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## Adsorption Behavior of Platinum Group Metals (Pd, Pt, Rh) on Nonylthiourea-Coated Fe<sub>3</sub>O<sub>4</sub> Nanoparticles

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**Abstract:** Magnetite nanoparticles coated with nonylthiourea (NTH) were synthesized and analyzed for the separation and recovery of platinum group metals (PGMs) from diluted aqueous chloride solutions. Physical characterizations of the coated nanoparticles were performed by Transmission Electron Microscopy (TEM), Thermogravimetric Analysis (TGA) and FT-IR Spectrometry. Separation efficiency of the coated nanoparticles and the equilibrium adsorption isotherm of PGMs were investigated. The maximum adsorption was attained in less than 30 minutes, and the maximum loading capacity of NTH-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles for Pt(IV) and Pd(II) was determined to be 10.7 and 8.1 mg g<sup>-1</sup>, respectively. The recovery of PGMs from the loaded nanoparticles was examined using different eluting solutions, including HNO<sub>3</sub>, thiourea, and NaClO<sub>4</sub>.

**Keywords:** Adsorption, platinum group metals, magnetite nanoparticles, nonylthiourea

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## INTRODUCTION

Interest towards nanoscale materials has increased in the last decade due to their unique characteristics such as a very large surface area, high surface reactivity, a large number of active sites on the surface, high catalytic efficiency, and strong adsorption ability. The reduction in size of the particles to below 100 nm results in extremely large surface area-to-volume ratio and increased surface reactivity (1), which also means increased metal ions adsorption capacity. The particles can be further functionalized with specific functional groups to enable selective binding.

Recently, sorption processes using magnetic nanoparticles have gained significant attention due to the value-added properties of these particles (2). Magnetic nanoparticles can obtain superparamagnetic properties below a certain particle size. Superparamagnetism is associated with finite size and surface effects that dominate the magnetic behavior of individual nanoparticles (3). This phenomenon arises when the thermal energy is sufficient to overcome the magnetic coupling forces, causing the atomic magnetic moments to fluctuate randomly. When an external magnetic field is applied, the particles acquire a certain magnetization but, because of the high thermal energy, the long range order is lost when the field is removed, and the particles have no remanent magnetization (4). This makes magnetic nanoparticles excellent candidates for combining metal binding and selective adsorption properties with ease of phase separation. These characteristics provide better kinetics for selective sorption of metal ions from aqueous solutions.

The recovery of platinum group metals (PGMs) including palladium, platinum, and rhodium from dilute solutions is of great interest due to the increasing industrial demand for these metals and their scarcity (5). Solvent extraction and ion exchange are the two primary technologies currently used for the separation of PGMs from process or waste solutions (6–8). For low metal concentrations, however the processes using these technologies are inefficient and complex, in some cases expensive, involving bulky equipment and large chemical inventories. Furthermore, they generate significant amounts of secondary waste. The magnetically assisted chemical separation (MACS) can be considered as an alternative cost-effective process for separating metal ions from waste solutions (9, 10). This process has the advantage of less complex equipment compared to solvent extraction and ion exchange. The MACS process, which uses extractant-coated magnetic particles combined with the use of external magnetic field, has provided a more efficient chemical separation (11, 12). Such magnetic particles demonstrated higher efficiency than that in traditional solvent extraction techniques (13).

In our previous work (14), we demonstrated that nanosized magnetite ( $\text{Fe}_3\text{O}_4$ ) particles can efficiently adsorb Pt(IV), Pd(II) and Rh(III) chlorocomplexes from diluted aqueous solutions. High loading capacity and short equilibrium time were achieved. The maximum sorption capacity of Pt(IV), Pd(II), and Rh(III) was determined to be 76, 102, and 144  $\mu\text{mol g}^{-1}$ , respectively, at

pH = 2.5. The sorption of PGMs was fast and equilibrium was attained in less than 30 minutes. Moreover, we have studied the solvent extraction of Pd(II) (15) and Pt(IV) (16) from hydrochloric acid solutions using nonylthiourea (NTH) as the extractant. NTH has shown to be selective for extraction of Pd(II) against some base metals and other PGM. A large difference in extraction kinetics allows the effective separation between Pd(II) and Pt(IV).

In the present study the feasibility of using magnetite nanoparticles coated with NTH is demonstrated for selective sorption of PGMs from diluted hydrochloric acid solutions. The sorption properties were studied for single metal solutions as well as for multi-metal solutions, in order to evaluate the selectivity of the sorption process.

## EXPERIMENTAL

### Chemicals and Reagents

Stock solutions of Pd(II), Rh(III) and Pt(IV) ( $500 \text{ mg L}^{-1}$ ) were prepared from  $\text{PdCl}_2$  (Merck, Germany),  $\text{RhCl}_3$ , and  $\text{PtCl}_4$  (both from Johnson Matthey, Germany) and the required amount of standardized HCl solution. Working solutions were prepared by dilution of the stock solutions. Analytical grade  $\text{FeCl}_2$ ,  $\text{FeCl}_3$  (Fluka), thiourea, nitric acid, sodium perchlorate, hydrochloric acid, ammonium hydroxide, and sodium hydroxide (Panreac, Spain) were used as received. Tetramethyl ammonium hydroxide (TMAOH, Aldrich 95%) was used without further purification and high purity water with a resistivity of  $18 \text{ M}\Omega\text{-cm}$  was used throughout all the experiments (Milli-Q, Millipore).

### Preparation of NTH-Coated $\text{Fe}_3\text{O}_4$ Nanoparticles

The respective synthesis procedures of NTH ( $\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2-\text{NH}-\text{CS}-\text{NH}_2$ ) and  $\text{Fe}_3\text{O}_4$  nanoparticles ( $\sim 10 \text{ nm}$ ) have been described elsewhere (15, 17). The NTH was synthesized through a two-temperature step reaction. The alkyl group was introduced by using nonylamine which was reacted with ammonium thiocyanate.  $\text{Fe}_3\text{O}_4$  nanoparticles were prepared by co-precipitation from a mixture of  $\text{FeCl}_2$  and  $\text{FeCl}_3$  (1:2 molar ratio) upon addition of  $\text{NH}_3$  at  $70^\circ\text{C}$ . NTH was coated on the surface of  $\text{Fe}_3\text{O}_4$  nanoparticles by mixing a known amount of magnetite with 50 mL of NTH in chloroform using rotary shaker for 24 hours. After phase separation using magnetic settlement, the particles were washed with chloroform three times to remove the NTH deposited on the surface of the particles. The particles were dried at room temperature ( $22 \pm 1^\circ\text{C}$ ). FT-IR (Nicolet Instrument model Avatar-100 equipped with ATR diamond at 303 K) was used to check whether the reagent was bound to the surface of the particles. The thermal gravimetric analysis (TGA) was carried out with TGA Q 500 with a heating rate of  $20^\circ\text{C}/\text{min}$  in nitrogen.

### Metal Adsorption and Desorption

The adsorption experiments were performed by mixing 10 mg of NTH-coated  $\text{Fe}_3\text{O}_4$  nanoparticles with aqueous solutions of Pt(IV), Pd(II) and Rh(III) in  $1 \times 10^{-3} \text{ mol L}^{-1}$  HCl media using a Griffin rotary shaker at room temperature ( $22 \pm 1^\circ\text{C}$ ). The pH of the solutions was controlled using either nitric acid or sodium hydroxide standardized solutions and confirmed by pH measurements (Microprocessor pH-meter, pH 537, Germany). After mixing, the aqueous phase was separated from the solid phase by magnetic settlement and centrifugation at 14000 rpm using a Genofuge 16 M (Technique, USA) centrifuge. The amount of metal ions in the supernatant was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a Liberty series II spectrometer (Varian, Australia). Metal adsorption was calculated by mass balance and the effect of different parameters, such as time, pH, and initial metal concentration have been investigated. The dissolution of iron oxide was monitored by determining the concentration of iron in aqueous solutions. The dissolution percentage was less than 0.5% of the total iron oxide used (pH = 1–3), no iron was detected in the aqueous solution at pH > 3.

In the desorption experiments, 20 mL of the elution solution was added to an accurate quantity of nanoparticles loaded with metal ions. After 30 minutes of contact, the aqueous and the solid phases were separated by centrifugation and the amount of metal ions in the supernatant was measured.

The sorption percentage of metal ions removed from the solution and the distribution coefficient ( $K_d$ ) are defined as;

$$\text{Sorption} = \frac{(C_i - C_{aq})}{C_i} \times 100 \quad (\%) \quad (1)$$

$$K_d = \frac{(C_i - C_{aq})}{C_{aq}} \times \frac{V}{m} \quad (\text{mL g}^{-1}) \quad (2)$$

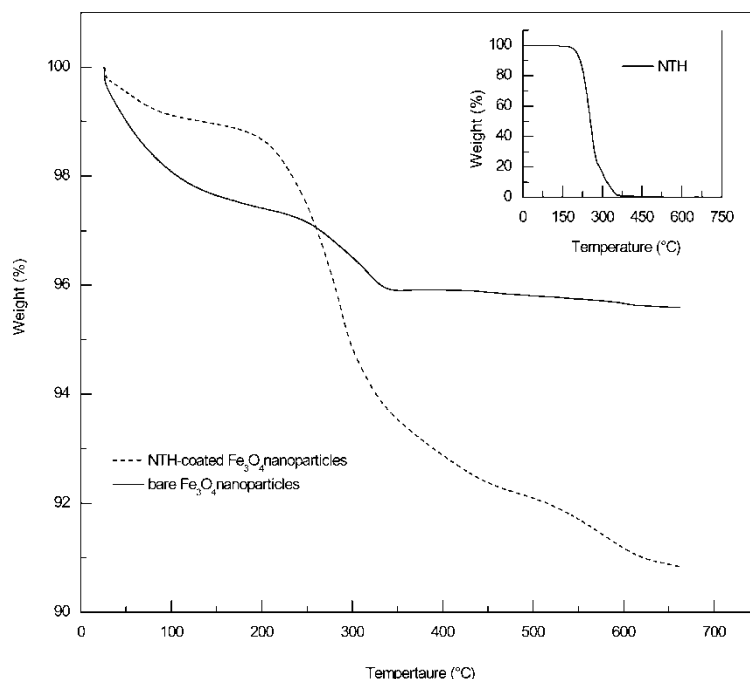
where  $C_i$  is the initial metal concentration ( $\text{mmol L}^{-1}$ ),  $C_{aq}$  is the metal concentration in the aqueous solution ( $\text{mmol L}^{-1}$ ),  $V$  is the volume of aqueous phase (mL), and  $m$  is the weight of the oxide (g).

## RESULTS AND DISCUSSION

### Characterization of NTH-coated $\text{Fe}_3\text{O}_4$ Nanoparticles

#### TGA and TEM Analysis

The amount of NTH coated on the surface of magnetite nanoparticles was determined from the percentage weight loss measured by the thermogravimetric analysis (TGA). As shown in Fig. 1, the TGA curve for  $\text{Fe}_3\text{O}_4$  nanoparticles shows a weight loss over 100–350°C of about 2%. This is most likely

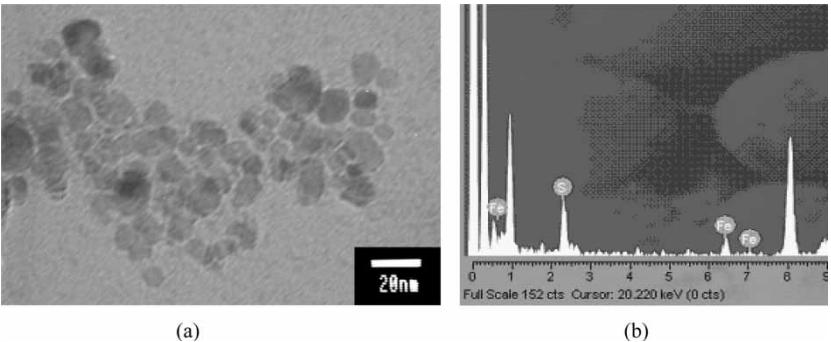


**Figure 1.** TGA curves of bare Fe<sub>3</sub>O<sub>4</sub> nanoparticles, NTH-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles, and the organic reagent (NTH).

due to the loss of adsorbed water and dehydration of internal OH groups. However, for NTH-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles, the TGA curve shows two weight loss steps. The first weight loss step over 100–180°C might be due to the loss of residual water adsorbed physically in the sample. The second weight loss over 200–600°C was due to the decomposition of NTH. TGA analysis of NTH alone (inset Fig. 1) show that the decomposition of the reagent starts at 200°C. Based on the TGA data, the amount of NTH coated on the surface of magnetite nanoparticles is determined to be 0.49 mmol g<sup>-1</sup>. When assuming the nanoparticles as completely coated, mono-dispersed, and mono-sized spheres of 10 nm in diameter, the thickness of the reagent layer was estimated to be 1 nm. The TEM image of NTH-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles is shown in Fig. 2a. Energy Dispersive X-ray (EDX) analysis data (Fig. 2b) shows that the main compositions of the sample are Fe, O, and S. The presence of sulphur in the sample is a confirmation of the coating process.

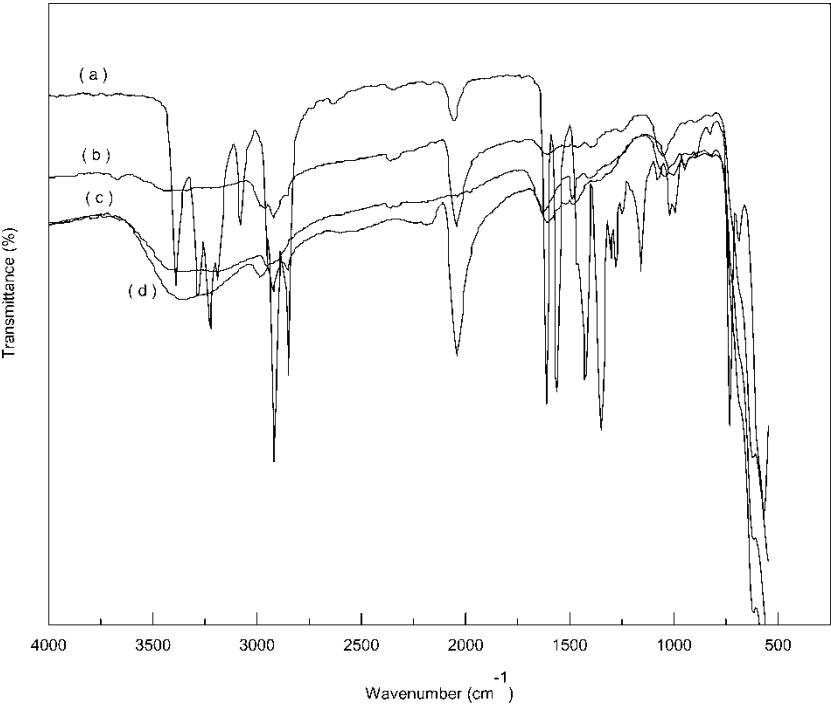
#### FT-IR Analysis

In order to confirm the coating of the magnetite nanoparticles surface with NTH, an FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub> nanoparticles, NTH-coated Fe<sub>3</sub>O<sub>4</sub>



**Figure 2.** (a) TEM images of the coated magnetite nanoparticles, (b) EDX analysis of the coated magnetite nanoparticles.

nanoparticles, and NTH were obtained (Fig. 3). As can be seen in Fig. 3, the bonding of NTH onto the surface of magnetite nanoparticles was observed with two strong spectral responses at  $2919\text{ cm}^{-1}$  and  $2849\text{ cm}^{-1}$  assigned to  $\nu(\text{C-H})$  vibration. Since C-H structures are present only in the reagent,



**Figure 3.** FT-IR spectra of (a) NTH, (b & c) NTH-coated magnetite nanoparticles at different NTH loading, (d)  $\text{Fe}_3\text{O}_4$  nanoparticles.

therefore, the presence of these vibrations in the spectrum of functionalized material indicates successful coating. The strong and relatively wide band at  $2041\text{--}2056\text{ cm}^{-1}$  is present in all spectra except the spectrum of initial magnetite. We cannot assign this vibration but it definitely belongs to the structure of the reagent. The strong response around  $1006\text{ cm}^{-1}$  corresponds to  $\rho(\text{NH}_2)$ . The response is recognizable in all samples of the coated magnetite as a peak at  $1003\text{ cm}^{-1}$ . Such a peak is absent in the spectrum of initial magnetite. Three lines at  $1250$ ,  $1281$ , and  $1303\text{ cm}^{-1}$  in the spectrum of the reagent are assigned to the combination of  $\nu(\text{C-N})$ ,  $\nu(\text{N-H})$ , and  $\nu(\text{N-C=S})$  (18). Weak responses can be recognized in this region in the spectra of coated samples while the magnetite does not have corresponding spectral lines. In addition, the effect of the reagent vibrations at  $1609\text{ cm}^{-1}$   $\delta(\text{NH}_2)$  and  $1561\text{ cm}^{-1}$   $\nu(\text{C-N})$  can be recognized. The magnetite has a spectral line at  $1620\text{ cm}^{-1}$  that overlaps with these two responses. As a result, the coated sample has one response at  $1605\text{ cm}^{-1}$ , most probably caused by a combination of these responses. Contribution of these two vibrations coming from the reagent is certainly reduced; this may be explained by the involvement of the nitrogen-containing groups in interactions binding the reagent to the surface. The spectrum of initial reagent has strong responses at  $735\text{ cm}^{-1}$   $\nu(\text{C=S})$  and  $1471\text{ cm}^{-1}$   $\nu_{\text{S}}(\text{C-S})$  which cannot be recognized in the spectra of the coated samples. A reasonable conclusion would therefore be that the reagent is bonded to the surface of magnetite primarily through sulphur atoms.

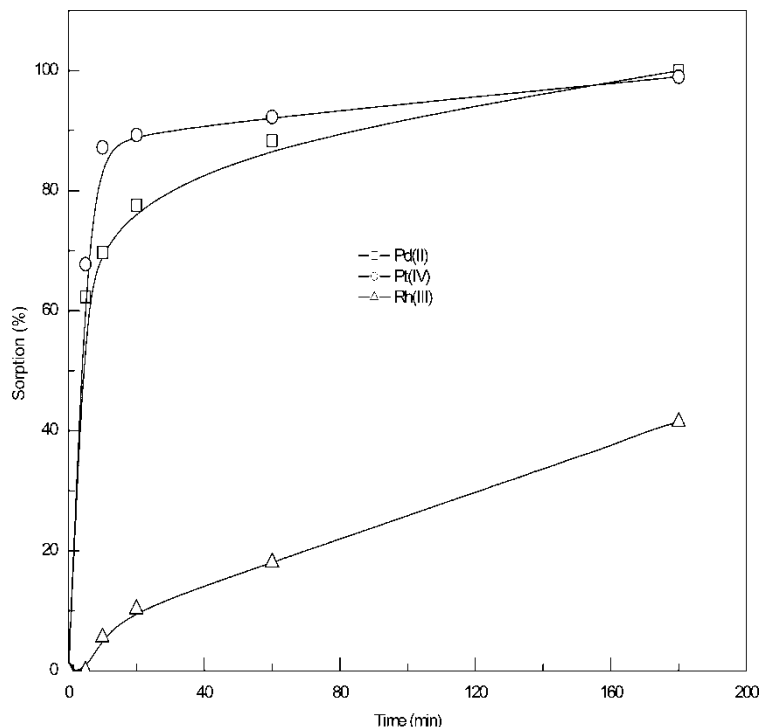
### Sorption Properties of PGMs

The selectivity of a sorbent material toward different metal ions generally depends on the oxidation state of metal ion, the geometry of the adsorption surface, and the physicochemical property of the functional groups incorporated on the surface (19). The sorption properties of Pt(IV), Pd(II), and Rh(III) under single and multi-metal solutions conditions have been investigated. Recovery of PGMs from the loaded particles was also examined using different compositions of stripping solutions.

### Effect of Contact Time

In these experiments the effect of contact time on the adsorption of Pd(II), Pt(IV), and Rh(III) was studied for single-metal solutions as well as for multi-metal solutions. The results obtained for single-metal solutions are presented in Fig. 4. As can be seen, the NTH-coated  $\text{Fe}_3\text{O}_4$  nanoparticles exhibit high sorption kinetics both for Pd(II) and Pt(IV), the 50% of the equilibrium sorption ( $t_{1/2}$ ) being reached in less than 5 minutes. In contrast the equilibrium time of Rh(III) is relatively slow, even though about 40% of

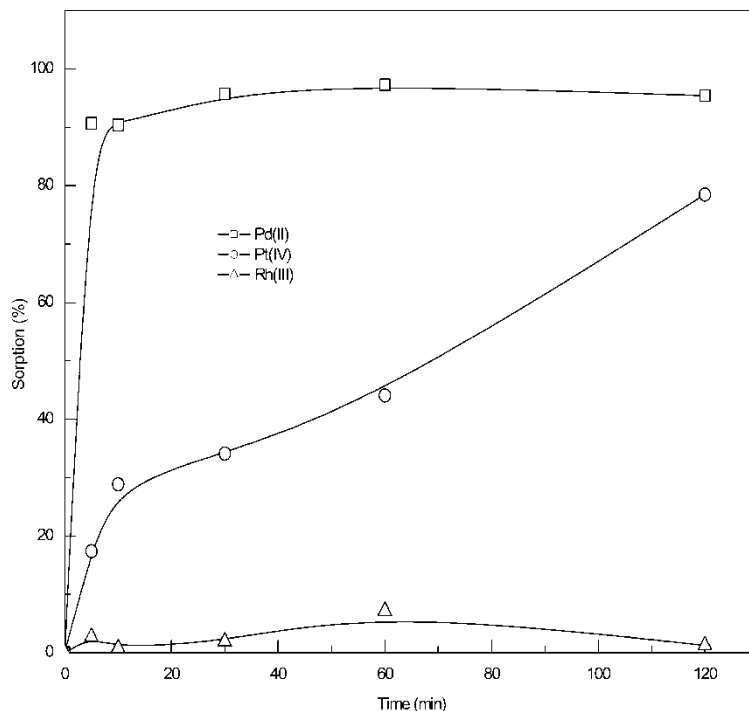




**Figure 4.** The effect of contact time on the sorption of Pd(II), Pt(IV), and Rh(III) under single-metal solutions.  $[M]_i = 3 \times 10^{-5} \text{ mol L}^{-1}$ ,  $\text{pH} = 2.7$ , amount of  $\text{Fe}_3\text{O}_4 = 10 \text{ mg}$ , total aqueous volume =  $20 \text{ mL}$ , temperature =  $22 \pm 1^\circ\text{C}$ .

Rh(III) was extracted after 3 hours of contact time. In our previously reported work (15, 16), the organic reagent NTH, dissolved into chloroform, was investigated for the extraction of Pd(II) and Pt(IV) from hydrochloric acid solutions. The results showed that the equilibrium time for Pd(II) can be attained in less than 5 minutes, but 72 hours are needed in the case of Pt(IV). In comparison to solvent extraction the fast sorption of Pt(IV) may be related to the large contact area offered by the high surface area of the particles. The surface area of the NTH-coated  $\text{Fe}_3\text{O}_4$  nanoparticles should be higher than that achievable in solvent extraction. In solvent extraction the droplet size is expected to be in the micron range. It has been reported that a longer time was needed to attain equilibrium between PGMs (Pd and Rh) and biopolymer enclosing Cyanex 302 extractant (20). In that study, the equilibrium time was found to be 7 days, which was explained by the low contact area of the extractant on the microcapsules.

On the other hand, Fig. 5 shows that, from multi-metal solutions, the adsorption of Pd(II) is fast with  $t_{1/2}$  less than 5 minutes, while  $t_{1/2}$  is



**Figure 5.** The effect of contact time on the sorption of Pd(II), Pt(IV), and Rh(III) under multi-metal solutions.  $[M]_i = 2.5 \times 10^{-5} \text{ mol L}^{-1}$ ,  $\text{pH} = 2.7$ , amount of  $\text{Fe}_3\text{O}_4 = 10 \text{ mg}$ , total aqueous volume =  $20 \text{ mL}$ , temperature =  $22 \pm 1^\circ\text{C}$ .

60 minutes for the adsorption of Pt(IV). The adsorption of Rh(III) was negligible. Solvent extraction studies indicated the possibilities of the complexation of Pd(II) and Pt(IV) via nitrogen or sulphur. In addition, the complexation of Pd(II) and Pt(IV) with sulphur and nitrogen cannot be excluded. In the present work, the FT-IR analysis suggested the possibility of binding NTH to magnetite surface through the reagent sulphur atoms. Therefore, it is most probable that PGM ions will bind through the reagent nitrogen atoms. The different extraction kinetics of PGMs may be explained by the following extraction mechanisms:

- As mentioned earlier the reagent sulphur atoms are being bound to magnetite surface, so the reagent nitrogen atoms will be easy to fulfil the geometry of square planar (Pd(II)), thus the extraction is fast, while more complex structures such as Pt(IV) and Rh(III) might take a longer time to be extracted.
- Based on TGA analysis the thickness of the adsorbed layer of NTH was estimated to be about  $1 \text{ nm}$ . As expected Pd(II) will be extracted first and

occupy all the sites on the adsorbed layer. As long as the surface is saturated with Pd(II), there is very little sites available for Pt(IV) to bind. When the reagent becomes available, the reaction is taking place with Pt(IV). The reagent becoming available may be due to the metal diffusion inside the layer to get the surface regenerated.

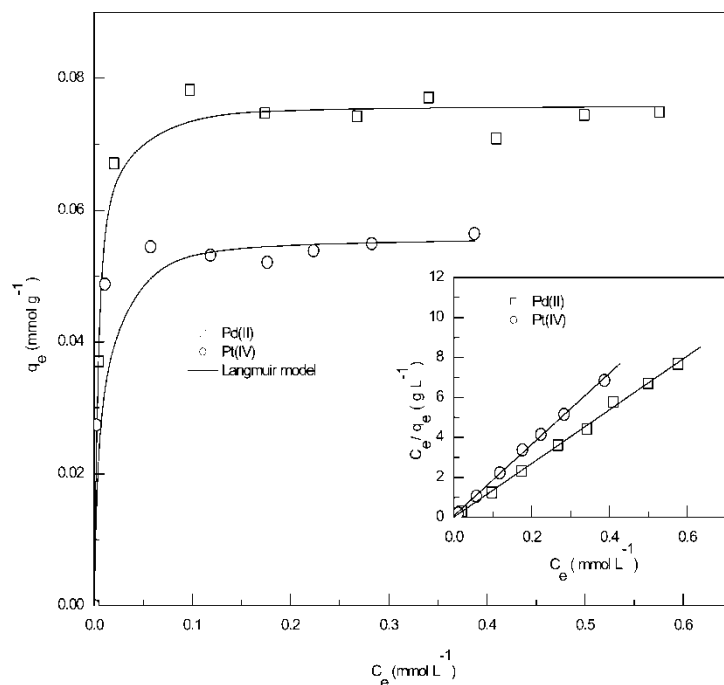
The results obtained in this work showed that Pd(II) has stronger affinity towards the extractant than Pt(IV) and Rh(III) in multi-metal solutions. The affinity of the NTH-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles for PGMs is in the order: Pd(II) > Pt(IV) > Rh(III). In comparison to the case of using bare Fe<sub>3</sub>O<sub>4</sub> nanoparticles as sorbent (14), it has been found that Rh(III) has stronger affinity towards the sorbent than that of Pd(II) and Pt(IV) under similar experimental conditions studied in this work. This confirms the role of NTH bound to the surface of magnetite nanoparticles.

### Effect of pH

The effect of pH on the adsorption of PGMs from single-metal and multi-metal solutions was studied in pH range of 1 to 6. The results obtained for both solutions conditions revealed that the adsorption of PGMs by NTH-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles is independent of pH. This is in agreement with the results obtained from solvent extraction studies using NTH as extractant (15, 16). Our previous results (14) showed that when using bare Fe<sub>3</sub>O<sub>4</sub> nanoparticles as the sorbent, the adsorption of PGMs is strongly effected by pH. It appears that the coating of NTH on the surface of Fe<sub>3</sub>O<sub>4</sub> nanoparticles resulted in the suppression of the proton influence due to the difference adsorption mechanism from ion exchange mechanism for bare Fe<sub>3</sub>O<sub>4</sub> nanoparticles. Similar observation was reported when thiourea derivatives were grafted on chitosan for the sorption of Pd and Pt (21).

### Effect of Initial Metal Ion Concentration

The distribution of metal species between the sorbent and the metal solution at the equilibrium conditions is important in determining the maximum adsorption capacity of the sorbent for design purposes (22). In these experiments the effect of initial metal ion concentration on the sorption of Pd(II) and Pt(IV) was studied in order to estimate the maximum loading capacity of NTH-coated nanoparticles. The initial metal concentration was in the range of  $5.7 \times 10^{-5} \text{ mol L}^{-1}$  and  $7.5 \times 10^{-4} \text{ mol L}^{-1}$ . The relationship between the equilibrium aqueous concentration and the equilibrium loading capacity for Pd(II) and Pt(IV) is shown in Fig. 6. The experimental is in good agreement with the Langmuir adsorption model, which is given



**Figure 6.** The relationship between the equilibrium loading capacity and the equilibrium concentration of Pd(II) and Pt(IV). Amount of  $\text{Fe}_3\text{O}_4 = 10$  mg, total aqueous volume = 10 mL, temperature =  $22 \pm 1^\circ\text{C}$ , contact time = 30 min, pH = 2.5. The inset shows the Langmuir profile for Pd(II) and Pt(IV) sorption.

by the following equation;

$$q_e = \frac{q_{\max} k_L C_e}{1 + k_L C_e} \quad (3)$$

or

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} k} + \frac{C_e}{q_{\max}} \quad (4)$$

where  $q_e$  is the equilibrium loading capacity ( $\text{mmol g}^{-1}$ ),  $C_e$  is the equilibrium metal concentration in the aqueous phase ( $\text{mmol L}^{-1}$ ),  $q_{\max}$  is the maximum loading capacity ( $\text{mmol g}^{-1}$ ) corresponding to a monolayer coverage, and  $k_L$  is Langmuir constant ( $\text{L mmol}^{-1}$ ). The values of the maximum loading of Pd(II) and Pt(IV) and Langmuir constant can be determined from the intercept and slope of the linear line by plotting  $C_e$  versus  $C_e/q_e$  (Eq. 4) as shown in the inset of Fig. 6 and listed in Table 1. The maximum loading capacity is determined to be  $0.076 \text{ mmol g}^{-1}$  ( $8.1 \text{ mg g}^{-1}$ ) and  $0.055 \text{ mmol g}^{-1}$  ( $10.7 \text{ mg g}^{-1}$ ) for Pd(II) and Pt(IV), respectively.

**Table 1.** Langmiur parameters for the adsorption of Pd(II) and Pt(IV) onto NTH-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles

Metal ions	Langmuir parameters		r <sup>2</sup>
	$q_{max}$ (mmol g <sup>-1</sup> )	$K_L$ (L mmol <sup>-1</sup> )	
Pd(II)	0.076	414	0.9897
Pt(IV)	0.055	208	0.9986

The maximum loading capacity of Pd(II) and Pt(IV) corresponded to 16% and 11% (molar basis) of the total binding sites (0.49 mmol NTH g<sup>-1</sup>), respectively. The major part of the reagent is likely to be inaccessible to PGM ions. The sorption capacity of Pd(II) is higher than that of Pt(IV). The differences observed in the case of Pd(II) and Pt(IV) sorption may be explained by

- (a) The difference in the affinity of the sorbent for these metals.
- (b) The speciation of the metals. The latter strongly depends on parameters such as the pH, the total metal concentration, and the total concentration of chloride ions (23).

Selectivity

In order to examine the separation of Pd(II) from a mixture containing other metals, the selective sorption of Pd(II) from a solution containing mixture of Pt(IV), Rh(III), Cu(II), Zn(II), and Fe(III) was investigated. The results obtained are listed in Table 2. The separation factor *S*, for metal *M*<sub>1</sub> over

**Table 2.** Separation factors for extraction of Pd(II) over Pt(IV), Rh(III) and some base metals (Cu, Zn, Fe)

Metal ions	Separation factor ( <i>S</i> )
Pd(II)/Pt(IV)	29
Pd(II)/Rh(III)	42
Pd(II)/Cu(II)	83
Pd(II)/Zn(II)	87
Pd(II)/Fe(III)	15

**Table 3.** The recovery efficiency of Pd, Pt and Rh in a mixture using different eluting solutions

Stripping solution	Recovery (%)		
	Pd(II)	Pt(IV)	Rh(III)
0.5 M HNO <sub>3</sub>	4	27	0
0.5 M Thiourea	66	96	25
0.5 M NaClO <sub>4</sub>	0	3	46

metal  $M_2$  is defined as;

$$S_{M_1/M_2} = K_{dM_1}/K_{dM_2} \quad (5)$$

Palladium(II) was extracted selectively using NTH-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles from a mixture containing 100-folds amount of base metals. The initial PGMs concentration was  $3 \times 10^{-5} \text{ mol L}^{-1}$ . The results obtained are in agreement with that of solvent extraction studies (15). It indicates that NTH-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles can be used to extract Pd(II) selectively from aqueous solutions under the experimental conditions studied.

### Desorption of PGM

The recovery of PGM species from loaded Fe<sub>3</sub>O<sub>4</sub> nanoparticles coated with NTH was tested using different eluting solutions. The adsorption experiments were performed at pH = 2.5 and initial metal concentration of  $1 \times 10^{-4} \text{ mol L}^{-1}$ . As shown in Table 3, the separation of Pt(IV), Pd(II), and Rh(III) from each other can be almost accomplished taking the advantage of their different elution behavior, and using a three steps elution sequence: the first step with NaClO<sub>4</sub> to elute Rh(III), the second with HNO<sub>3</sub> to elute Pt(IV), and the third with thiourea to elute the remaining Pd(II). Thiourea can be used for the stripping of all metals. The low recovery values of all metals may be attributed to the formation of stable complexes with NTH.

### CONCLUSIONS

In this study, the feasibility of using magnetite nanoparticles coated with NTH (extractant) has been demonstrated for the selective separation of PGMs from diluted chloride solutions. The time needed to reach maximum adsorption was attained in less than 30 minutes and the loading capacity of NTH-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles for Pd(II) and Pt(IV) was determined to be 8.1 and 10.7 mg g<sup>-1</sup>, respectively. The adsorption behavior of Pd(II) and Pt(IV) at  $22 \pm 1^\circ\text{C}$  was similar to Langmuir isotherm. The order of affinity of NTH-coated Fe<sub>3</sub>O<sub>4</sub>

nanoparticles for PGMs from single-metal and multi-metal solutions is  $\text{Pd(II)} > \text{Pt(IV)} > \text{Rh(III)}$ . This order of the affinity is opposite to that of bare  $\text{Fe}_3\text{O}_4$  nanoparticles:  $\text{Rh(III)} > \text{Pt(IV)} > \text{Pd(II)}$ . The NTH-coated  $\text{Fe}_3\text{O}_4$  nanoparticles have been shown to be selective for Pd(II) against Pt(IV) and Rh(III) and some base metals such as Cu(II), Zn(II), and Fe(III).

FTIR analysis suggested that NTH is bound to the magnetite surface through sulphur atoms. The binding of metal ions is suggested to be most probably through nitrogen atoms of NTH bound to the magnetite surface. The different kinetic behavior of PGMs in single-metal and multi-metal solutions was explained by:

- (a) the difference in structure and geometry of PGMs chlorocomplexes;
- (b) the extraction of the strongest species and then diffusion in the layer of organic reagent.

The possibility of combining the superparamagnetic properties of  $\text{Fe}_3\text{O}_4$  nanoparticles with the selectivity of the reagent (NTH) could result in the development of a more effective sorbent for the selective recovery of PGMs from dilute solutions. The particles could be manipulated magnetically and exhibit quite a high adsorption capacity and fast adsorption and desorption rates for the extraction of PGMs due to high specific area and the decrease of internal diffusion resistance.

In this study, sufficiently high loading capacity and high selectivity of Pd(II) were obtained using NTH-coated  $\text{Fe}_3\text{O}_4$  nanoparticles. This proposed approach has a number of advantages:

- (a) no need for complex equipment, as compared to traditional separation techniques;
- (b) simplicity that will facilitate scale-up;
- (c) relatively inexpensive starting materials. Therefore industrial application of this system, providing a simple and efficient way to recover Pd(II) from dilute solutions, could be feasible. This system might be useful for treatment of process streams of palladium(II) and platinum(IV), specially since such streams usually contain low concentrations of these metals.

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