

Liquid-liquid Extraction and Recovery of Pd(II) from Nitric Acid Medium Using Green Diesel as Extractant

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ABSTRACT: *A cost-effective method for the extraction of palladium (Pd) from HNO₃ solution by green diesel as extractant in kerosene was investigated. Several parameters such as extractant, nitrate, hydrogen ion, nitric acid and metal ion concentrations, phase ratio, and thermodynamic parameters were studied. The extracted species were deduced using slope analysis method and infrared (IR) measurements. The results showed that the extraction efficiency of Pd(II) is 95% with 10% (v/v) diesel in kerosene, and 97% was recovered from the loaded organic solution using 0.05 M thiourea or ammonium thiocyanate solutions as stripping agents. The maximum loading capacity of diesel was found to be 2×10^{-2} moles of Pd(II) per mole extractant. The effect of diluents on the extraction of Pd(II) from nitric acid solution by green diesel indicated that, under the used experimental conditions, kerosene gave the highest extraction percent compared to cyclohexane, benzene, toluene, chloroform and carbon tetrachloride. Extraction of Pd(II) from different acidic media was also carried out and the extraction percent was found to decrease in the order: H₂SO₄ > HNO₃ > HCl. The possibility of extraction and recovery of Pd from the sulphate leach solution of spent automotive catalyst was explored and a modified process is proposed and evaluated.*

Keywords: Green diesel, palladium, nitric acid, extraction, automotive catalyst

1. INTRODUCTION

Nowadays, extraction and recovery of precious metals, especially palladium (Pd), from wastes of industrial and nuclear applications are of major concern due to their scarcity and economic value. Pd has unique physical and chemical properties

that are suitable for manufacturing industrial materials such as catalysts, electrical and corrosion-resistant alloys.¹ Pd is also very important in fuel cell industry. Therefore, it is important to develop an effective and cheap recovery process for Pd from nuclear and industrial applications. Among the most simple and efficient techniques which can be employed for the separation and recovery of Pd ions is solvent extraction process, which has already been industrially used for the recovery of precious metals in industrial scale.² In this context, the extraction of Pd(II) from nitric acid medium with various ketones in nitrobenzene has been reported.³ The authors concluded that both methylalkylketones and ketones containing symmetrical alkyl configuration effectively extracted Pd(II) from nitric acid medium, especially 2-tridecanone and 2-nonanone which exhibited efficient extraction of Pd(II) and provided a feasible extraction system at 3.0 M ligand concentration and HNO₃ above 2.0 M.

Extraction of Pd from aqueous nitrate solution was studied with solvents containing 3,4-dithio toluene (H₂TDT), bis(2,4,4-trimethylpentyl) monothiophosphinic acid (CYANEX 302) and its dithio analogue (CYANEX 301).⁴ The selectivity of Pd separation from nitric acid took the sequence H₂TDT > CYANEX 301 > CYANEX 302 in kerosene.⁴ CYANEX 302 provided good extraction performance as a carrier where almost 100% Pd was extracted and 90% was stripped with 2.0 M thiourea in 1.0 M sulfuric acid as stripping solution.¹ The extraction of Pd(II) from HNO₃ solution with 1-benzoyl-3-[6-(3-benzoyl-thioureido)-hexyl]-thiourea (Ia) and several monodentate thiourea derivatives in 1,2-dichloroethane has been studied; the increase in the number of thioamide groups in the molecule of Ia increased its extraction efficiency towards Pd(II).⁵ Extraction and separation of Pd, platinum (Pt) and rhodium (Rh) using CYANEX 923 and their recovery from real samples was carried out.⁶ The extraction behaviour of Pd(II) showed a positive dependence on the acidity of sulphuric acid indicating that the use of sulphuric acid favoured the formation of extractable species.⁶ The extraction studies of Pd from hydrochloric acid (HCl) medium with triphenylphosphine (Ph₃P), triphenylphosphine oxide (Ph₃PO) or triphenylphosphine sulphide (Ph₃PS) showed high extraction of Pd(II) with Ph₃P.⁷ The authors reported that the use of 1 M stabilised thiosulfate solution was efficient for stripping Pd from its loaded Ph₃P-benzene solution. The selective extraction of Pd from nitric acid medium using CYANEX 471X in kerosene using n-octanol as modifier was carried out.⁸ The extraction from other acidic media indicated that the extraction decreased in the order sulphuric > nitric > hydrochloric acids.⁸

The extraction performance and separation behaviour of Pd(II) and Pt(IV) were studied using a synthetic sulfoxide (MSO) as extractant from HCl medium. The Pd(II) transfer depended strongly on the MSO and HCl concentration, phase

ratio, contact time and Pd(II) concentration in stock solution.⁹ Phosphonium ionic liquids such as trihexyl (tetradecyl) phosphonium chloride and bromide (Cyphos IL 101 and 102) and bis-(2,4,4-trimethylpentyl) phosphinate (Cyphos IL 104) were used for the removal of Pd(II) ions from aqueous chloride solutions by liquid-liquid extraction and transport across polymer inclusion membranes (PIM).¹⁰ The results showed that the addition of NaCl and the increase in HCl content in the feed aqueous phase slightly reduced the efficiency of Pd(II) extraction. In addition, CyphosIL 101 was used in the presence of toluene to extract Pd(II) from HCl solutions of various concentrations.¹¹ Successful stripping of Pd(II) from the loaded organic phase was achieved with 0.5 M ammonia solution and CyphosIL 101 could be reused for at least 5 cycles of extraction-stripping processes.¹¹

Green diesel is known to be a cheap source of sulphide extractants and has been used as extracting agent for liquid-liquid extraction of Pd from nitric acid mixtures. Such use has been proposed as a mean of separating the fission product Pd from PUREX raffinate which comes from spent nuclear fuel.¹² Diesel oil in benzene and lacquer petroleum were used for an effective extraction of Pd(II) from nitrate medium and the authors reported that the distribution was almost independent of the acidity and nitrate concentration in the aqueous phase.¹³

In the present work, the solvent extraction of Pd ions from nitric acid medium using green diesel in kerosene has been studied. The effects of several parameters, such as the shaking time, acid concentration, diluent type, nitrate ion, hydrogen ion and extractant concentration, as well as temperature, were separately investigated. The stoichiometry of the extracted species was deduced using the slope analysis method and verified by Fourier transform infrared (FTIR) measurements. Stripping of Pd from loaded organic solutions was also carried out. Extraction of Pd(II) from sulphate and chloride media was investigated and the results were compared with those obtained in case of nitric acid medium. Based on the obtained results, the possible use of the studied system for the extraction and recovery of Pd(II) from spent automotive catalyst leached with sulfuric acid was explored and a developed recovery process is proposed and evaluated.

2. EXPERIMENTAL

2.1 Chemicals

Most of the chemicals and reagents used in this work are of analytical reagent (AR) grade and were used without further purification. PdCl₂ was obtained from Fluka and nitric acid from BDH. Odourless non-aromatic kerosene was obtained from Misr Petroleum Company, Egypt. The commercial extractant (green diesel)

was obtained from Total petroleum company, Egypt, and was used as received. Petroleum-derived diesel (green diesel) is composed of about 75% saturated hydrocarbons (primarily paraffins including n, iso and cycloparaffins), and 25% aromatic hydrocarbons (including naphthalenes and alkylbenzenes).¹⁴ The average chemical formula for common diesel fuel is $C_{12}H_{23}$, ranging from $C_{10}H_{20}$ to $C_{15}H_{28}$.¹⁵ Diesel oil is stable in nitric acid solution up to 5 M. At high acidity (8 M), a possible oxidation of the extractant may take place leading to a slight decrease in its extraction properties.¹³

2.2 General

Pd concentration was measured with atomic absorption spectrometer (Thermo Scientific). Extraction experiments were carried out using a water-thermostated shaker of the type G.F.L 1083, Germany. The two phases were separated completely using a centrifuge of the type Z-230 obtained from Hermle, Germany.

2.3 Liquid-liquid Extraction

Extraction experiments were carried out by mixing equal volumes (5 ml) of the aqueous phase (9.40×10^{-4} M Pd(II) in 3 M nitric acid) and organic phase (0.25 M (6% (v/v) green diesel in kerosene as diluent and n-octanol as a modifier) using a water-thermostated shaker for 60 min, which were found to be enough to reach equilibrium. After the disengagement of phases, the aqueous phase was analysed to determine the concentration of Pd using atomic absorption spectroscopy.

The general equation of extraction is the following:

$$D = \frac{[Pd]_{i(aq.)} - [Pd]_{f(aq.)}}{[Pd]_{i(aq.)}} \quad (1)$$

where D is the distribution ratio of the Pd ions between the aqueous and organic phases, $[Pd]_{i(aq.)}$ is the initial Pd concentration in the aqueous phase and $[Pd]_{f(aq.)}$ is the Pd concentration in the aqueous phase after extraction.

The percentage of extraction (%E) was determined from D values as:

$$\%E = \frac{100D}{D + (V/V')} \quad (2)$$

where V and V' denote the volume of the aqueous and organic phases, respectively.

The stripping percent (S%) was calculated as:

$$S\% = \frac{[\text{Pd}]_{\text{fs(aq.)}}}{[\text{Pd}]_{\text{li(org.)}}} \times 100 \quad (3)$$

where $[\text{Pd}]_{\text{fs(aq.)}}$ is the Pd concentration in the aqueous phase after stripping and $[\text{Pd}]_{\text{li(org.)}}$ is the Pd concentration in the organic phase after extraction.

3. RESULTS AND DISCUSSION

3.1 Extraction of Pd(II)

3.1.1 Effect of shaking time

The effect of shaking time on the extraction of 9.40×10^{-4} M Pd(II) from 3 M HNO_3 using 0.25 M green diesel in kerosene was studied in the range of 5–160 min. The extraction percent was found to increase with the increase in time from 5 min to 60 min. Further increase in the shaking time up to 160 min did not affect the extraction percent (Figure 1). Therefore, a shaking time of 60 min was maintained in all the extraction experiments of Pd(II) carried out in this work.

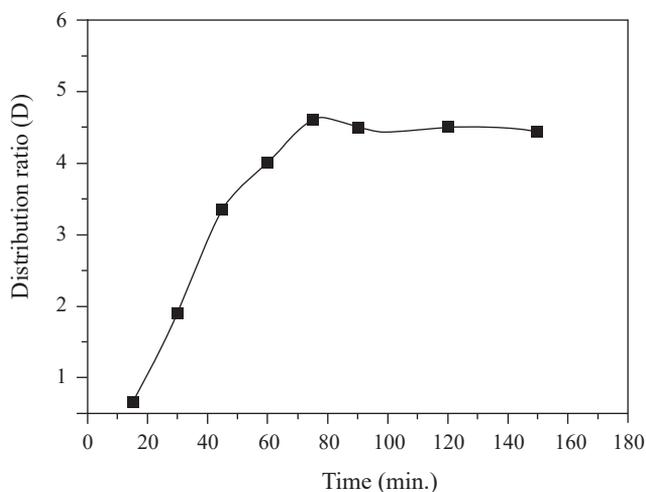


Figure 1: Effect of shaking time on the extraction of Pd(II) with green diesel in kerosene from 3 M nitric acid solution; O:A = 1:1, $T = 25^\circ\text{C} \pm 1^\circ\text{C}$, $[\text{diesel}] = 0.25$ M, $[\text{Pd(II)}] = 9.4 \times 10^{-4}$ M.

3.1.2 Effect of green diesel concentration

The effect of green diesel concentration on the extraction of 9.40×10^{-4} M Pd(II) from 3 M HNO₃ was studied in the range 0.085–0.42 M (2%–10% v/v). It was found that the extraction of Pd ions increased with the increase in the concentration of green diesel and reached a maximum of 95% when the concentration of extractant was 0.42 M (10% v/v). The plot of log D vs. log [diesel] yielded a straight line of slope 1.99, which indicates that the extracted metal species contains two molecules of green diesel (Figure 2).

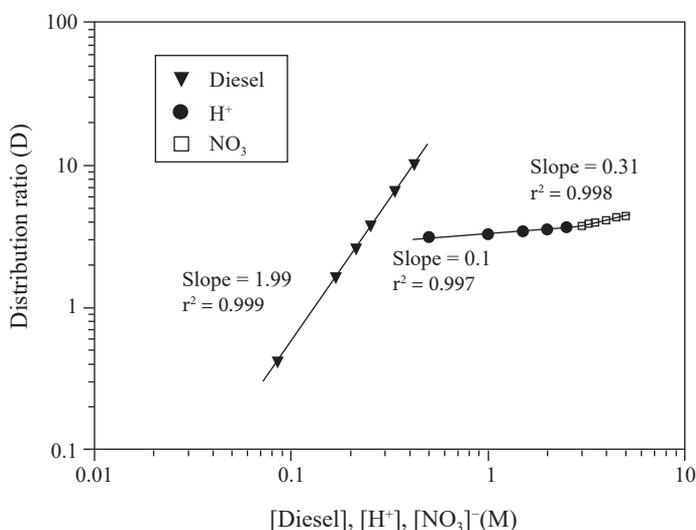


Figure 2: Effect of extractant, hydrogen ion and nitrate concentration on the extraction of Pd(II) from 3 M nitric acid solution by green diesel in kerosene; O:A = 1:1, T = 25°C ± 1°C, shaking time = 60 min, [Pd(II)] = 9.4×10^{-4} M.

3.1.3 Effect of nitric acid concentration

The extraction behavior of Pd(II) by 0.25 M green diesel from nitric acid solution of different concentrations ranging from 0.50 M to 5.0 M was carried out. The extraction percent of Pd(II) was found to increase from 53.50% to 80% at 3 M nitric acid then remained nearly constant with further increase in the acid concentration, as shown in Figure 3. The increase in the extraction process in the low nitric acid concentrations may be due to the salting out effect of the nitrate ion which increases in the range 0.50–3.0 M then becomes negligible at higher acidities leading to a constant extraction percentage.

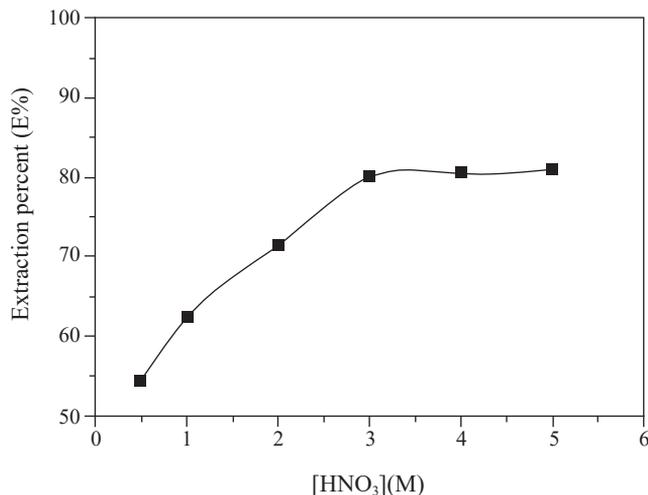


Figure 3: Effect of nitric acid concentration on extraction of Pd(II) by green diesel in kerosene; O:A = 1:1, $T = 25^{\circ}\text{C} \pm 1^{\circ}\text{C}$, $[\text{diesel}] = 0.25 \text{ M}$, $[\text{Pd(II)}] = 9.4 \times 10^{-4} \text{ M}$, shaking time = 60 min.

3.1.4 Effect of hydrogen ion concentration

The effect of hydrogen ion concentration on the extraction of $9.40 \times 10^{-4} \text{ M}$ Pd(II) by 0.25 M green diesel was studied in the 0.5–3 M range by using different nitric acid solutions in the same concentration range and addition of the proper amounts of sodium nitrate which keeps the total nitrate ion concentration in the solution fixed at 3 M. When $\log D$ was plotted against $\log [\text{H}^+]$, a straight line was obtained with slope 0.1 (Figure 2), indicating that no H^+ was released in the aqueous medium during extraction. This also indicates that the increase in $[\text{H}^+]$ in the investigated range had nearly no effect on the extraction of Pd(II) under the used experimental conditions.

3.1.5 Effect of nitrate ion concentration

The effect of nitrate ion concentration on the extraction of $9.40 \times 10^{-4} \text{ M}$ Pd(II) from HNO_3 by 0.25 M green diesel in kerosene was studied in the concentration range 3–5 M at constant $[\text{H}^+]$ of 3 M. The obtained data indicate that when the total nitrate ion concentration increased, the distribution ratio slightly increased. The plot of $\log D$ versus $\log [\text{NO}_3^-]$ was found to give a straight line with positive slope of about 0.31, which indicates that the increase in nitrate ion concentration had a negligible effect on the extraction of $9.40 \times 10^{-4} \text{ M}$ of Pd(II) under the used experimental conditions (Figure 2).

3.1.6 Effect of Pd ion concentration

The effect of Pd(II) concentration on its extraction from 3 M nitric acid by 0.25 M green diesel in kerosene was carried out in the range ($4.7 \times 10^{-4} - 4.6 \times 10^{-3}$ M). The results indicate that the extraction process decreased with the increase in Pd(II) concentration. The relation between the equilibrium concentration of Pd⁺² in the organic and aqueous phases plotted in Figure 4 indicates that the molar ratio of Pd(II) to the extractant is equal to 1:2 in the extracted metal species, which supports the results represented in Figure 2.

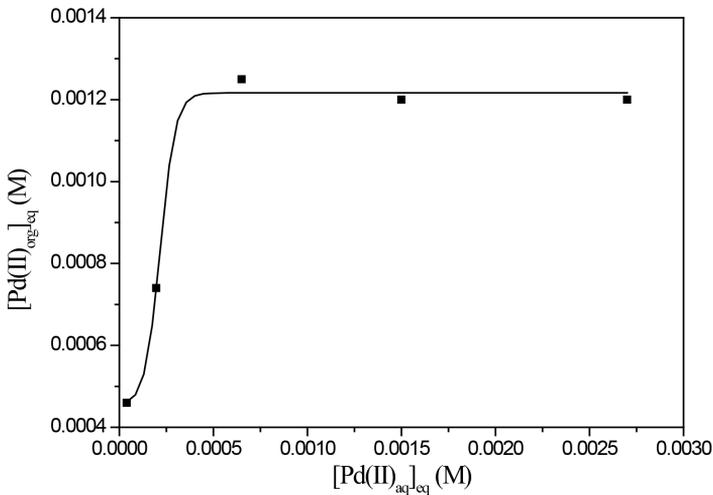
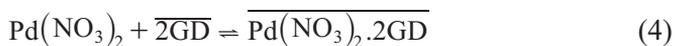


Figure 4: The isotherm of Pd(II) extraction from 3 M nitric acid solution with green diesel in kerosene; O:A = 1:1, T = 25°C ± 1°C, [diesel] = 0.25 M, shaking time = 60 min.

3.1.7 Extraction equilibrium

Based on the experimental results and the slope analysis values of the above log-log relations which indicate that 1 mole of Pd(II) chelates with 2 moles of the extractant, and assuming that Pd(NO₃)₂ is the predominant species in the aqueous nitrate medium, the extraction equilibrium of Pd(II) from nitric acid solution with green diesel can be represented by:¹⁶⁻¹⁹



where GD denotes green diesel extractant.

The extraction constant K_{ex} can be expressed as (in M^{-2}):

$$K_{ex} = \frac{[\text{Pd}(\text{NO}_3)_2 \cdot 2\text{GD}]}{[\text{Pd}(\text{NO}_3)_2] \cdot [\text{GD}]^2} \quad (5)$$

Since the distribution ratio is given by the relation:

$$D = \frac{[\text{Pd}(\text{NO}_3)_2 \cdot 2\text{GD}]}{[\text{Pd}(\text{NO}_3)_2]} \quad (6)$$

Therefore, the extraction constant is expressed as (in M^{-2}):

$$K_{ex} = \frac{D}{[\text{GD}]^2} \quad (7)$$

The average K_{ex} value calculated using Equation 7 at different green diesel concentrations was found to be $58 \pm 0.6 M^{-2}$.

3.1.8 Infrared spectroscopic investigations

To learn about the Pd(II) complex extracted by green diesel in kerosene from nitrate medium, the IR of the organic phase was studied before and after the Pd extraction in the wave length region $4000\text{--}450 \text{ cm}^{-1}$.

The IR spectrum of 0.25 M green diesel in kerosene with n-octanol as a modifier before extraction of Pd(II) showed bands at 2955.1 cm^{-1} , 2916.6 cm^{-1} and 2854.7 cm^{-1} that belong to aliphatic C-H stretching vibrations of CH_3 and CH_2 present in the extractant which is a mixture of hydrocarbons.²⁰ Furthermore, the bands at 1459.1 cm^{-1} and 1376.8 cm^{-1} are related to the deformation caused by CH_2 groups next to the sulphur atom in green diesel and to the attached CH_3 groups. The band at 1096.4 cm^{-1} is related to the C-SH stretching of sulfated diesel. The bands at 721.7 cm^{-1} and 671.7 cm^{-1} are due to the stretching vibrations related to C-S bond, shown in Figure 5(a).²⁰

After Pd(II) extraction, a new band assigned to the nitrate group appeared at 1652.2 cm^{-1} , shown in Figure 5(b), which indicates the presence of NO_3^- groups in the extracted metal species and supports the proposed equilibrium reaction given in Equation 4.²⁰

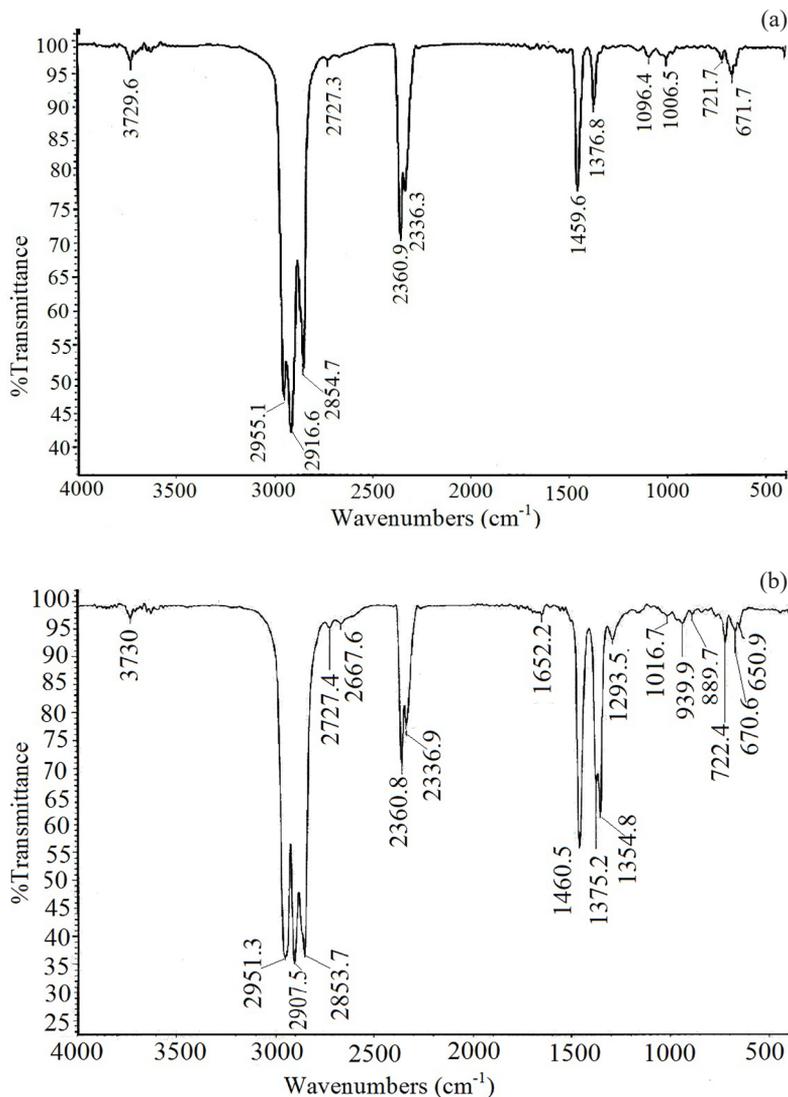


Figure 5: IR spectra of green diesel in kerosene, illustrated for (a) before extraction of Pd(II), and (b) after extraction of Pd(II).

3.1.9 Effect of temperature

The effect of temperature on the extraction of 9.40×10^{-4} M Pd(II) from 3 M HNO_3 using 0.25 M green diesel in kerosene was studied in the 15°C – 60°C range. The extraction was found to decrease with the increase in temperature. The relation between $(1/T)$ and the corresponding K_{ex} values gave a straight line as shown in

Figure 6. From the slope of this line and using the van't Hoff equations, the enthalpy change (ΔH), the entropy change (ΔS) and free energy change were calculated and the data are given in Table 1. The negative value of the enthalpy change (ΔH) indicates that the extraction of Pd(II) in the investigated system is an exothermic process, with an increase in the randomness of the system shown by the positive value of the entropy change (ΔS).

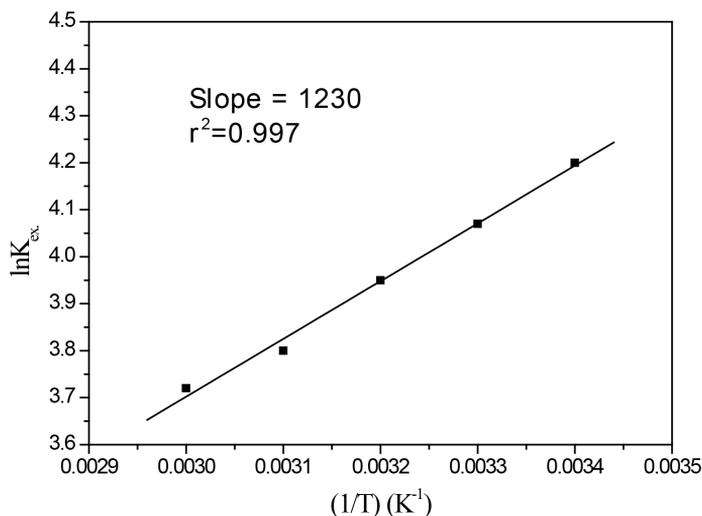


Figure 6: Relation between (K_{ex}) and ($1/T$) for the extraction of Pd(II) with green diesel in kerosene from 3 M nitric acid solution; O:A = 1:1, shaking time = 60 min, [diesel] = 0.25 M, [Pd(II)] = 9.4×10^{-4} M.

Table 1: Thermodynamic parameters of the extraction of Pd(II) from 3 M HNO₃ solution by green diesel in kerosene at phase ratio O:A = 1.

Thermodynamic parameter	ΔH (kJ mole ⁻¹)	ΔG (kJ mole ⁻¹)	ΔS (J mole ⁻¹ K ⁻¹)
Calculated value	-10.26 ± 0.47	-10.00 ± 0.39	0.87 ± 0.004

3.1.10 Effect of phase ratio

The effect of organic to aqueous (O/A) phase ratio on the extraction of 9.40×10^{-4} M Pd(II) from 3 M HNO₃ with 0.25 M green diesel in kerosene was investigated in the range between 1:2 and 5:2. The extraction was found to increase with increasing O/A phase ratio in the range 1:2–2:1, and the extraction of Pd(II) was almost complete after reaching the organic to aqueous phase ratio 2, as shown in Figure 7.

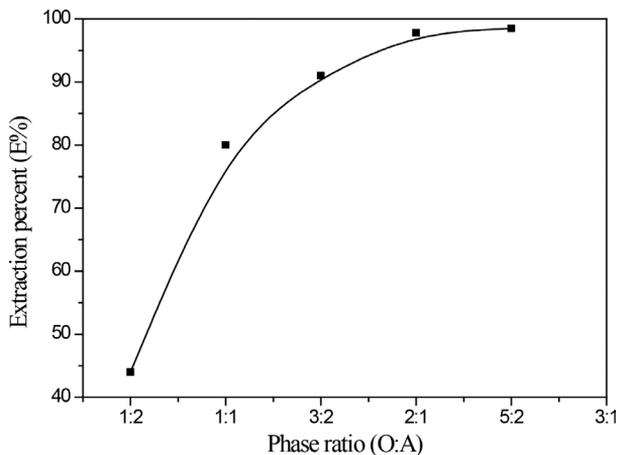


Figure 7: Effect of phase ratio on the extraction of Pd(II) with green diesel in kerosene from 3 M nitric acid solution; shaking time = 60 min, $T = 25^{\circ}\text{C} \pm 1^{\circ}\text{C}$, $[\text{diesel}] = 0.25 \text{ M}$, $[\text{Pd(II)}] = 9.4 \times 10^{-4} \text{ M}$.

3.1.11 The loading capacity

The loading capacity of one mole of green diesel which achieved the extraction of Pd(II) from 3 M nitric acid solution was determined by shaking an organic solution containing 0.25 M green diesel in kerosene with an equal volume of an aqueous solution containing $9.4 \times 10^{-4} \text{ M}$ Pd(II); after equilibration and separation of the two phases, the amount of the metal loaded in the organic phase was determined. The aqueous phase was discarded and a fresh aqueous solution was used for another round of extraction with the same organic solution. These stages were repeated until the extractant became unable to extract more amounts of Pd(II). As shown in Figure 8, the maximum concentration of Pd(II) in the organic phase is 0.001 M and was reached after four extraction stages. This indicates that the maximum loading of green diesel is 2×10^{-2} moles of Pd(II) per mole extractant.

3.1.12 McCabe-Thiele diagram

The number of the theoretical stages required for complete Pd extraction by green diesel in kerosene from 3 M nitric acid solution could be determined using the McCabe-Thiele diagram presented in Figure 9. The extraction isotherm which represents the relation between Pd(II) concentration in the aqueous phase and its concentration in the organic phase was first drawn. The operating line, the slope of which is equal to the phase ratio (O:A) to be used, was then inserted. A vertical line was drawn from the concentration of Pd(II) in the feed solution on the X-axis, and starting from the point where this vertical line meets the operating line, a

horizontal line was drawn to the extraction isotherm and then a vertical line to the operating line. This diagram indicates that two extraction stages are sufficient for the extraction of 9.40×10^{-4} M Pd(II) from 3 M nitric acid with 0.25 M green diesel.

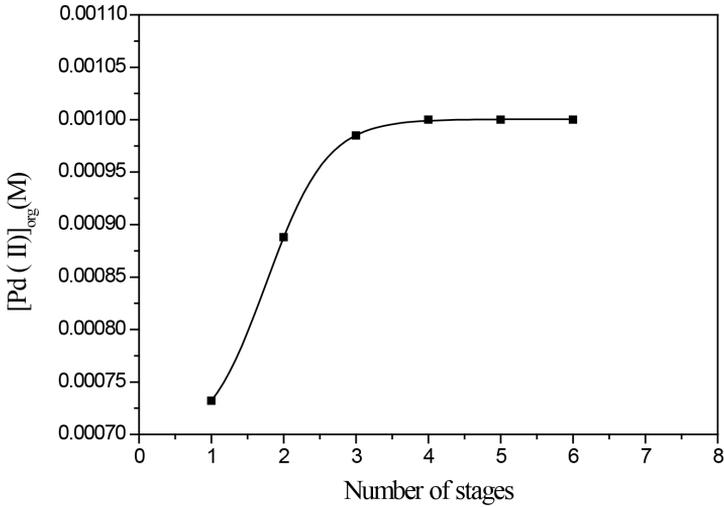


Figure 8: Effect of number of stages on the extraction of Pd(II) with green diesel in kerosene from 3 M nitric acid solution; O:A = 1:1, T = 25°C ± 1°C, [diesel] = 0.25 M, [Pd(II)] = 9.4×10^{-4} M, shaking time = 60 min.

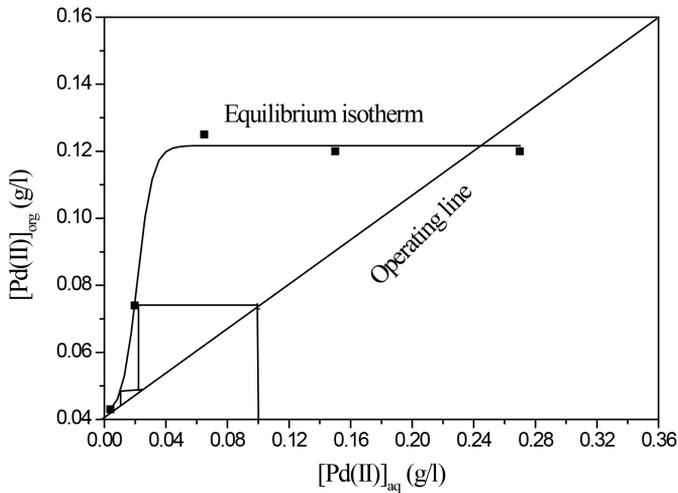


Figure 9: McCabe-Thiele diagram for extraction of Pd(II) from HNO₃ solution by green diesel in kerosene at 25°C and O:A = 1.

3.1.13 Effect of diluents

The effect of different diluents such as kerosene, cyclohexane, benzene, toluene, chloroform and carbon tetrachloride on the extraction of 9.40×10^{-4} M Pd from 3 M nitric acid solution by 0.25 M green diesel was carried out. The results shown in Figure 10 indicate that kerosene gave the highest extraction percent and is the most favourable diluent under the used experimental conditions. The values of the dielectric constant (ϵ) and the dipole moment (μ), as well as the extraction percentage of the investigated diluents are given in Table 2. The decrease in the extraction percentage from 80% in case of kerosene ($\epsilon = 1.8$) to 68% in case of cyclohexane and $\sim 52\%$ in case of chloroform ($\epsilon = 4.81$) may be related to the water solubility in the organic phase, which is a factor that decreases the extraction, and is generally low in aliphatic diluents and high in polar molecules and in diluents with high dielectric constant.²¹ On the other hand, the decrease in the extraction process when using benzene or toluene is related to the interaction between the aromatic hydrocarbons and the extractant, which is usually stronger than that of non aromatic ones, and subsequently decreases the metal extraction.^{22,23} This explains the increase in the extraction percentage of Pd(II) with green diesel in case of kerosene which has a low dipole moment ($\mu = 0$) compared with toluene or chloroform which have higher values of dipole moment. It has to be mentioned that in addition to its high extraction percent, kerosene is commercially available at low cost and gives a good phase separation, which made it a preference choice for the investigations carried out in this work.

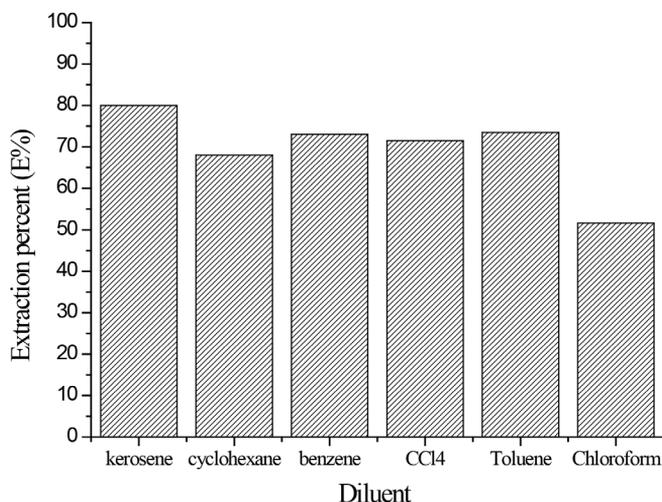


Figure 10: Effect of different diluents on the extraction of Pd(II) from 3 M nitric acid solution using green diesel; O:A = 1:1, T = $25^\circ\text{C} \pm 1^\circ\text{C}$, [Pd(II)] = 9.4×10^{-4} M, [diesel] = 0.25 M, shaking time = 60 min.

Table 2: The effect of different diluents on the extraction of 9.4×10^{-4} M Pd(II) from 3 M nitric acid solution by 0.25 M green diesel.

Diluent	Extraction percent	Dipole moment (μ)	Dielectric const. (ϵ)
Kerosene	80	0	1.8
Cyclohexane	68	0	2.02
Carbon tetrachloride	71.5	0	2.24
Benzene	73	0	2.27
Toluene	73.5	0.43	2.38
Chloroform	51.6	1.15	4.81

3.1.14 Extraction of Pd(II) from other acidic media

Most of the leaching processes for PGMs in hydrometallurgy, especially Pd, are generally carried out with hydrochloric and sulfuric acids. Therefore, the extraction of 9.40×10^{-4} M Pd by 0.25 M green diesel in kerosene from these media was studied in the acid concentration range of 0.5–5 M. The results shown in Figure 11 indicate that the extraction of Pd(II) from chloride medium increased with the increase in the acid concentration and reached its maximum at 1 M HCl due to the salting out effect of the chloride ions which increased with the increase in HCl concentration up to 2 M. This effect becomes negligible due to the known tendency of Pd to form stable chlorocomplexes at high acidities, which is an obvious reason for the decrease in the distribution ratio of Pd.^{7,13,24,25} In addition, the decrease in the metal extraction with the increase in the acidity of the medium may be also related to the possible extraction of HCl leading to the decrease in the concentration of the extractant available for Pd(II) extraction.

The extraction of Pd(II) from sulfuric acid medium was found to be more efficient, where the extraction percentage increased from 72% to 95% with increasing the acid concentration from 0.5 M to 5 M (Figure 10). The extraction of Pd from nitric acid, hydrochloric and sulfuric acid media was found to decrease in the order $\text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HCl}$.

3.2 Stripping Process

The loaded organic phase containing 7.5×10^{-4} M Pd(II) after extraction from 3 M nitric acid with 0.25 M green diesel in kerosene was stripped with various concentrations of different stripping agents namely, citric acid, oxalic acid, HNO_3 , H_2SO_4 , HCl, NaOH, aqueous ammonia, NaCl, thiourea, NH_4SO_4 , EDTA, ammonium thiocyanate and Na_2CO_3 , as well as H_2O at equal phase ratio and shaking time 60 min. The values of the stripping percent were calculated and are given in

Table 3. The tabulated data show that a maximum of 98.5% stripping was achieved with 0.5 M ammonium thiocyanate solution; 97% of Pd(II) was stripped with 0.5 M ammonium acetate or ammonium hydroxide. However, an efficient stripping of 96% was obtained with 0.05 M thiourea or ammonium thiocyanate; other stripping agents gave low stripping percent. The effect of time on the stripping with 0.05 ammonium thiocyanate indicated that 45 min was sufficient for stripping more than 98% of the loaded Pd(II) in one stage and further increase in the shaking time decreased the stripping percent, as shown in Figure 12.

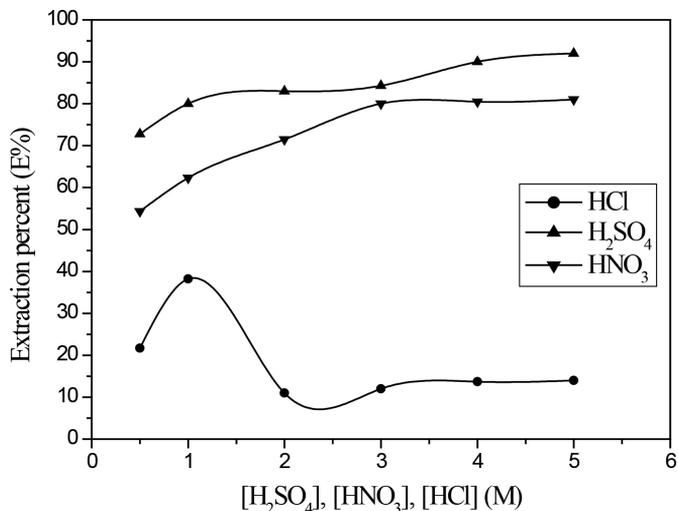


Figure 11: Effect of acid concentration on the extraction of Pd(II) by green diesel in kerosene from H₂SO₄, HNO₃ and HCl solutions; O:A = 1:1, T = 25°C ± 1°C, [diesel] = 0.25 M, [Pd (II)] = 9.4 × 10⁻⁴ M, shaking time = 60 min.

Table 3: Stripping percent of 9.4 × 10⁻⁴ M Pd(II) from loaded 0.25 M green diesel in kerosene.

Stripping agent	Conc. (M)	Stripping %
H ₂ O	–	5
[Thiourea]	0.01	95.50
	0.05	96.0
	0.1	98
	0.5	98

(continued on next page)

Table 3: (Continued)

Stripping agent	Conc. (M)	Stripping %
[NH ₄ SCN]	0.01	95
	0.05	96
	0.1	98
	0.25	98
	0.50	98.50
[Ammonium acetate]	0.1	77.50
	0.5	97.0
	1.0	94
[Ammonium nitrate]	0.50	20
[Ammonium sulphate]	0.5	30
Aqueous ammonia	0.15	52.50
	0.5	97
	1.0	98
[NaOH]	0.5	38.0
	1	40
[NaCl]	0.75	35
	1	37
	2.0	40
[Na ₂ CO ₃]	0.5	38
	1	40
H ₂ SO ₄	0.50	9
	1	11.50
HCl	0.50	30
	1	36.50
HNO ₃	1	8
	5	6
Citric acid	0.50	15
	1	21.50
Oxalic acid	0.25	47.30
	1	47.80
EDTA	0.1	62.50
	2.0	40

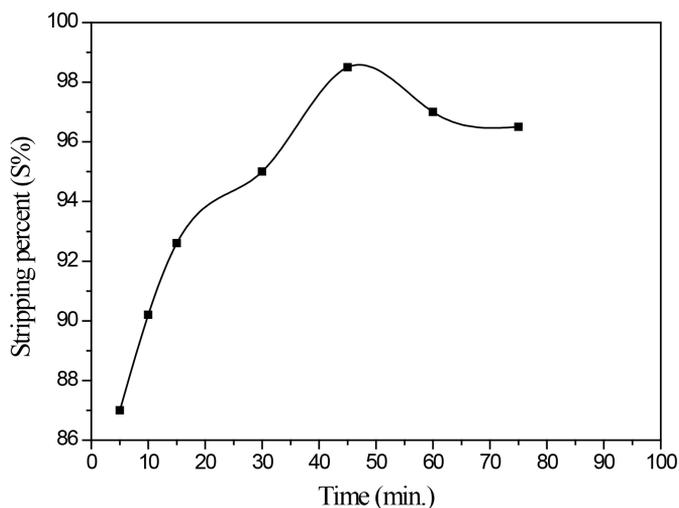


Figure 12: Effect of time on the stripping of Pd(II) loaded on green diesel in kerosene with 0.05 M ammonium thiocyanate; O:A = 1:1, $T = 25^{\circ}\text{C} \pm 1^{\circ}\text{C}$, $[\text{NH}_4\text{SCN}] = 0.05 \text{ M}$.

3.3 Industrial Application on Spent Automotive Catalyst

Catalytic converters, which allow the purification of automotive exhaust emissions, contain significant amounts of platinum group metals (PGM), especially Pd, Pt and Rh. Spent automobile catalytic converters which are considered as the main secondary source of PGM, are recycled by the metallurgical industry, through the use of pyro and/or hydrometallurgical methods. When the matrix containing PGM is leached in acidic media, Pd, Pt and Rh would be separated using conventional techniques such as solvent extraction and ion exchange. In this context, and in order to test the viability of the investigated extraction system for the recovery of Pd(II) from the spent automotive catalysts, a developed process is proposed and discussed.

3.3.1 Leaching process

A spent automotive catalyst supplied from Magar Brothers service center (Egypt) was grounded to a mesh size less than 300 mesh. Chemical analysis of the catalyst powder was carried out by X-ray fluorescence (XRF) analysis and the results are given in Table 4. The tabulated data indicate that the spent catalysts contains 0.114 wt% Pd, 0.032 wt% Rh, 4.8 wt% zirconium and high percent of cerium and other rare earth elements.

Table 4: XRF analysis of the used sample of automotive spent catalyst.

Metal	Weight (%)
Pd(II)	0.114
Rh(III)	0.032
Zr(IV)	4.80
Zinc(II)	0.062
Ni(II)	0.342
Fe(III)	16.230
Al(III)	19.749
Si(IV)	9.315
Pb(II)	0.327

Different characterisation techniques were also used for the evaluation of the physicochemical properties of the spent catalyst and the residue. In this context, scanning electron microscopic (SEM) analysis was used to study the morphology of the spent automotive catalyst and the SEM analysis of the powdered catalyst was performed at magnification of 200X and 1000X, shown in Figure 13. Energy dispersive X-ray analysis (EDX) was also carried out to investigate the quantitative analysis of metals present in the spent automotive catalyst; the EDX spectrum of the spent catalyst shown in Figure 14 indicates that the major elements are cerium, alumina, silicon, Pd and others.

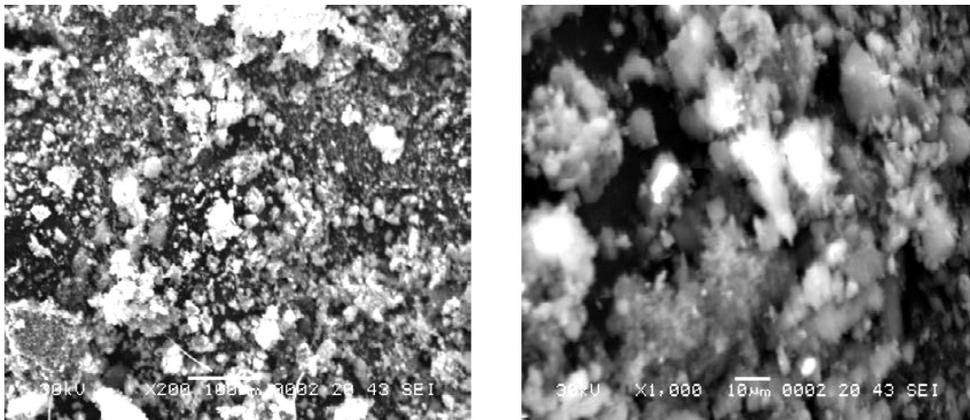


Figure 13: SEM images of the used spent automotive catalyst (magnification 200X on the left, and 1000X on the right).

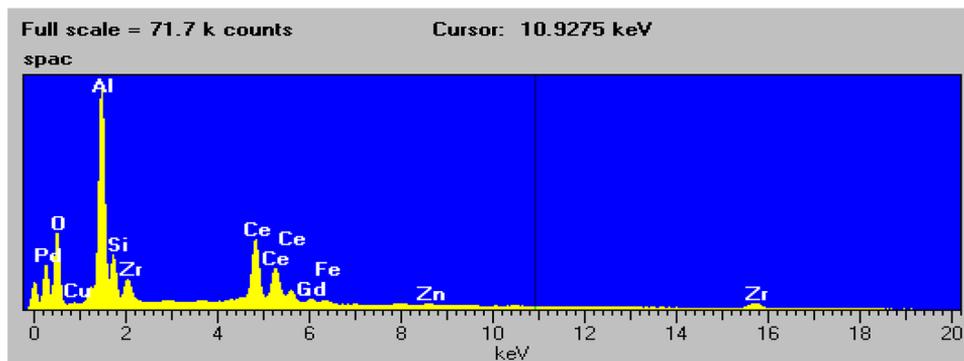


Figure 14: EDX analysis of the used spent automotive catalyst.

A sample weighing 15 g of the grounded catalyst powder was digested with two leaching solutions, namely aqua regia and (10 H₂SO₄:1 H₂O₂) solution at 60°C–70°C for 2 h. The results indicated that H₂SO₄-H₂O₂ mixture was a better leaching solution. The leached sample solution was scanned using a prodigy high dispersion Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Leeman, USA, after dilution to 100 ml with deionised water and the results are given in Table 6.

Table 6: ICP-OES analysis of leached solution of the used spent catalyst before and after extraction using 0.25 M green diesel in kerosene.

Metal	Conc. (before extraction), ppm	Conc. (after extraction), ppm
Pd(II)	160	16
Rh(III)	100	98
Zr(IV)	69.6	67.0
Zn(II)	1.5	1.30
Mn(III)	0.4	0.4
Fe(III)	20.50	20.0
Al(III)	879.20	874.0
Cu(II)	2	1.9
Pb(II)	10.4	9
Cs(II)	0.6	0.5
Cr(III)	0.4	0.4
Si(IV)	15.0	15.0

3.3.2 Extraction process

Based on the experimental data and the results given in section 3.1.14 for extraction of Pd(II) from sulphuric acid medium, 25 ml of the leached solution (diluted to 4 M H_2SO_4) was shaken with 25 ml solution of 0.25 M (6%) green diesel in kerosene at phase ratio O:A = 1:1 in two stages for 60 min. After extraction and separation of the two phases, the aqueous phase was analysed by ICP-OES and the results given in Table 4 indicate that Pd extraction percent was about 90% while the extraction percent of the other metals collected was less than 1%. On the other hand, Pd loaded in the organic phase was stripped with 0.05 M ammonium thiocyanate at equal O:A phase ratio, and the regenerated extractant was used for another cycle. The proposed process for the recovery of Pd from a spent automotive catalyst in sulphuric acid is summarised in Figure 15.

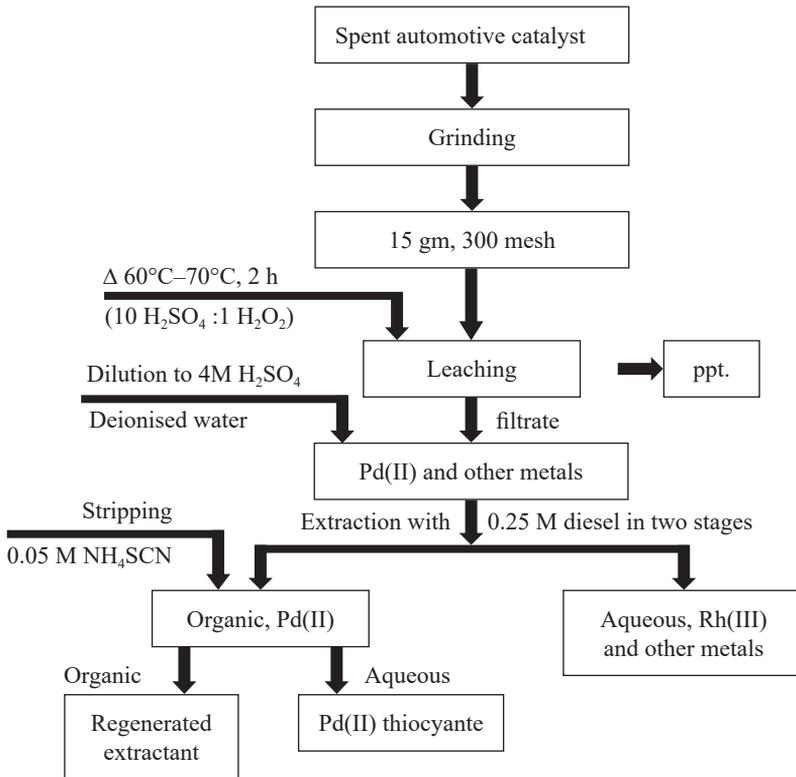


Figure 15: Flowchart for the recovery of Pd(II) from automotive spent catalyst in sulphuric acid solution.

4. CONCLUSION

Green diesel has high extraction ability towards Pd ions from nitrate medium and the extraction equilibrium was reached after 60 min. The stoichiometry of the extracted metal species was determined as $[\text{Pd}(\text{NO}_3)_2 \cdot 2\text{GD}]$, where GD denotes green diesel. The mean value of the extraction constant equals $58 \pm 0.6 \text{ M}^{-2}$, under the used experimental conditions. Increasing temperature had an inhibiting effect on the extraction of Pd indicating the exothermic nature of the extraction process. The loading capacity of one mole of green diesel was found to be 2×10^{-2} moles of Pd(II) per mole extractant. Pd was strongly stripped from the organic phase using different stripping agents; 0.05 M of thiourea or ammonium thiocyanate had a stripping efficiency of about 96% and 98%, respectively. The effect of diluents on the extraction of Pd(II) from nitric acid solution by green diesel indicated that, under the used experimental conditions, kerosene gave the highest extraction percent compared to cyclohexane, benzene, toluene, chloroform and carbon tetrachloride. Green diesel could also extract Pd(II) from hydrochloric and sulfuric acid media with higher extraction from sulfuric acid solution. The extraction from the investigated acidic media took the sequence $\text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HCl}$. Based on the results obtained, a developed process for the recovery of Pd(II) from the sulphate leach solution of spent automotive catalyst using green diesel was proposed and the obtained results indicate the efficiency of the proposed process.

5. ACKNOWLEDGEMENTS

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