Research Article

Recovery of Rhodium and Palladium from Spent Automotive Catalyst by a New Extractant

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Abstract

This work examines a hydrometallurgical route for processing spent commercial catalysts containing Rh-Pd supported on a substrate of metals such as Al/Mg/ Ce used in Iranian car for recovery of the noble metal with less final wastes generation. Samples were initially pre-oxidized (650°C, 2 h, 1atm) in order to eliminate coke and the other pollutants. The basis of the present route is the partial dissolution of the pre-oxidized catalyst in a non aqua-regia medium. Temperature and time necessary to dissolve all Pd and Rh were optimized in order to reduce the operation severity and support substrate solubilization Then, the solvent extraction and precipitation methods have been used to develop a process to separate palladium and rhodium from a synthetic chloride solutions containing other associated metals such as Al, Mg, Zr,Ce and Sr in a the same concentration and condition of leach solutions obtained by processing the spent catalyst at <1 M HCl acidity. At pH 3.3, the quantitative precipitation of Al ,Zr and Sr was achieved using 15 wt% $Na_3PO_4 \cdot 12H_2O$, with ~6% loss of Pd and Rh due to adsorption phenomenon. The synsesized extractant 4-(4-Methoxybenzylideneamino)-5-methyl-4H-1,2,4-triazole-3-thiol (MBIMTT) is a ligand of the class Schiff bases contains N-S that could separate rhodium at an unit aqueous to organic ratio (A/O) and concentration of 0.01 M. Stripping of Rh from loaded organic with 0.5 M thiourea (Tu) and 0.3M HCl indicated that ~99.9% stripping efficiency. The selective precipitation of palladium was performed with NH_4Cl from rhodium free raffinate with a recovery of >98%.

Keywords: Palladium; Rhodium; MBIMTT; Solvent extraction; Hydrometallurgy

NO	Complete Name	Abbreviation
1	4-(4-Methoxybenzylideneamino)-5-methyl-4H-1,2,4-triazole-3-thiol	MBIMTT
2	Organic ratio	A/O
3	Thiourea	Tu
4	Platinum Group Metals	PGMs
5	Three-way catalyst	TWC
6	Ammonium Persulfate	APS
7	Di –n-octyl sulphoxide	DOS
8	Tri Iso Butyl Phosphine Sulfide	TIBS
9	Energy Dispersive X-ray flourcence	ED-XRF
10	Inductive Coupled Plasma Optical Emission Spectrometer	ICP-OES
11	X-ray Diffraction	XRD
12	3-Methyl-4-amino-5-mercapto-1,2,4-triazole	MAMT

13	Infrared Spectra	IR
14	loaded organic	LO
15	Iranian Academic Center for Education, Culture & Research	ACECR
16	Geological Survey of Iran	GSI
17	Atomic Energy Organization of Iran	AEOI

Introduction

The platinum group metals (PGMs) are increasingly used in the industry for various purposes such as dental applications, electronic and electrical devices, jewelry, biomedical devices and catalysts, mainly in automobile exhaust emission control catalysts . The main mineral sources of these precious metals are very low and limited to the copper-nickel ores, sperrylite (Platinum Arsenide, $PtAs_2$), cooperite (Platinum Sulfide, PtS). Due to this limitation of natural resources, the PGMs recycling from industrial wastes and secondary resources has been much studied in recent decades [1].

PGM based catalysts used to reduce pollutants such as CO , NOx and SOX in catalytic converters of automotive industry. Three metals of platinum group metals i.e. platinum (Pt), palladium (Pd) and rhodium (Rh) are employed as active materials in Three-way catalyst (TWC)[2].

In the year 2000, it was reported that automotive exhaust catalysts consumed approximately 60% PGMs worldwide [3]. These catalysts like the other catalysts after a period of active life get deactivated and at this stage it is considered as a waste. Spent catalysts are harmful to the environment due to the presence of soluble/leachable organic and inorganic compounds [4], so their disposal in landfills is restricted. Recycling and recovery of spent automobile catalysts provide a growing secondary source of PGMs production. Worldwide efforts recover and refine palladium and platinum from different spent materials, by an efficient and cost effective method [5].

Since the physical and chemical properties of these metals are very similar, it is difficult to separate these metals from each other. Traditional PGMs recovery methods involve physical treatment, acid dissolution, chemical separation and refining [6]. Recovery of PGMs are reported by a variety of methods such as classical precipitation methods [7, 8] with a relatively poor selectivity, numerous unit operations, recycle streams and refining steps. On the other hand, hydrometallurgical leaching followed by solvent (liquid-liquid) extraction offers a number of advantages over the classical precipitation methods due to their higher selectivity, scrubbing step to achieve high metal purity, and complete removal of metals by multi-stage extraction steps [9].

Literature survey revealed that the extraction of PGMs, in particular Pd and Pt, have been reported extensively by many researchers from acidic (chloride) media, mostly from synthetic solutions at low metal concentrations employing a variety of extractants such as TBP [10] amines [11,12], oximes [13,14], thio-phosphoric acid [15], phosphonic acid [16], thiophosphinic acid [17], TIBPS [18], sulphoxides [19], thiol [20], thiourea [21], tributyl phosphate [2] and bis-(2-ethylhexyl) phosphoric acid [3]. Alamine336 [4], HMAINH [5] have been tested for liquid-liquid extraction of platinum group metals . In comparison to these extractants, ones containing Schiff bases such as Nitrogen-sulphur showed promising effects in the field of analytical chemistry for the separation of platinum group metals [6].

Among PGMs, rhodium has the poorest extraction yield especially in chloride medium. This is because of steric hindrance of the highly charged octahedral complexes and the difficulty of packing two or three cationic organic molecules around a single cation. Furthermore, the Rh^{+3} aquo-chloro complexes are kinetically inert therefore, replacement of Cl/H_2O in the inner coordination sphere by extractants is generally unsuccessful.
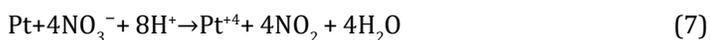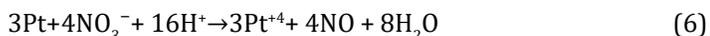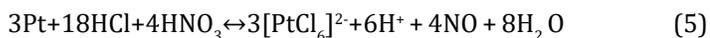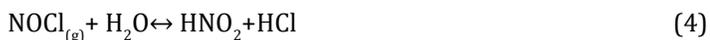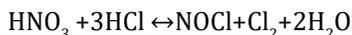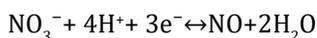
Although the addition of stannous chloride to Rh^{3+} in HCl solution drastically improves Rh extraction, there are two problems: the use of a large amount of stannous chloride and the difficulty of back-extraction. The capacity to both extract and back-extract Rh^{3+} from the chloride media without additives is preferable for a new extractant. An ion-pair extraction using protonated extractants is considered for the Rh aquo-chloro anion complex because of their inert properties, although such a simple mechanism is insufficient to achieve high extraction efficiency. Hence, additional effects onto the ion-pair reaction seem to be required [22].

On the other hand, rhodium being a soft acid, can be selectively extracted with soft donor base extractants containing 'N' or 'S' atoms. Based upon this presumption, several extractants, namely, N,N-Dialkyl-N′-benzoylthioureas [7], Kelex100 [8], Dioctyl sulphides [9], trialkylphosphinesulphide [10] have been studied for the extraction of Rhodium (III).

The main objective of the present study was to develop a simple process flowsheet involving precipitation and solvent extraction methods for the selective separation of rhodium from a chloride solution containing Pd(IV), Rh(III), Al(III), Mg(II) and other metals similar to leach solutions obtained by the processing spent PGM-containing catalysts.

The leaching of PMG in aqua regia(HNO_3/HCl) is not environmentally friendly method because of its toxic gas emissions such as nitrogen oxides(NO_x) due to the reactions (1)–(7) even

in the absence of any dissolution process.

$$NO_3^- + 4H^+ + 3e^- \leftrightarrow NO + 2H_2O \tag{1}$$

$$HNO_3 + 3HCl \leftrightarrow NOCl + Cl_2 + 2H_2O \tag{2}$$

$$2NOCl_{(g)} \rightarrow 2NO_{(g)} + Cl_2 \tag{3}$$

$$NOCl_{(g)} + H_2O \leftrightarrow HNO_2 + HCl \tag{4}$$

$$3Pt + 18HCl + 4HNO_3 \leftrightarrow 3[PtCl_6]^{2-} + 6H^+ + 4NO + 8H_2O \tag{5}$$

$$3Pt + 4NO_3^- + 16H^+ \rightarrow 3Pt^{+4} + 4NO + 8H_2O \tag{6}$$

$$Pt + 4NO_3^- + 8H^+ \rightarrow Pt^{+4} + 4NO_2 + 4H_2O \tag{7}$$

On mixing HCl and HNO_3, toxic gases nitrosyl chloride (NOCl) and chlorine gas are formed. Afterwards, NOCl decomposes into nitrogen oxides and chlorine that are main air pollutants. All of these gases are toxic and causes ozone layer depletion . In the atmosphere, they may convert to nitric acid, an important contributor of acid rains [23, 24].

Further studies showed the presence of an oxidizing agent like hydrogen peroxide improved the PMG leaching kinetics to less than 1 h in the absence of strong mineral acid [25]. The most common oxidizing agent in the recent researches is H_2O_2 with a standard electrode potential(E°) of +1.77 V.

The more studies showed the possibility of replacing the HNO_3 of aqua regia with hydrogen peroxide [26] So, based on the above mentioned, we decided to use $HCl/H_2SO_4/F^-$ plus a strong oxidizing agent such as ammonium persulfate (APS) to leach the pretreated spent catalyst powder in this study.

APS is a more strong oxidizing agent with a E°of 2.1 V and has been employed to improve PGM leaching from spent catalysts and other materials.

So, we investigated the leaching and separation conditions for recovery of palladium and rhodium from the spent automobile catalyst. Oxidative acid leaching followed by either chemical precipitation and solvent extraction for Rh extraction was examined. The extractant was a new ligand of the class Schiff bases contains N-S namely MBIMTT and studied for its extraction behavior for Rhodium (III) .

Various process parameters such as extractant concentration, aqueous phase pH, stripping agent concentration and other ones were studied. Palladium was also found to be leached with an oxidative $HF/HCl/H_2SO_4$ media. The leaching residue and the filtrate after palladium separation were used for Rh recovery via extraction with the extractant mentioned above. Based on the results a separation and recovery scheme was proposed.

Experimental

Materials and apparatus

The spent catalyst was a cylindrical honeycomb TWC from Johnson Matthey Inc (Model: JM403). This convertor is used in the Pegout Model-206 car in Iran. The extractants used for comparison tests are cyanex 923(a mixture of four trialkylphosphine oxides) from Cytec Canada Inc ,Alamin336(tri-N-octylamine) from Henkel Corp, DOS(Di –n-octyl sulphoxide) from Aldrich and TIBS(tri iso butyl phosphine sulfide) from Cyanimide Co.

All other materials and chemicals were of analytical reagent grade from Merck or Fluka.

Chemical analysis of the spent catalyst ,products and solutions was determined by using high resolution ED-XRF(Energy Dispersive X-ray flourcence) analyser(Oxford Model ED2000 and thermo fisher inductive coupled plasma optical emission spectrometer (ICP-OES), model IRIS Intrepid II XDL, USA ICP-OES and XRD (X-ray Diffraction analyser Model: X'Pert Pro MPD , PANalytical).

Procedure

Pretreatment

The sample was pulverized with a disc mill and then sieved. The powder with a size of less than 200 μm was prepared in the end of this step. This step purpose was to make the sample more homogenous during the sampling and easier to agitate during the leaching via increasing its surface area. The powder sample was kept in a desiccator to avoid contamination.

Then, this powder was oxidized in temperature 650°C, atmospheric pressure with the rate of 2°C.min^{-1} in a furnace for 2h. This process eliminates hydrocarbons, charcoal, water and other pollutant volatile that exist probably on the catalyst after fuel consuming in the car engine.

The roasted mass was cooled down in the furnace and transferred to a desiccator before running the experiments.

Acidic-Oxidative leaching

50 grams of the mentioned above powder was added in a 1-L glass container immersed in a thermostatically controlled water bath equipped with magnetic stirrer. A mixture containing 1%NH_4F /10% HCl/50% H_2SO_4/1% APS(wt%) , was used as the leaching agent. The fluoride ion was also employed by adding NH_4F, which improved the dissolution efficiency by attacking the interface between the PGMs and the catalyst substrates. H2SO4 as a proton source also improves the leaching of Rh.

A reflux system (glass condenser) was used to recover gases and any escaped gases were scrubbed in water. The liquid/solid ratio of this leaching agent employed was 5 ml g^{-1} sample,

which was the minimum amount to cover all powdered spent catalyst. The next step was to dissolve quantitatively all Pd and Rh along with minimum simultaneous dissolving of other elements of the catalyst.Leaching was performed with slow magnetic stirring (50 rpm) for 3 hours at 85°C.

After the experiments residues were separated from the liquid phase by filtration, washed with water and dried at 150°C for 1.5 h. Washing waters were added to the leachate. All experiments were run in triplicate, and data obtained were within ± 3%.

Aqueous feed solution containing Pd, Rh and other metal impurities Al, Zr, Ce, Sr and Mg were prepared from respective metal salts (G.R grade $PdCl_4$, $RHCl_3.3H_2O$, $AlCl_3$, $Zr(SO_4)_2$, $CeCl_3$,$SrCl_2.6H_2O$,$MgCl_2$).The composition of this synthetic solution was simmilar to leach liquor generated by the processing of the spent automobile catalyst mentioned above

Precipitation of contaminants

The precipitation experiments were conducted by adding $K_3PO_4.3H_2O$ at room temperature and different pH values in a 1-L beaker equipped by a magnetic stirrer and a pH meter electrode. The solid residue was separated from liquor by filtration. The liquors were analyzed by ICP-OES to calculate the precipitation yield in the removal of impurities cations. The precipitated cake of metal phosphates was washed with double distilled water and acidized water (pH≈ 4.0) respectively several times and dried in oven temperature (65 ± 3°C). All the experiments were conducted in duplicate and the errors associated with the extraction and precipitation percentages varied within ±3%.

Pd extraction

In order to separation of Pd from the solution, a solution of NH_4Cl 10 wt% added to supertant gained from the above mentioned filtration step. Then, Pd was precipitated as $(NH_4)_2PdCl_6$ .After drying, the precipitate was ignited at 400°C to produce sponge Pd white –silvery powder.
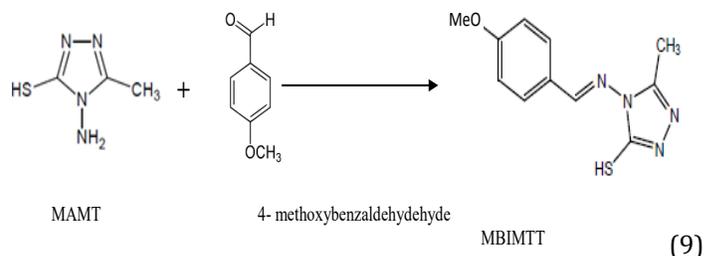
Solvent Extraction of Rh

Synthesis of MAMT

3-Methyl-4-amino-5-mercapto-1,2,4-triazole(MAMT)as synthesized and re-crystallized as the reported procedure in one step reaction of thiocarbohydrazide and glacial acetic acid [27]. A mixture of thiocarbohydrazide (10 g) and acetic acid (60 ml) was taken in a round bottomed flask. The reaction mixture was refluxed for about 4 h. The precipitated product was purified by recrystallization from hot water and was identified by melting point (203 – 204°C), elemental analysis and infrared spectra (IR). The equation of this reaction is mentioned below.

Acetic acid   Thiocarbohydrazide   3-Methyl-4 amino-5-mercapto-1,2,4-triazole
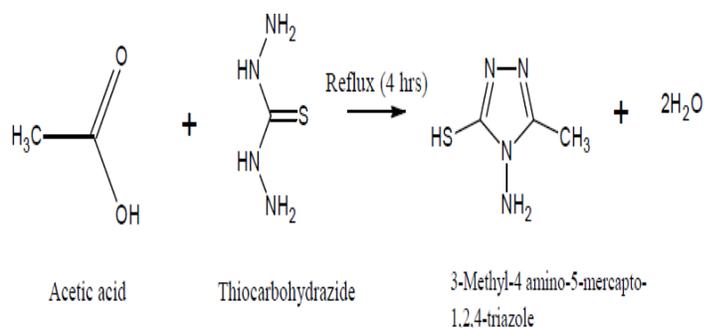
Synthesis of extractant

MBIMTT was synthesized by taking the equimolar concentration of MAMT and 0.02 mole of 4- methoxybenzaldehyde in 50 ml ethanol containing 3 drops of glacial acetic acid and was refluxed for 3-4 h. The product obtained was separated and recrystallized from hot ethanol as pale yellow shiny needles (m.p.165°C). Then, it's solution (0.1M) was prepared in chloroform [28].

MAMT   4- methoxybenzaldehydehyde   MBIMTT   (9)

Solvent extraction of Rh

The typical composition of solution used for the present study contains Pd-144, Rh-28, Ce-1344 and Mg-974 in mg/l.

Solvent extraction experiments used 0.01M MBIMTT in kerosene and were performed in 250- ml cylindrical glass vessels with equal volumes of the organic and aqueous phases. The vessels were shaken in a thermostatted shaker (GFL Model 1083) for the required time at room temperature (30 ± 1°C).

After phase separation a sample from the aqueous phase was withdrawn for chemical analysis The metal ion concentration in the aqueous was determined by ICP-OES/AAS. The metal ion concentration in the organic phase was calculated by mass balance before and after the extraction. In some cases, the loaded organic (LO) phases were stripped with acidified thiourea (Tu) and the strip solution were analyzed for metal contents by ICP-OES/AAS. The distribution ratio, D, was calculated as the concentration of metal present in the organic phase to that part in the aqueous phase at equilibrium. From the D values, the percentage extraction (%E = D × 100/D +(V_{aq} / V_{org}) where V_{aq} and V_{org} are the volumes of aqueous and organic phases, respectively), and separation factor (β = $DM1$ /$DM2$, M1 represents Rh and M2 represents other metals (Pd, Cr, Mn, Fe and

Ni) were calculated. Experiments are conducted twice and the percentage of precipitation, extraction and stripping of metals varied within 3%. Blank determinations and corrections were carried out wherever necessary. Recovery of Rh as a white-silvery powder was tried using magnesium powder as a reducing agent. This reducing agent was added slowly.

Results and discussions

The chemical composition of catalyst

The chemical composition of the spend catalyst powder is listed in Table 1 (XRF). This table shows the sample contained more than 90% mass of support materials such as Al_2O_3, SiO_2 CeO_2, ZrO_2 , SrO and other oxides.

Sample	Concentration (wt%)	Sample	Concentration (wt%)
Al_2O_3	35.3	SrO	4.7
SiO_2	34.8	Ce_2O_3	7.1
MgO	7.0	PdO_2	0.4
ZrO_2	7.6	Rh_2O_3	0.06

Table 1. Chemical composition of powdered spent catalyst.

Removal of troublesome cations by precipitation method

In order to remove interfering cations such as Al, Mg, Zr, Ce and Sr from the the feed solution containing (mg/l) Al- 4670, Mg-1025, Zr- 1395, Ce-1415, Sr-950, Pd-150,Rh-30, the precipitation method with addition of 15 wt% potassium phosphate solution was performed. As it can be seen from Figure 1, the precipitation of Al, Zr and Sr started at pH≈ 2, reached nearly 100% at pH≈3 and remained in the same value despite of futher additional of potassium phosphate up to nearly pH ≈8, whereas that of Ce and Mg were about less than 5% only.

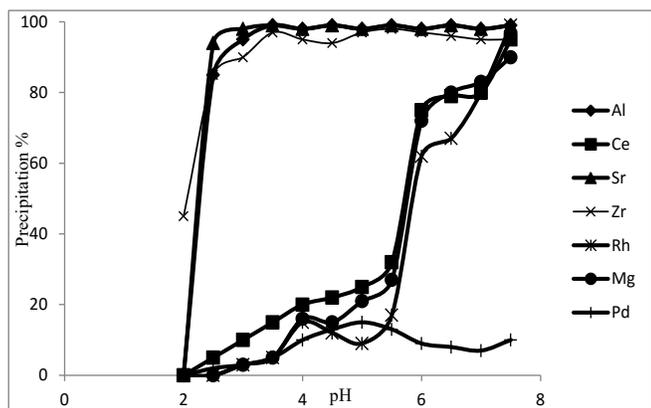**Figure 1.** Precipitation of metals as a function of pH in the HCl/H_2SO_4 system.

The loss of Pd and Rh was ~6% due to adsorption on aluminum and phosphates produced in situ [29]. Although, at pH ≈ 7.5, there was a complete removal of impurities (Al, Ce and Zr), but at the same time rhodium and palladium

loss increased to 100% and 5% respectively. As a result, aluminum ,zirconium and strantium free solution (generated at pH ≈ 3.3) containing(mg/l) Pd-144, Rh-28, Mg-974 and Ce-1344 was processed for the separation and recovery of palladium and rhodium.

Comparation of synthesized extractant with the other ones

In this step, to evaluate strength of MBIMTT in Rh extraction, it's D_{Rh} and four other current commercial extractants' D_{Rh}, are determined and mentioned in Table 2. These four extractants are Cyanex 923, Alamin 336, DOS and TIBS.

Extractant concentration in (vol%)	Cyanex 923	Alamin 336	DOS	TIBS	MBIMTT
5	2.1	2.9	3	4.5	4.2
10	4.2	5.4	5.5	6.2	6.5
15	20	24.2	25	35	30
20	25	30.2	32	41	40

Table 2. D values for MBIMTT and the other extractants (A/O phase ratio = 1 ,25°C, 1stage).

The results show that MBIMTT is better extractant specially in higher concentrations. This maybe because of S and N atoms in MBIMTT. In Cyanex 923, Alamin 336 and DOS there is just one donor soft base atom (S, N or P), Whereas MBIMTT has two atoms S and N. So, it can adsorb and extract Rh(III) pieces in the solution with the better yield.

Besides, the data from this table shows that TIBS have the same or better Dpd in comparation with MBIMTT. This maybe return to existence of P atom in TIBS. Since Phosphorus has a lower electronegativity rather than nitrogen in MBIMTT, so, TIBS can act as a better donor soft base and adsorb an acceptor acid like Rh(III) with the more yield.

Effect of concentration of extractant on the extraction of metals

Figure 2 shows the extraction behavior of palladium, rhodium , magnesium and cerium as a function of MBIMTT in the range 0.001–0.5 M in kerosene at pH 3.4 and unit phase ratio. In the studied concentration range the percent extraction of Mg and Ce are nil. It was found that quantitative extraction of rhodium from palladium and cerium is possible using 0.01 M MBIMTT. The co-extraction of Pd is ~5.5%, indicating effective separation of rhodium from palladium with a separation factor (β) of 2×10⁴. Above 0.01 M MBIMTT concentration, β value decreased to less than 3800 due to co-extraction of palladium. From these studies 0.01M MBIMTT was selected to ensure best separation of rhodium from palladium, cerium and magnesium.
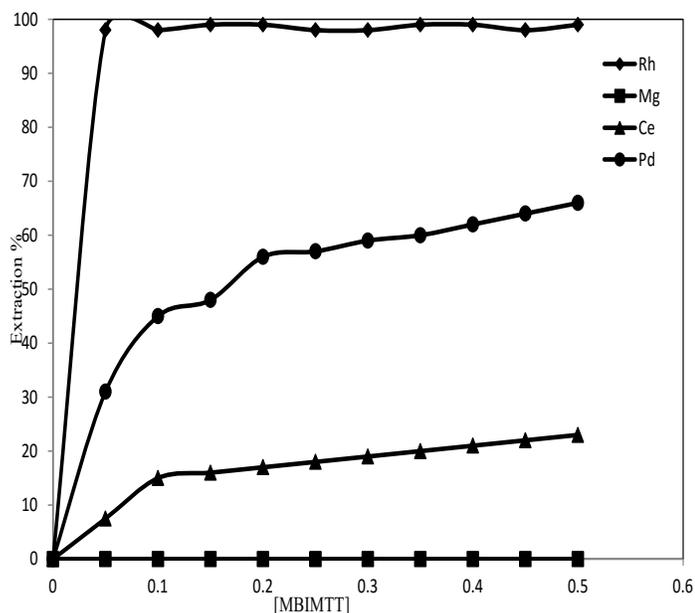
Figure 2. Effect of MBIMTT concentration on extraction of metals at pH= 3.4. [MBIMTT] = 0.001–0.5 M in kerosene, aqueous phase: Pd= 144 mg/l, Rh = 28 mg/l, Mg = 974 mg/l, Ce=1344, A/O phase ratio = 1, equilibrium time = 5 min.

Nature of the extracted species

The metal to extractant ratio in the extracted rhodium species was studied by varying MBIMTT concentration from 0.01 to 1.0 M at 1.0 M hydrochloric acid and sulfuric acid for Rh(III). The extraction increases with the increase in the extractant concentration. The plot drawn between log [Extractant] and log D (Figure 3) gave straight line with a slope value around 1.5 for the cations, thus suggesting the involvement of 1.5 molecules of the extractant in the formation of the extracted species (Eq10&11).
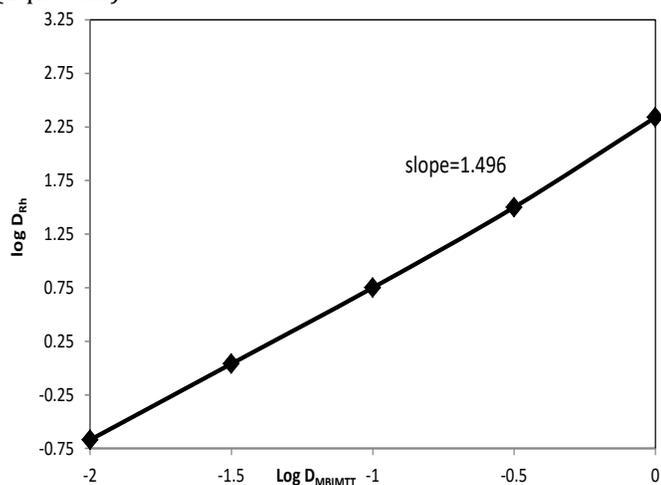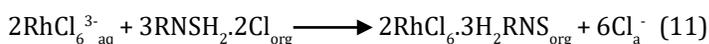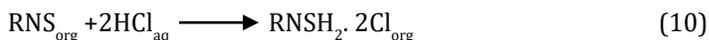

Figure 3. log plot of log D[Rh(III)] against log C[MBIMTT] .

It was because MBIMTT has N and S atoms in its structure (Eq.1). This has two loin pairs that adsorb 2 positive charges.

Since, rhodium cation has 3 positive charge, so each one Rh(III) complex can be extracted by 1.5 MBIMTT molecules.

$$RNS_{org} + 2HCl_{aq} \longrightarrow RNSH_2 \cdot 2Cl_{org} \tag{10}$$

$$2RhCl_6{}^{3-}{}_{aq} + 3RNSH_2 \cdot 2Cl_{org} \longrightarrow 2RhCl_6 \cdot 3H_2RNS_{org} + 6Cl_a{}^- \tag{11}$$

Stripping of rhodium from loaded organic phase

Stripping of Rh from the loaded organic phase was attempted using HCl, NH_4Cl, $Na_2S_2O_3$, aqueous NH_3 and aqueous mixed solution of NH3-NH4Cl as stripping reagents at unit phase ratio (Table 3). These reagents were found to be unsuitable for stripping of rhodium from loaded organic phase due to poor stripping efficiency (0.3–31%). On the other hand, stripping of rhodium with thiourea (Tu) individually showed better stripping efficiency of Rh (77–85%) but longer time for phases separation and hydrolysis of metal in stripping solution. Finally, combination of Tu and HCl in the range of 0.1–0.5 M and vice versa resulted clear phase separation and quantitative stripping of rhodium.

In the present study, 0.5 M each of HCl and Tu was used for rhodium stripping from loaded organic phase.

$$2RhCl_6 \cdot 3H_2RNS_{org} + 2Tu_{aq} \longrightarrow 2Rh(Tu)_{aq}{}^{+3} + RNS_{org} + 6H^+{}_{aq} + 12Cl^-{}_{aq} \tag{12}$$
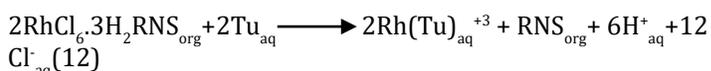
This is based on the fact that the rhodium ions may form a more stable cationic complex, $Rh(Tu)^{+3}$, with thiourea than an anionic complex with chloride ions $RhCl_6 \cdot 3H_2RNS$. Consequently, ligand replacement can occur and the more stable thiourea complex is released to aqueous phase as indicated by the equation.12.

Stripping reagent	Rh stripping efficiency (%)
3M Ammonia	31.3
3M Ammonium chloride	0.3
3M Ammonium chloride + 0.1M Ammonia	3.8
3M Ammonium chloride+ 0.5M Ammonia	12.4
3M Ammonium chloride+ 1M Ammonia	16.4
3M Ammonium chloride + 0.3M Ammonia	8.5
0.1-05 M NH_4SCN	14
0.3 M NaSCN	2
0.1-0.3M $Na_2S_2O_3$	5-12
1-5 M HCl	0-1.5
6-8 M HCl	5.5
0.1-1.0 M Thiourea	77-85
0.3 M Thiourea + 0.1M HCl	98
0.5 M Thiourea + 0.1M HCl	99.9
0.1 M Thiourea + 0.3M HCl	97
0.3-0.5 M Thiourea + 0.5M HCl	99
0.3 M Thiourea + 0.1M HCl	98
0.5 M Thiourea + 0.3M HCl	100
0.3-0.5 M Thiourea + 0.5M HCl	100

Table 3. Stripping of Rhodium from loaded organic phase.

Recovery of Palladium metal

Recovery of palladium from free raffinate was carried out with the addition of ammonium chloride to this solution then heating it to 60°C and kept at this temperature for 30 min, cooled and allowed the solution to settle down the precipitate. The content was filtered and precipitated, then washed with acidified distilled water (pH ≈ 4.0) for removal of any other metals impurity and oven dried to get pure white-silvery powder of pd. The precipitated palladium was further analyzed by XRD. The XRD data (Figure 4) shows that the observed d and 2θ values agree with those reported for palladium. It means that the observed intense peaks 40, 46, 68, and 87 deg are respectively representing the (111), (200), (220), and (222) Bragg reflection. Furthermore, the XRD pattern was compared with JCPDS standard (#05-0681) and confirmed the formation of palladium powder.
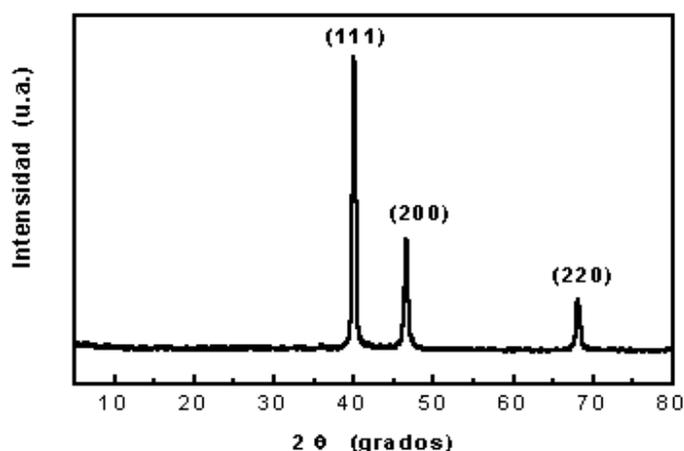

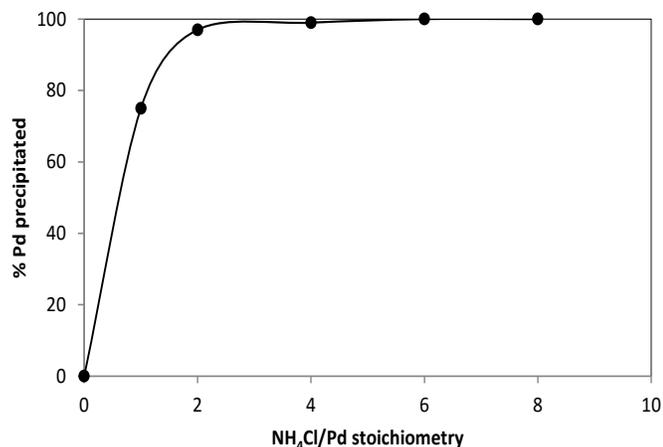**Figure 4.** X-ray diffractogram of obtained Palladium powder.

Figure 5. Precipitation of palladium as a function of NH4Cl/Pd ratio.

Figure 5 shows the effect of ammonium chloride addition on the precipitation of palladium at 25°C. It is obvious that the precipitation yield increases sharply with increasing amounts of ammonium chloride, reaching a value of 96% at the stoichiomteric ratio of 2. For 99.5% Pd recovery a ratio of 4 is required. This excess of ammonium chloride is needed to overcome the negative effect of excess HCl from leaching. The palladium precipitate was ignited to palladium powder according to:

$$(NH_4)_2PdCl_6 \xrightarrow{\text{Ignition}} Pd + 2NH_4Cl + 2Cl_2 \qquad (13)$$
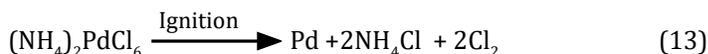
The optimal decomposition temperature of the pd salt (30 % Pd) was detected by the weight loss percentage.

Separation and recovery of rhodium from palladium free raffinate

Recovery of rhodium from pd free raffinate was carried out with the addition of 0.5 M thiourea/ 0.3M HCl to adjust pH around 3 and heating it to 60°C and keeping at this temperature for 30 min. After cooling, thiourea / HCl solution added as a stripping agent. Then Mg powder with the E° of -2.36 V was added to this solution in order to precipitate Rh as a powder based on the equation below.

$$3Mg + 2Rh(III) \longrightarrow 3Mg(II) + 2 Rh \quad (14)$$
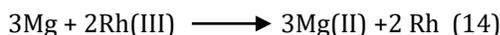
Acidified distilled water (pH 4.0) for removal of Mg impurity and oven dried to get pure rhodium sulfide. The filtrate contains 0.1 mg/l Rh, corresponding to more than 99% Rh recovery. Analysis of precipitate indicated about 10 wt% of this precipitated is Mg. The precipitated rhodium was further analyzed by XRD. The XRD data (Figure 6) shows that the observed *d* and 2θ values agree with those reported for Rh ,indicating the formation of rhodium powders (JCPDF # 05-0685).
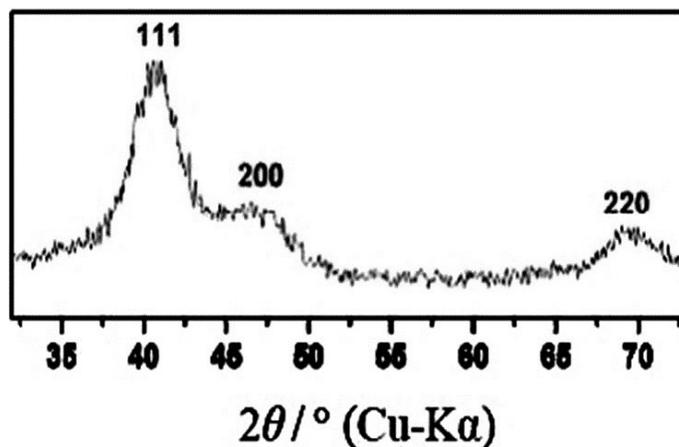

Figure 6. X-ray diffractogram of obtained rhodium powder.

A complete process flowsheet describing the phase ratio, the stages for the quantitative separation and recovery of rhodium and selective precipitation of palladium as a powder from synthetic chloride leach liquor was demonstrated in Figure 7.
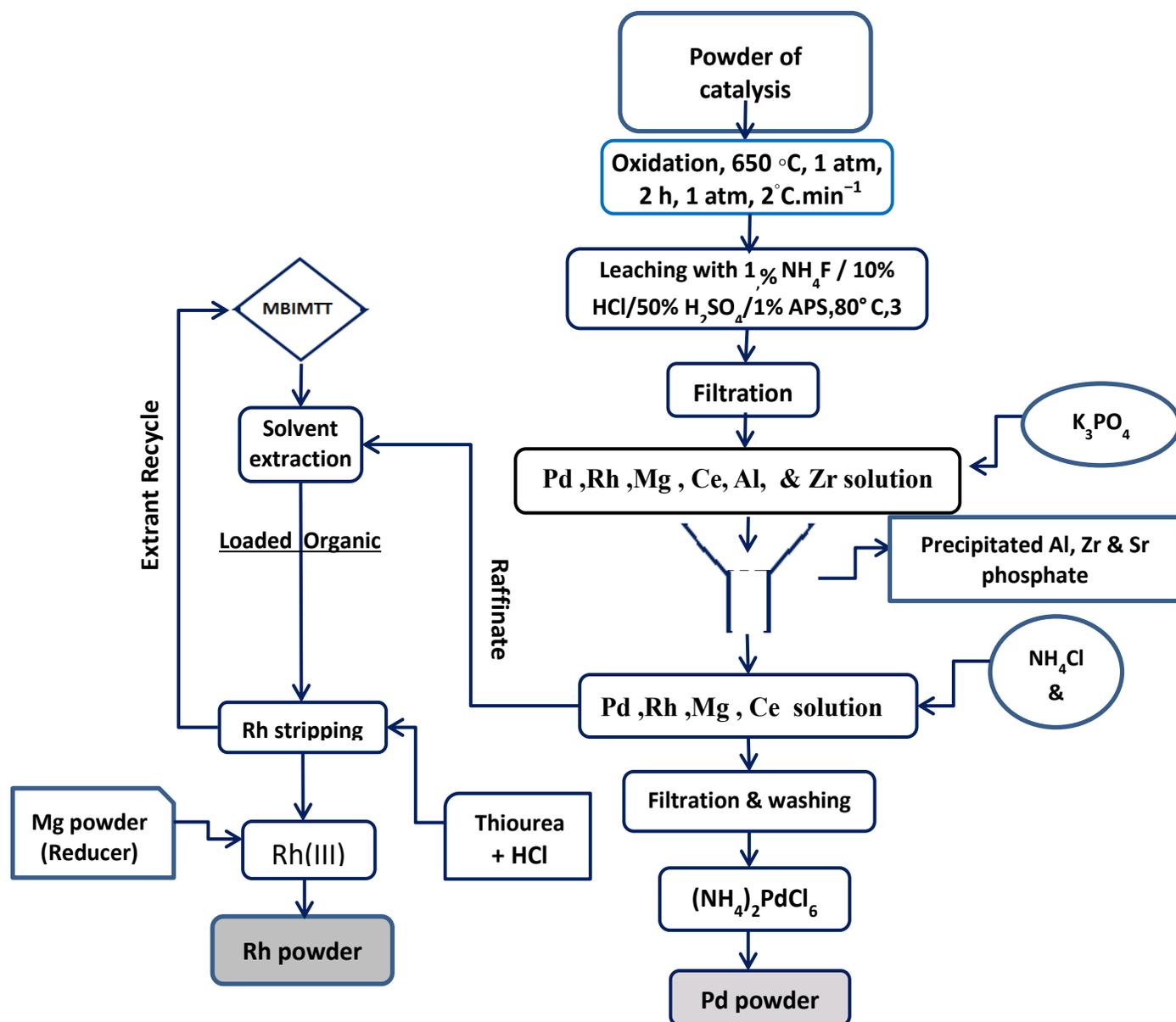
Figure 7. Overall flowsheet of the process.

Conclusions

In this study, acidic leaching and separation conditions for the recovery of palladium and rhodium from spent catalyst dust arising from an Iranian car factory have been evaluated. We have developed a process flowsheet for the separation and recovery of palladium and rhodium from the chloride solution containing other impurities such as Al, Mg and Zr. At first, a more practical chemical precipitation method has been used to remove impurities such as Al ,Zr and Sr. Then, employing 0.01 M synthesized MBIMTT in kerosene gave a selective and quantitative extraction of rhodium from the raffinate was obtained without any palladium, cerium and magnesium impurities.

Stripping of palladium from loaded organic was achieved with acidified thiourea. The selective precipitation of palladium as a pure powder from rhodium, magnesium and cerium was achieved by a simple NH_4Cl precipitation process.

The overall recovery nearly 99% rhodium and palladium was achieved. The present results show a possible application to the separation and recovery of Pt and Rh from chloride leach liquor of spent catalysts, or any other related sources.

Acknowledgements

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