be due to foreign ions which inhibits the ion-pair formation of rhodium(III) with the 2-DDAP. The measurements were repeated with different concentrations of foreign ions and the tolerance was set at the amount of foreign ion that presents to cause an error ±2% in the recovery of rhodium(III). The results obtained are shown in **Table 3**.

4. Selective separation of rhodium(III) by 2-DDAP

4.1 Separation of Rh(III) from Ru(III) and Pd(II)

Different researchers have studied the extraction and separation of PGMs from low concentration of aqueous solutions. Separation of rhodium(III) from palladium(II) and ruthenium(III) was carried by taking the advantages of their ion-pair formation and stripping conditions. The selectivity shown for rhodium(III) by extractant 2-DDAP is determinant and again focusing the research on the use of 0.05 M citric acid solution with a more practical interest. Separation of rhodium(III) from palladium(II) and ruthenium(III) was carried using the present extraction and stripping conditions. Separation of rhodium(III) from these metals depends on the ability of formation of ion pair complex by controlling the extraction conditions and stripping with particular reagents. For this separation, the aqueous solution of 0.05 M citric acid with mixture of 100 µg Rh(III), 100 µg Pd(II) and 50 µg Ru(III) at pH 9 equilibrated with 5×10^{-4} M 2-DDAP for 60 seconds. Rhodium(III) was quantitatively extracted and determined by the proposed method. Palladium(II) and Ruthenium(III) are not form ion pair complex with 2-DDAP in basic pH condition and remained in aqueous phase and strippants are also different for these metal ions[42-45].

Table 3. Effect of foreign ions on the extraction of Rh(III)

Foreign ions	**Added as**	**Tolerance limit (mg)**
Au (III)	$HAuCl_4$	5
Cr (III)	$CrCl_3$	10
Mn(II)	$MnCl_2.6H_2O$	10
Fe (III)	$NH_4Fe(SO_4)_2.12H_2O$	15
Fe(II)	$FeSO_4.7H_2O$	20
Mg(II)	$MgCl_2.6\ H_2O$	10
Zn(II)	$ZnSO_4.7H_2O$	15
Cu(II)	$CuSO_4.5H_2O$	20
Ni(II)	$NiCl_2.6H_2O$	15
Co(II)	$CoCl_2.6H_2O$	15
Sn (II)	$SnCl_2\ .\ 2H_2O$	10

4.2 Separation of rhodium (III) from commonly associated elements

In order to investigate the utility of proposed method, it was successfully applied for the separation and determination of Rh(III) from commonly associated metal ions such as Pt(IV), Au(III), Cu(II), Co(II), Ni(II) and Fe(III) in 0.05 M citric acid media at pH 9. A solution containing 100 µg of Rh(III) and known amounts of other metal ions were added and Rh(III) solution was equilibrated with 5×10^{-4} M 2-DDAP for 60 seconds. **Table 4** shows the results of extraction of Rh(III) in the presence of commonly associated metal ions**.** As expected, there is no significant difference in the results obtained, indicates that the associated metal ions with rhodium(III) are not extracted practically by 2-DDAP under optimized conditions.

Table 4: Separation of rhodium(III) from commonly associated metals

Amount of metal ions (µg)	**Average (%) recovery**
Rh(III) 100;Pt(IV) 100	99.40
Rh(III) 100; Au(III) 100	99.25
Rh(III) 100; Cu(II)1000	99.60
Rh(III) 100; Co(II) 1000	99.35
Rh(III) 100; Ni(II) 500	99.70
Rh(III) 100; Fe(III) 500	99.50

Conclusions

We have investigated that the new selective and efficient extractant 2-DDAP, is successful for practical use for the extraction of trivalent rhodium from citric acid solution at pH 9. The separation of Rh(III) from Pd(IV) and Ru(III) was carried out on the basis of differences in their extraction and stripping properties towards 2-DDAP. The extraction behavior of Rh(III) in the presence of Pt (IV), Au(III), Cu (II), Ni(II), Co(II) and Fe(III) has been tested with 2-DDAP and the percentage extraction in the case of Rh(III) was found to be very high. The proposed method requires fewer amounts of extractant concentration and equilibrium time. The results obtained concludes that 2-DDAP have excellent potential as extractant to recover rhodium(III) from mixtures of commonly associated metals

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