Adsorption of platinum(IV) and palladium(II) from aqueous solution by thiourea-modified chitosan microspheres

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ABSTRACT

The chitosan microparticles were prepared using the inverse phase emulsion dispersion method and modified with thiourea (TCS). TCS was characterized by scanning electron microscope (SEM), the Fourier transform infrared (FT-IR) spectra, sulfur elemental analysis, specific surface area and pore diameter. The effects of various parameters, such as pH, contact time, initial concentration and temperature, on the adsorption of Pt(IV) and Pd(II) by TCS were investigated. The results showed that the maximum adsorption capacity was found at pH 2.0 for both Pt(IV) and Pd(II). TCS can selectively adsorb Pt(IV) and Pd(II) from binary mixtures with Cu(II), Pb(II), Cd(II), Zn(II), Ca(II), and Mg(II). The adsorption reaction followed the pseudo-second-order kinetics, indicating the main adsorption mechanism of chemical adsorption. The isotherm adsorption equilibrium was well described by Langmuir isotherms with the maximum adsorption capacity of 129.9 mg/g for Pt(IV) and 112.4 mg/g for Pd(II). The adsorption capacity of both Pt(IV) and Pd(II) decreased with temperature increasing. The negative values of enthalpy (ΔH°) and Gibbs free energy (ΔG°) indicate that the adsorption process is exothermic and spontaneous in nature. The adsorbent was stable without loss of the adsorption capacity up to at least 5 cycles and the desorption efficiencies were above 95% when 0.5 M EDTA–0.5 M H_2SO_4 eluent was used. The results also showed that the preconcentration factor for Pt(IV) and Pd(II) was 196 and 172, respectively, and the recovery was found to be more than 97% for both precious metal ions.

1. Introduction

Platinum group are precious metals (PGM) and are widely used in industries because of their specific physical and chemical properties. Therefore, the effective recovery of PGM from both natural ore and industrial waste is quite important from the viewpoint of full utilization of resources. There are several methods, such as solvent extraction [1], ion-exchange [2], membrane separation [3] and adsorption [4], available in the literature for the removal of these precious metals from aqueous solutions. Comparatively, the adsorption seems to be the most suitable method for the recovery of PGM in the case of low concentration due to low cost and high efficiency. Due to the technical and economical point of view, now much attention has been focused on low cost adsorbents, such as chitosan for the removal and recovery of precious metal ions [5,6].

Chitosan is a partially acetylated glucosamine biopolymer and mainly results from deacetylation of chitin. It is an aminopolysac-

charide constituted of both glucosamine and acetylglucosamine moieties. Chitosan is nontoxic, bioabsorbable and possesses various biofunctionalities, including antithrombogenic, homeostatic, immunityenhancing, and wound-healing properties [7]. Chitosan has already been described as a suitable natural polymer for the removal of metal ions [5]. The high content of nitrogen atoms in the chitosan allows the uptake of several metal ions through various mechanisms such as chelation, electrostatic attraction or ion-exchange, depending on the metal ion and the pH of the solution [6]. The amine and two hydroxyl groups on each glucosamine in the repeating unit of chitosan can act as a reactive site for chemical modification. The acido-basic properties of chitosan lead to a cationic behavior in acidic conditions (pK_a near 6.2). The cationic properties of chitosan make the biopolymer efficient at sorbing anionic compounds, including metal anions or anionic dyes through electrostatic attraction [4,6].

However, chitosan can be dissolved in acid media and its applications are limited. To overcome these problems chitosan was modified with different crosslinking agents. Several crosslinkers such as glutaraldehyde [8], epichlorohydrin [9], and ethyleneglycoldiglycidylether [10] have been used to modify the chitosan for metal ion removal. The selectivity for a specific metal ion depends

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on what kind of complexing agent is introduced into the polymeric chain. Several chelating ligands such as poly(ethylenimine) [4], ethylenediaminetetraacetic acid [11], thiocarbamonyl [12], crown ethers [13], L-lysine [14], and thiourea [15] were used to functionalize the crosslinked chitosan for adsorption of metal ions. According to the theory of hard and soft acids and bases (HSAB) defined by Pearson, metal ions will have a preference for complexing with ligands that have more or less electronegative donor atoms. Chelating agents with N and S groups are highly efficient for the selective sorption of precious metal ions. The sulfur group is known to form stable complexes with metals such as Hg, Pt, Ag, Au, and to a lesser extent, Cd and Zn [16]. Due to their high nitrogen content and porosity, chitosan-based sorbents have exhibited relatively high sorption capacities and fast kinetics for most metals [17–19]. However, lack of specificity towards several precious metals limits the use of chitosan as an effective sorbent.

In the present work, chitosan microspheres were prepared and modified with sulfur groups. The high content of sulfur groups makes possible chemical modification in chitosan with the purpose of improving its features as an adsorbent, such as selectivity and adsorption capacity. The influences of experimental parameters such as pH, contact time, initial concentration and temperature on adsorption were studied. The kinetic models used to describe the rate data were discussed. Desorption studies were conducted by suitable agents to regenerate the spend adsorbent.

2. Experimental

2.1. Materials

Chitosan with 40 mesh, 90% degree of deacetylation (DD) and molecular weight of 1.3×10^5 was purchased from Yuhuan Ocean Biology Company (Zhejiang, China). All the other reagents used in this work were of analytical grade. Thiourea, HCl, NaOH and buffer solutions (Wako chemicals, Japan) were used. K_2PtCl_6 (>99%, Sigma) and $PdCl_2$ (>99%, Sigma) were analytical reagents. The stock solutions were prepared by dissolving these metal salts in deionized water and were further diluted as required.

2.2. Preparation of chitosan microspheres

The water/oil (W/O) emulsion crosslinking technique was used for the preparation of chitosan microspheres. 1.0 g of chitosan powder was dissolved in 100 mL of 2 wt.% aqueous acetic acid solution. The W/O emulsion was prepared by dropwising the acetic acid solution containing chitosan into the dispersion medium, which was composed of cyclohexane, n-hexanol (11:6, v/v) and an emulsifier (2.5 mL Triton X-100). The W/O ratio of the W/O emulsion was 4:17 (v/v). During this process, the dispersion medium was stirred with a mechanical stirrer at about 1000 rpm at room temperature. Ten minutes later, an additional 1 mL of glutaraldehyde was added to the dispersion medium. Similarly, 1 h later, another 1 mL of glutaraldehyde was added to the medium, which was then stirred for a further 2 h. At the end of this period, the chitosan microspheres

(CS) were collected and rinsed with ethanol and deionized water for three times.

2.3. Modification of chitosan microspheres with thiourea

Grafting of sulfur groups using epichlorohydrin as a crosslinking agent was carried out according to the procedure described by Chassary et al. [4] with chitosan flakes. Four milliliters of epichlorohydrin was dissolved in 100 mL of acetone, the chitosan microspheres (2 g) were added, and the slurry was mixed at 308 K for 24 h. Thiourea (2 g) was added, and stirring was continued for 6 h at 333 K, followed by addition of further thiourea (4.6 g) with stirring at 333 K. NaOH (1 M, 50 mL) was added, and the slurry was agitated (4 h, 333 K). The solid product (thiourea derivative of chitosan, TCS) was filtered and successively washed with acetone, deionized water, and methanol, and dried in a vacuum oven at 333 K. The synthesis is shown in Scheme 1.

2.4. Characterization of the adsorbents

Scanning electron microscopy (SEM, Hitachi, S-4500) was used to analyze the surface morphology of the chitosan microspheres. FT-IR spectra were measured on a Nicolet, Magna-550 spectrometer. The unmodified and the modified chitosan was mixed with KBr and pressed to a pellet for measurement. The sulfur content of TCS was determined by a Thermo Finnigam 1112 Elemental Analyzer. The specific surface area was measured by N_2 adsorption isotherm using an ASAP 2010 Micromeritics instrument and by Brunauer–Emmett–Teller (BET) method, using the software of Micromeritics. Pore diameter greater than 20 Å were determined by mercury porosimeter up to 2000 kg/cm^2 using a Carlo Erba mercury porosimeter (model 200, Carlo Erba Co. Ltd.). Temperature controlled bio-shaker (BR-30L, Taitec) was used for agitating the sample solutions.

2.5. Effect of pH

Uptake experiments were performed at controlled pH (1–9) and 298 K by shaking 0.1 g of dry TCS with 30 mL (30 mg/L) metal ion solution for 4 h at 150 rpm. The solution pH was adjusted to the desired value by adding hydrochloric acid or ammonia solution. After filtration, The concentrations of Pt(IV) and Pd(II) in aqueous solutions were analyzed using Inductively Coupled Plasma (ICP, ARL- 340, ICP-AES Fison Instruments).

2.6. Binary metallic systems

The relative higher uptake of Pt(IV) and Pd(II) at lower pH values was taken as indication for their selective separation from other metal ions. The initial concentration of all metal ions in the mixture was 30 mg/L. The uptake behavior of Pt(IV) and Pd(II) from a binary mixtures with Cu(II), Pb(II), Cd(II), Zn(II) and Ca(II) was studied at pH 2.0 and the same other adsorption conditions as those in Section 2.5. The procedures were similar to those of Section 2.5.
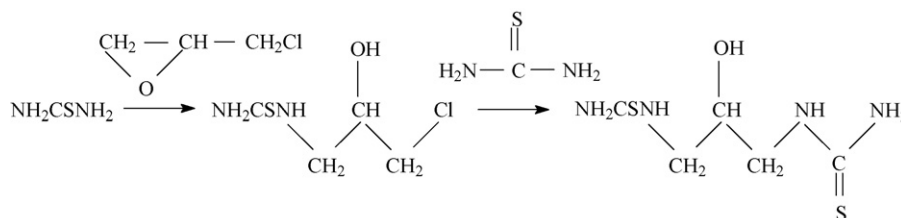
Scheme 1. Synthesis of thiourea-modified crosslinked chitosan.

2.7. Kinetics

Kinetic studies were conducted by placing 0.1 g TCS in a flask containing 200 mL (80 mg/L) metal ion solution at pH 2.0. The contents of the flask were agitated on a shaker at 150 rpm and 298 K. Three milliliters of samples were taken at time intervals for the analysis of residual metal concentration in solution. The concentrations of metal ions in the aqueous solutions were calculated after the correction of volume.

2.8. Adsorption isotherms

The effect of initial concentration of the metal ion on the uptake by TMCS obtained was carried out by placing 0.1 g TCS in a series of flasks containing 30 mL of metal ions at definite concentrations (10–400 mg/L) and pH 2.0. The flasks were agitated on a shaker at 150 rpm for 4 h while keeping the temperature at 298, 308, 318, or 328 K. After adsorption, solution was filtered and the residual concentration of the metal ions was determined.

2.9. Desorption of precious metals and reuse

Batch desorption experiments were carried out using various concentrations of H_2SO_4, EDTA, and EDTA–H_2SO_4 solutions. The adsorbed precious metal ions (100 mg/L) onto TCS were washed with deionized water several times and transferred into stoppered reagent bottles. To this 30 mL of the desorption agent was added, and then the bottles were shaken at room temperature (298 K) using mechanical shaker for 4 h. The concentration of precious metal ion released from the TCS into aqueous phase was analyzed by ICP-AES. The TCS after desorption was reused in adsorption experiment, and the process was repeated for five times.

2.10. Preconcentration and recovery

The sample solution contained the Pt(IV) or Pd(II) in the concentration of 10 μg/L, and the pH was adjusted to desired value with HCl or ammonia solution. The solution was passed through the microcolumn (50 mm × 3.0 mm i.d.) containing 0.15 g of TCS, at a flow rate of 1.0 mL/min. Then the column was rinsed with 5 mL of deionized water. Afterwards, the retained metal ions were eluted with 5 mL of 0.5 M EDTA–0.5 M H_2SO_4 solution at a flow rate of 1.0 mL/min. The concentrations of the analytes were determined by ICP-AES. The preconcentration factor was calculated as the ratio of the concentration of Pt(IV) and Pd(II) after preconcentration to that prior to preconcentration.

2.11. Replication of batch experiment

Each batch adsorption experiment above was conducted twice to obtain reproductive results with error <5%. In the case of deviation larger than 5%, more tests were carried out. The experimental data could be reproduced with an accuracy greater than 95%. All the data of batch adsorption experiments listed in Section 3 are the average values of two tests.

3. Results and discussions

3.1. Characterization of the adsorbents

SEM micrograph of TCS is shown in Fig. 1a. Most of the TCS microspheres have a diameter between about 6 μm and around 30 μm. The FT-IR spectra of CS and TCS are shown in Fig. 1b. The adsorption band around 3420 cm^{-1}, revealing the stretching vibration of N–H group bonded with O–H group in chitosan, and at 1661 cm^{-1} confirms the N–H scissoring from the primary amine,
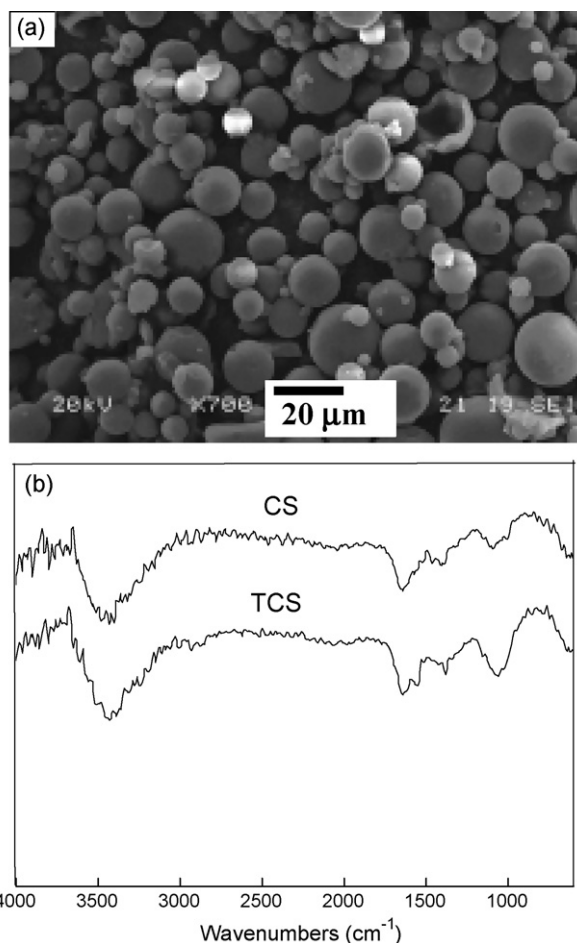

Fig. 1. (a)SEM of TCS and (b) infrared spectra of CS and TCS.

due to the free amino groups in the crosslinked chitosan [20]. The band around 1065 cm^{-1} is attributed to the combined effects of C–N stretching vibration of primary amines and the C–O stretching vibration from the primary alcohol in chitosan. The spectrum of TCS displays new bands near 1548 cm^{-1} which are assigned to νC–N of thiourea moiety [21]. The increasing intensity at 1661 and 1062 cm^{-1} in the spectrum of TCS indicates that TCS has more amine groups than the unmodified chitosan. The peak due to sulfur group vibration was not detected, probably due to the weak signal [21]. Elemental analysis of sulfur indicated that the chitosan modification with thiourea resulted in a product with a sulfur content of 3.26 mmol/g. The BET surface area for TCS was 95.6 m^2/g. According to mercury porosimetry data, the average pore size of TCS microspheres was 869 nm.

3.2. Effect of pH

The effect of pH on the adsorption of Pt(IV) and Pd(II) was studied individually by varying the pH of 30 mg/L initial metal concentration for a fixed adsorbent dosage of 3.33 g/L at 298 K and the results are presented in Fig. 2. The results demonstrated that the maximum adsorption capacity occurred at pH 2.0 for both Pt(IV) and Pd(II). The data indicated that the adsorption percentage was slightly changed between pH 1.0 and 4.0, later it decreased drastically for tested precious metal ions. At low pH, when the solution pH was controlled by HCl, the amount of chloride in the solution is high enough to favor the formation of chloro-anioinc species that will be adsorbed on protanated amine groups of TCS [4]. Moreover, the protanation of amine groups on the TCS induced an electrostatic
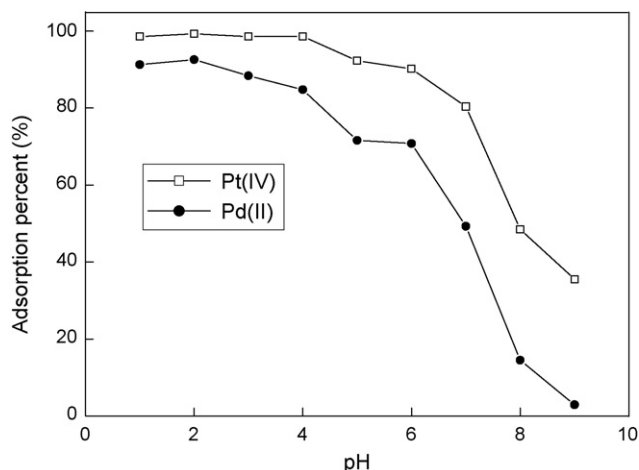
Fig. 2. Effect of pH on the uptake of Pt(IV) and Pd(II) by TCS (initial metal ion concentration 30 mg/L, contact time 4 h, adsorbent dose 0.1 g). The symbols represent the average values of two tests under the identical conditions with error <5%.

attraction of anionic metal complexes and increased the number of available binding sites for precious metal ions uptake. At acidic solutions the dominant mechanism of interaction is probably due to the formation of salts [(R NH$_3^+$)$_2$PtCl$_6^{2-}$ or (R NH$_3^+$)$_2$ PdCl$_4^{2-}$] [4]. This interaction mechanism may take place along with adduct formation (R–S → PtCl$_6^{2-}$ or R–S → PdCl$_4^{2-}$) due to the strong oxidizing power of PtCl$_6^{2-}$ or PdCl$_4^{2-}$ species. At higher pH values the sorption capacity decreases, this may be explained by the presence of less adsorbable Pt(IV) and Pd(II) species because of the lower availability of chloride anions. Previous results also indicated that higher adsorption capacity for precious metal ions was obtained at pH 1.0–4.0 [22–24].

3.3. Binary metallic systems

Selective separation of Pt(IV) and Pd(II) from binary mixtures with Cu(II), Pb(II), Cd(II), Zn(II) or Ca(II) was studied at pH 2.0 and same other adsorption conditions. The uptake obtained for Cu(II), Pb(II), Cd(II), Zn(II) and Ca(II) in the presence of Pt(IV) was 0.10, 1.10, 0.24, 0.15 and 0.30 mg/g, respectively, while that for Pt(IV) was 8.54–8.86 mg/g. The uptake obtained for Cu(II), Pb(II), Cd(II), Zn(II) and Ca(II) in the presence of Pd(II) was 0.50, 0.70, 0.55, 0.40 and 0.35 mg/g, respectively, while that for Pd(II) was 8.02–8.28 mg/g. This data indicate no appreciable uptake for the studied metal ions relative to that of Pt(IV) and Pd(II).

3.4. Kinetic

The effect of contact time on the adsorption of Pt(IV) and Pd(II) is shown in Fig. 3. The kinetic curve for Pt(IV) and Pd(II) showed that the adsorption was rapid for the first 30 min, when the removal rate reached 73% and 67%, respectively, and then slowed considerably. Experimental results suggest that the amount of Pt(IV) and Pd(II) adsorbed (mg/g) increased with increasing contact time and reached equilibrium at 300 min for Pt(IV) and around 150 min for Pd(II). Hence, in the present study, we used 4 h contact time for further experiments.

In order to evaluate the kinetic mechanism that controls the adsorption process, pseudo-first-order, pseudo-second-order, and intra-particle diffusion models were employed to interpret the experimental data [25,26]. A good correlation of the kinetic data explains the adsorption mechanism of the metal ions on the solid phase [27].
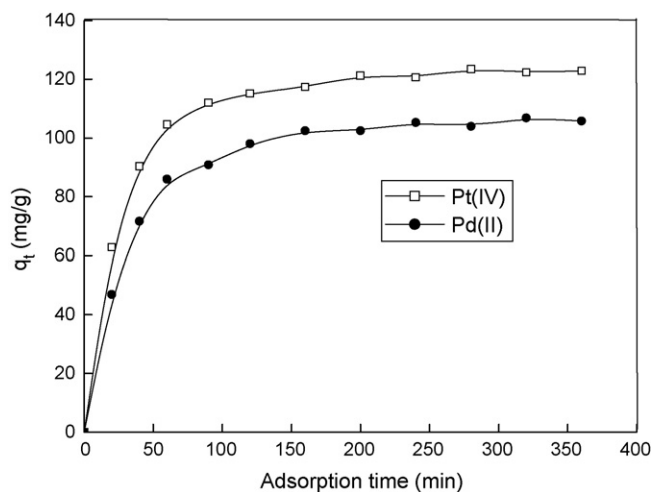
Fig. 3. Effect of adsorption time on the uptake of Pt(IV) and Pd(II) by TCS (initial metal ion concentration 80 mg/L, solution pH 2.0, adsorbent dose 0.1 g). The symbols represent the average values of two tests under the identical conditions with error <5%.

The pseudo-first-order equation was represented by

$$\frac{1}{q_t} = \frac{k_1}{q_e t} + \frac{1}{q_e} \tag{1}$$

where k_1 (min^{-1}) is the pseudo-first-order adsorption rate constant, q_t is the amount adsorbed at time t (min), and q_e denotes the amount adsorbed at equilibrium, both in mg/g.

The linear form of pseudo-second-order equation can be written as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2}$$

where k_2 (g/(mg min)) is the adsorption rate constant of pseudo-second-order.

The initial adsorption rate (h) can be determined from k_2 and q_e values [25] using

$$h = k_2 q_e^2 \tag{3}$$

The linear form of the intra-particle diffusion equation is given by

$$\ln q_t = \ln k_{id} + 0.5 \ln t \tag{4}$$

where k_{id} (mg/(g min$^{1/2}$)) is the intra-particle diffusion rate constant.

Table 1
Kinetic Parameters for Pt(IV) and Pd(II) adsorption by TCS.

Metals	First-order model		
	k_1 (min^{-1})	$q_{e,1}$ (mg/g)	R^2
Pt(IV)	21.92	135.14	0.9829
Pd(II)	29.91	120.48	0.9849

Metals	Second-order model			
	h (mg/(g min))	k_2 (g/(mg min))	$q_{e,2}$ (mg/g)	R^2
Pt^{4+}	10.04	6.11×10^{-4}	128.20	0.9995
Pd^{2+}	6.37	5.05×10^{-4}	112.36	0.9987

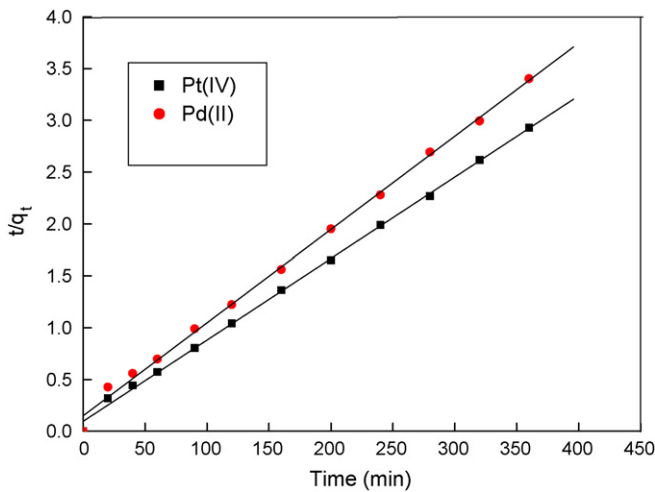| Metals	Intra-particle diffusion model	
	k_{id} (mg/(g min$^{1/2}$))	R^2
Pt^{4+}	41.66	0.8173
Pd^{2+}	27.65	0.8391

Fig. 4. Pseudo-second-order kinetics of the uptake of Pt(IV) and Pd(II) by TCS.

The results of kinetic parameters are shown in Table 1. The validity of each model could be checked by the fitness of the straight lines (R^2 values). Accordingly as shown in Table 1 and Fig. 4, adsorption of Pt(IV) and Pd(II) on TCS is perfectly fit pseudo-second-order model rather than other ones. In addition, the experimental and theoretical values of q_e (obtained from pseudo-second-order model) are closely similar, confirming the validity of that model to the adsorption system under consideration. This suggests the main adsorption mechanism of chemical adsorption. It is more likely to predict that the adsorption behavior may involve valency forces through sharing of electrons between precious metal anions and adsorbent. The pseudo-second-order rate constant (k_2) and initial sorption rate (h) for Pt(IV) were higher when compared to Pd(II). The adsorption of Pt(IV) and Pd(II) onto TCS may be consist of two processes: the first process is interpreted to be the instantaneous adsorption stage or external surface adsorption. The second process is interpreted to be the gradual adsorption stage where intraparticle diffusion controls the adsorption rate until finally the metal uptake reaches equilibrium.

In many cases, the pseudo-second-order kinetic model provided better results on the adsorption of Fe on chitosan and crosslinked chitosan beads [28], Cu, Cd and Ni on chemically modified chitosan [18], Cr and Cu ions on chitosan [29].

3.5. Adsorption isotherms

Fig. 5 shows the isotherms of adsorption of Pt(IV) and Pd(II) on TCS, respectively at 298, 308, 318 and 328 K. The results found that the adsorption capacity decreased with increasing temperature. This indicates that the adsorption process is exothermic in nature. The adsorption data were plotted according to Langmuir equation

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \tag{5}$$

where q_e and C_e are the amount adsorbed (mg/g) and the adsorbate concentration in solution (mg/L), both at equilibrium. q_m and K_L are the Langmuir constants which are related to the adsorption capacity and energy of adsorption, respectively, and can be calculated from the intercept and slope of the linear plot, with C_e/q_e versus C_e.

The values of K_L and q_m at different temperatures for adsorption of Pt(IV) and Pd(II) were reported in Table 2. It is seen that the value of q_m (obtained from Langmuir plots) is consistent with that experimentally obtained, indicating that the adsorption process is
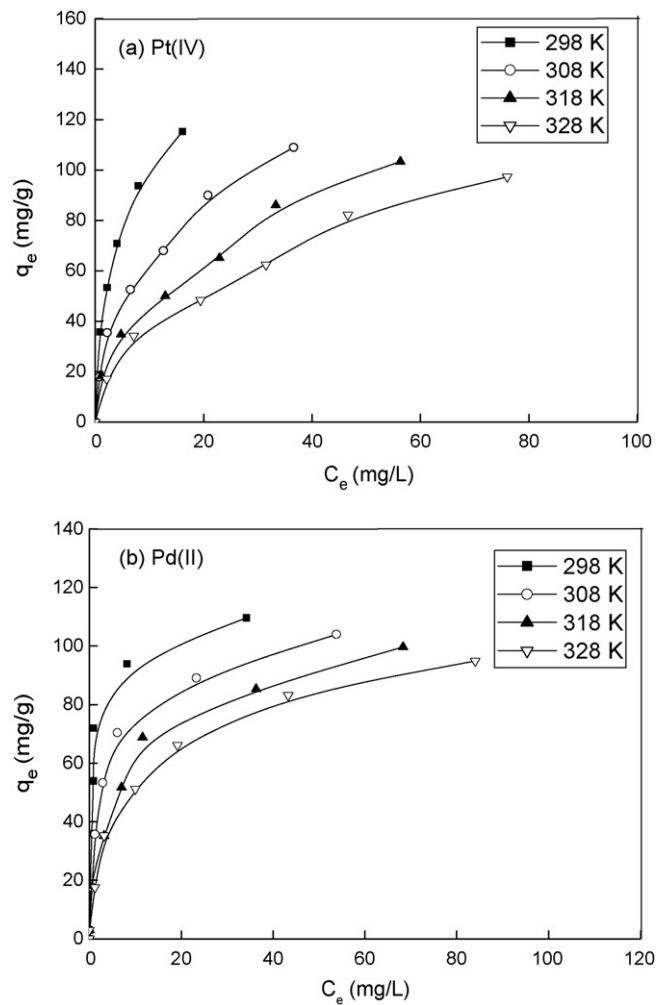

Fig. 5. Adsorption isotherms of Pt(IV) (a) and Pd(II) (b) at different temperatures (initial metal ion concentration 10–400 mg/L; solution pH 2.0; adsorbent dose 3.33 g/L; contact time 4 h). The symbols represent the average values of two tests under the identical conditions with error <5%.

mainly monolayer. The chelation adsorption mechanism for Pt(IV) and Pd(II) may give controlled monolayer adsorption [4,5].

The adsorption curves show that the maximum uptake values for Pt(IV) and Pd(II) are 129.87 and 112.36 mg/g. The q_m values of the unmodified chitosan microspheres (CS) obtained at 298 K and in the same other conditions as in TCS for Pt(IV) and Pd(II) are 101.2 and 80.6 mg/g, respectively, which are lower than those of TCS. The higher maximum adsorption capacity obtained for Pt(IV) and Pd(II) on TCS is because of the fact that the incorporation of thiourea in CS increases the number of sorption sites in TCS to interact with Pt(IV) and Pd(II) ions, which enhances the adsorption capacity.

Table 3 compares the adsorption capacity of different types of adsorbents [30–35] used for Pt(IV) and Pd(II) adsorption. The adsorption capacity of TCS was relatively high when compared

Table 2
Langmuir parameters for the adsorption of Pt(IV) and Pd(II) onto TCS.

Temperature (K)	Pt(IV)			Pd(II)		
	q_m (mg/g)	K_L (L/mg)	R^2	q_m (mg/g)	K_L (L/mg)	R^2
298	129.9	0.389	0.9858	112.4	0.978	0.9993
308	125.0	0.141	0.9704	108.7	0.308	0.9978
318	120.5	0.077	0.9623	104.2	0.192	0.9886
328	117.6	0.050	0.9692	102.0	0.123	0.9952

Table 3
Maximum adsorption capacities for the adsorption of Pt(IV) and Pd(II) onto various adsorbents.

Adsorbent	Adsorption capacity (mg/g)	
	Pt(IV)	Pd(II)
Sulfur-derivatives of chitosan [30]		213
Glycine-modified chitosan [31]	122.47	120.39
Fe$_3$O$_4$ nanoparticles [32]	13.27	10.96
PA-Lignin [33]	104.57	22.66
Amberlite IRC 718 [34]	42.93	40.43
Poly(vinylbenzylchloride–acrylonitryle–divinylbenzene) modified with tris(2-aminoethyl)amine [35]	245	280
TCS [this work]	129. 87	112.36

Table 4
Themodynamic parameters for the adsorption of Pt(IV) and Pd(II) onto TCS.

Metal ion	Temp. (K)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol K)	$T\Delta S°$ (kJ/mol)	R^2
Pt^{4+}	298	−27.52	−55.25	−92.99	−27.71	0.9293
	308	−26.60			−28.64	
	318	−25.66			−29.57	
	328	−24.73			−30.50	
Pd^{2+}	298	−28.18	−54.77	−89.19	−26.58	0.9929
	308	−27.29			−27.47	
	318	−26.39			−28.36	
	328	−25.50			−29.25	

to several other adsorbents. The differences of precious metal ion uptake on various adsorbents are due to the properties (function groups, surface area, particle size, etc.) of each of them.

The degree of suitability of resin towards metal ions was estimated from the values of separation factor constant (R_L) which gives indication for the possibility of the adsorption process to proceed. $R_L > 1.0$ unsuitable; $R_L = 1$ linear; $0 < R_L < 1$ suitable; $R_L = 0$ irreversible [36]. The value of R_L could be calculated from the relation

$$R_L = \frac{1}{1 + K_L C_0} \tag{6}$$

where K_L (L/mg) is the Langmuir equilibrium constant and C_0 is the initial concentration of Pt(IV) and Pd(II). The values of R_L lie between 0.0064 and 0.6667 for Pt(IV), 0.0026 and 0.4484 for Pd(II), indicating that the adsorption of Pt(IV) and Pd(II) on TCS is favorable and useful for the removal of precious metal ions.

The observed decrease in both values of q_m and K_L at elevated temperature indicates the exothermic nature of the adsorption process. The values of K_L at different temperatures were treated according to van't Hoff equation [37]

$$\ln K_L = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{7}$$

where $\Delta H°$ (J/mol) and $\Delta S°$ (J/mol K) are enthalpy and entropy changes, respectively, R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (in Kelvin). Plotting $\ln K_L$ against $1/T$ gives a straight line with slope and intercept equal to $-\Delta H°/R$ and $\Delta S°/R$, respectively. The values of $\Delta H°$ and $\Delta S°$ were calculated from Fig. 6 and reported in Table 4. The negative values of $\Delta H°$ confirming the exothermic nature of adsorption process whereas the negative values of $\Delta S°$ suggests the high orderness of adsorption system at equilibrium due to the interaction between active sites and metal ions. Gibbs free energy of adsorption ($\Delta G°$) was calculated from the following relation

$$\Delta G° = \Delta H° - T\Delta S° \tag{8}$$

The values of $\Delta G°$ at different temperatures were calculated and also reported in Table 4. The negative value of $\Delta G°$ indicates that the adsorption reaction is spontaneous. The observed decrease in negative values of $\Delta G°$ with increasing temperature implies that the adsorption becomes less favorable at higher temperatures [37].

The data given in Table 4 also show a slight change in the value of $T\Delta S°$ at all temperatures and $|\Delta H°| > |T\Delta S°|$. This indicates that the adsorption process is dominated by enthalpic rather than entropic changes [37].

3.6. Desorption of precious metals, and reuse after desorption

For the adsorption to be useful, the adsorbate has to be desorbed and spend adsorbent reused. In the present study the desorption efficiency of adsorbed precious metals (100 mg/L) onto TCS (3.33 g/L) was studied by various concentrations of 30 mL H$_2$SO$_4$, EDTA, and EDTA–H$_2$SO$_4$ solutions. The systematic influences of these desorbing solutions on adsorbed precious metals onto TCS are shown in Table 5. The results show that 0.5 M EDTA–0.5 M H$_2$SO$_4$ solution can effectively desorbed the Pt(IV) and Pd(II) (>97%) metal ions from adsorbent material. The high percentage of desorption obtained when 0.5 M EDTA–0.5 M H$_2$SO$_4$ solution was used may be explained by both stable complexes and the electrostatic interactions between the Pt(IV) and Pd(II) species and charged species from elution, through the comparison of the electric double layer,
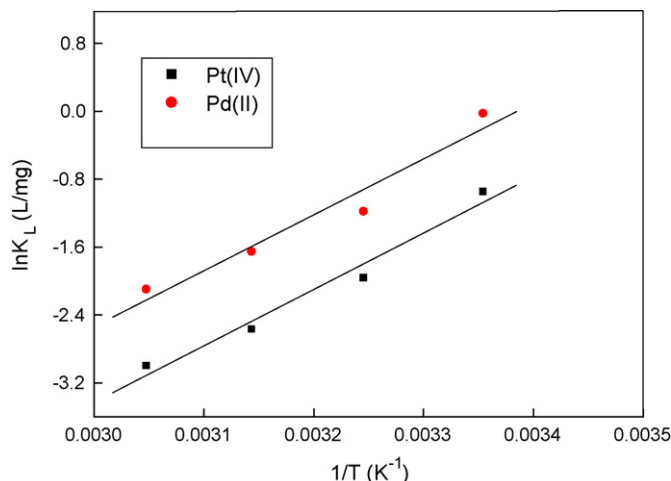
Fig. 6. Van't Hoff plots for the uptake of Pt(IV) and Pd(II) on TCS.

Table 5
Desorption of Pt(IV) and Pd(II) with different eluents.

Desorption agent	Desorption efficiency (%)	
	Pt(IV)	Pd(II)
0.1 M H_2SO_4	19.23	3.12
0.3 M H_2SO_4	28.08	5.36
0.5 M H_2SO_4	37.36	6.88
1.0 M H_2SO_4	38.18	7.68
0.1 M EDTA	36.28	43.28
0.3 M EDTA	70.86	75.16
0.5 M EDTA	90.09	93.09
1.0 M EDTA	92.26	95.26
0.1 M EDTA–0.5 M H_2SO_4	45.24	49.21
0.3 M EDTA–0.5 M H_2SO_4	77.06	79.08
0.5 M EDTA–0.5 M H_2SO_4	97.16	98.38
1.0 M EDTA–0.5 M H_2SO_4	98.48	99.64

which would weaken the interaction between the adsorbent and precious metal ions, promoting desorption.

The stability and the potential regeneration of the adsorbent were investigated. The adsorbent can be reused after desorption with 0.5 M EDTA–0.5 M H_2SO_4 solution. The results showed that the adsorbent was stable without loss of the adsorption capacity up to at least 5 cycles and the desorption efficiencies were above 95%. Therefore, TCS could be successfully applied for the recovery of Pt(IV) and Pd(II) from aqueous solution.

3.7. Preconcentration and recovery

From the measured results, recovery was found to be more than 97% for both Pt(IV) and Pd(II). The preconcentration factor for the metal ions with TCS was also studied. The results showed that the preconcentration factor for Pt(IV) and Pd(II) was 196 and 172, respectively.

4. Conclusions

The recovery of Pt(IV) and Pd(II) from aqueous solutions was studied using resin derived from thiourea-modified chitosan. The results demonstrated that the adsorption process is dependent on contact time, initial metal ion concentration, solution pH and temperature. The adsorption capacity of TCS is higher than that of CS. The maximum adsorption capacity was obtained at pH 2.0 both for Pt(IV) and Pd(II). Kinetic studies indicated that the adsorption reaction follows the pseudo-second-order kinetics; this suggests the main adsorption mechanism of chemical adsorption. The adsorption isotherms could be well fitted by the Langmuir isotherm equation. Thermodynamic parameters obtained indicated that the adsorption process is spontaneous and exothermic. The resin obtained showed good durability and easy regeneration.

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References

[1] H.T. Nguyen, W. Masayuki, K. Takaumi, Solvent extraction of palladium(II) with various ketones from nitric acid medium, Solvent Extr. Ion. Exch. 25 (2007) 407–416.
[2] A. Hulanicki, Ion exchange preconcentration and separation of trace amounts of platinum and palladium, Anal. Lett. 33 (2000) 2805–2820.
[3] T.Z. Sadyrbaeva, Separation of copper(II) from palladium(II) and platinum(IV) by di(2-ethylhexyl)phosphoric acid-based liquid membranes during electro-dialysis, Biol. J. Membr. Sci. 275 (2006) 195–201.
[4] P. Chassary, T. Vincent, J.S. Marcano, L.E. Macaskie, E. Guibal, Palladium and platinum recovery from bicomponent mixtures using chitosan derivatives, Hydrometallurgy 76 (2005) 131–147.
[5] I.M.N. Volda, K.M. Varum, E. Guibal, O. Smidsrod, Binding of ions to chitosan-selectivity studies, Carbohydr. Polym. 54 (2003) 471–477.
[6] E. Guibal, Interactions of metal ions with chitosan-based sorbents: a review, Sep. Purif. Technol. 38 (2004) 43–74.
[7] R. Tang, Y. Du, L. Fan, Dialdehyde starch-crosslinked chitosan films and their antimicrobial effects, J. Polym. Sci. Part B: Polym. Phys. 41 (2003) 993–997.
[8] M. Ruiz, A.M. Sastre, E. Guibal, Palladium sorption on glutaraldehyde crosslinked chitosan, React. Funct. Polym. 45 (2000) 155–173.
[9] R.S. Vieira, M.M. Beppu, Interaction of natural and crosslinked chitosan membranes with Hg(II) ions, Colloids Surf. A 279 (2006) 196–207.
[10] N. Li, R. Bai, Development of chitosan-based granular adsorbents for enhanced and selective adsorption performance in heavy metal removal, Water Sci. Technol. 54 (2006) 103–113.
[11] R.S. Juang, C.Y. Ju, Kinetics of sorption of Cu(II)-ethylenediaminetetraacetic chelated anions on cross-linked, polyaminated chitosan beads, Ind. Eng. Chem. Res. 37 (1998) 3463–3469.
[12] Y. Baba, H. Noma, R. Nakayama, Y. Matsushita, Preparation of chitosan derivatives containing methylthiocarbamoyl and phenylthiocarbamoyl groups and their selective adsorption of copper(II) over iron(III), Anal. Sci. 18 (2002) 359–361.
[13] S. Ding, X. Zhang, X. Feng, Y. Wang, S. Ma, Q. Peng, W. Zhang, Synthesis of N,N1-diallyl dibenzo 18-crown-6 crown ether crosslinked chitosan and their adsorption properties for metal ions, React. Funct. Polym. 66 (2006) 357–363.
[14] K. Fujiwara, A. Ramesh, T. Maki, H. Hasegawa, K. Ueda, Adsorption of platinum (IV), palladium (II) and gold (III) from aqueous solutions onto L-lysine modified crosslinked chitosan resin, J. Hazard. Mater. 146 (2007) 39–50.
[15] L.M. Zhou, Y.P. Wang, Z.R. Liu, Q.W. Huang, Characteristics of equilibrium, kinetics studies for adsorption of Hg(II), Cu(II), and Ni(II) ions by thiourea-modified magnetic chitosan microspheres, J. Hazard. Mater. 161 (2009) 995–1002.
[16] S.M.C. Ritchie, K.E. Kissick, L.G. Bachas, S.K. Sikdar, C. Parikh, D. Bhattacharyya, Polycysteine and other polyaminoacid functionalized microfiltration membranes for heavy metal capture, Environ. Sci. Technol. 35 (2001) 3252–3258.
[17] W.S.W. Ngah, A. Kamari, Y.J. Koay, Equilibrium and kinetics studies of adsorption of copper(II) on chitosan and chitosan/PVA beads, Int. J. Biol. Macromol. 34 (2004) 155–161.
[18] K.C. Justi, V.T. Favere, M.C.M. Laranjeira, A. Neves, A.P. Rosely, Kinetics and equilibrium adsorption of Cu(II), Cd(II), and Ni(II) ions by chitosan functionalized with 2-[-bis-(pyridylmethyl) aminomethyl]-4-methyl-6-formylphenol, J. Colloid Interface Sci. 291 (2005) 369–374.
[19] A.A. Atia, Studies on the interaction of mercury(II) and uranyl(II) with modified chitosan resins, Hydrometallurgy 80 (2005) 13–22.
[20] R.K. Katarina, T. Takayanagi, M. Oshima, S. Motomizu, Synthesis of a chitosan-based chelating resin and its application to the selective concentration and ultratrace determination of silver in environmental water samples, Anal. Chim. Acta 558 (2006) 246.
[21] A.M. Donia, A.A. Atia, K.Z. Elwakeel, Recovery of gold(III) and silver(I) on a chemically modified chitosan with magnetic properties, Hydrometallurgy 87 (2007) 197–206.
[22] S. Doker, S. Malci, M. Dogan, B. Salih, New poly(N-(hydroxymethyl) methacrylamide-1-allyl-2-thiourea) hydrogels prepared by radiationinduced polymerization: selective adsorption, recovery and preconcentration of Pt (II) and Pd (II), Anal. Chim. Acta 553 (2005) 73–82.
[23] H.W. Ma, X.P. Liao, X. Liu, B. Shi, Recovery of platinum(IV) and palladium(II) by bayberry tannin immobilized collagen fiber membrane from water solution, J. Membr. Sci. 278 (2006) 373–380.
[24] C. Kavaklı, S. Malcı, S.A. Tuncel, B. Salih, Selective adsorption and recovery of precious metal ions from geological samples by 1,5,9,13-tetrathiacyclohexadecane-3,11-diol anchored poly(p-CMS-DVB) microbeads, React. Funct. Polym. 66 (2006) 275–285.
[25] Y.S. Ho, G. McKay, The kinetics of sorption of divalentmetal ions onto sphagnum moss peat, Water Res. 34 (2000) 735–742.
[26] M. Yurdakoc, Y. Scki, S.K. Yuedakoc, Kinetic and thermodynamic studies of boron removal by Siral 5, Siral 40, and Srial 80, J. Colloid Interface Sci. 286 (2005) 440–446.
[27] F.C. Wu, R.L. Tseng, R.S. Juang, Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan, Water Res. 35 (2001) 613–618.
[28] W.S.W. Nagh, S.A. Ghani, A. Kamari, Adsorption behavior of Fe (II) and Fe (III) ions in aqueous solution on chitosan and crosslinked chitosan beads, Bioresour. Technol. 96 (2005) 443–450.
[29] Y. Sag, Y. Aktay, Kinetic studies on sorption of Cr(VI) and Cu(II) ions by chitin, chitosan and Rhizopus arrhizus, Biochem. Eng. J. 12 (2002) 143–153.
[30] E. Guibal, O.S.N. Von, T. Vincent, J.M. Tobin, Sulfur-derivatives of chitosan for palladium soption, React. Funct. Polym. 50 (2002) 149–163.
[31] A. Ramesh, H. Hasegawa, W. Sugimoto, T. Maki, K. Ueda, Adsorption of gold(III), platinum(IV) and palladium(II) onto glycine modified crosslinked chitosan resin, Bioresour. Technol. 99 (2008) 3801–3809.
[32] A. Uheida, M. Iglesias, C. Fontas, M. Hidalgo, V. Salvado, Y. Zhang, M. Muhammed, Sorption of palladium(II), rhodium(III), and platinum(IV) on Fe$_3$O$_4$ nanoparticles, J. Colloid. Interface Sci. 301 (2006) 402–408.
[33] P. Durga, K. Hidetaka, I. Katsutoshi, F. Masamitsu, Recovery of gold(III), palladium(II), and platinum(IV) by aminated lignin derivatives, Ind. Eng. Chem. Res. 45 (2006) 6405–6412.

[34] C. Park, J.S. Chung, K.W. Cha, Separation and preconcentration method for palladium, platinum and gold from some heavy metals using Amberlite IRC 718 chelating Resin, Bull. Korean Chem. Soc. 21 (2000) 121–124.

[35] D. Jermakowicz-Bartkowiak, B.N. Kolarz, A. Serwin, Sorption of precious metals from acid solutions by functionalised vinylbenzyl chloride–acrylonitryle–divinylbenzene copolymers bearing amino and guanidine ligands, React. Funct. Polym. 65 (2005) 135–142.

[36] P.K. Malik, Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics, J. Hazard. Mater. 113 (2004) 81–88.

[37] A. Atia, A.M. Donia, H.A. El-Boraey, D.H. Mabrouk, Adsorption of Ag(I) on glycidyl methacrylate/N,N-methylene bis-acrylamide chelating resins with embedded iron oxide, Sep. Purif. Technol. 48 (2006) 281–287.