

Adsorption of platinum(IV) and palladium(II) from aqueous solution by magnetic cross-linking chitosan nanoparticles modified with ethylenediamine

Limin Zhou^{a,b,*}, Jianping Xu^a, Xizhen Liang^a, Zhirong Liu^b

^a Key Laboratory of Nuclear Resources and Environment (Ministry of Education), East China Institute of Technology, Fuzhou, Jiangxi 344000, PR China

^b Key Laboratory of Radioactive Geology and Exploration Technology Fundamental Science for National Defense, East China Institute of Technology, Fuzhou, Jiangxi 344000, PR China

ARTICLE INFO

Article history:

Received 27 January 2010

Received in revised form 2 May 2010

Accepted 15 June 2010

Available online 19 June 2010

Keywords:

Magnetic nanoadsorbents

Chitosan

Ethylenediamine

Adsorption

Platinum(IV)

Palladium(II)

ABSTRACT

The adsorption characteristics of platinum(IV) and palladium(II) from aqueous solutions onto the ethylenediamine-modified magnetic chitosan nanoparticles (EMCN) have been investigated. The magnetic chitosan nanoparticles were prepared by adding the basic precipitant of NaOH solution into a W/O microemulsion system. The transmission electron microscope showed that the diameter of EMCN was from 15 to 40 nm. The adsorption experiments indicated that the maximum adsorption capacity occurred at around pH 2.0 for both Pt(IV) and Pd(II). Due to the small diameter and the high surface reactivity, the adsorption equilibrium of Pt(IV) and Pd(II) onto the EMCN reached very quickly. The maximum loading capacity of EMCN for Pt(IV) and Pd(II) was determined to be 171 and 138 mg/g, respectively. Sorption isotherms were determined both in single component with pure metal solutions and bicomponent systems with different Pd/Pt mass ratios. The results showed that the sorbents had a greater affinity for Pt(IV) than for Pd(II). The total sorption capacity was comparable to that of each metal individually, indicating that the metals compete for the same sorption sites. It was found that 0.4 M HNO₃–1.0 M thiourea solution provided effectiveness of the desorption of Pt(IV) and Pd(II) from EMCN, while 5 M ammonia exhibited the highest selectivity for the tested metal ions.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The increasing demand for the platinum group metals (PGMs) for production of catalysts and in related industries, combined with the limited resources available, has led to increasing interest in the recovery of these strategic elements [1,2]. Separation of these metal ions is still problematic and, because of their complex chemistry and the overlapping properties, represents a real challenge. The conventional methods for the separation of metal ions from aqueous solution include solvent extraction, oxidation, reduction, precipitation, membrane filtration, ion-exchange and adsorption [3–5]. Among the all above methods adsorption is highly effective and economical.

Chitosan is an *N*-deacetylated derivative of chitin, a cationic polysaccharide composed of β -D-glucosamine and acetyl- β -D-glucosamine residues with a 1,4 linkage [6]. Chitosan has been reported to be a suitable biopolymer for the removal of metal ions from aqueous solution [5–9], since the amino and hydroxyl groups

present on chitosan can act as chelation sites. It is noteworthy that metal adsorption may involve different mechanisms (chelation versus electrostatic attraction), depending on solution composition, pH, and speciation of the metal ions [6].

Chitosan beads and chitosan-inorganic composites for the adsorption of metal ions were usually prepared by crosslinking the amine groups on chitosan with glutaraldehyde [8–10]. They were submicron to micron-sized and need large internal porosities to ensure adequate surface area for adsorption. However, the diffusion limitation within the particles led to the decreases in the adsorption rate and available capacity. Compared to the traditional micron-sized supports used in separation process, nano-sized adsorbents possess quite good performance due to high specific surface area and the absence of internal diffusion resistance [11,12]. However, the nano-adsorbents could not be separated easily from aqueous solution by filtration or centrifugation. Magnetic nano-adsorbents can be manipulated by an external magnetic field and hence be ease of phase separation.

Numerous types of magnetic nanoparticles have been reported for metals ions removal [11–15]. Chang et al. [11,12] reported chitosan-bound Fe₃O₄ magnetic nanoparticles for removal of Cu(II) and Co(II) ions. Hu et al. [13] employed δ -FeOOH-coated maghemite as adsorption material for the removal and recovery of Cr(VI) from

* Corresponding author. Tel.: +86 794 8829625; fax: +86 794 8258320.

E-mail addresses: minglzh@sohu.com, minglzh@shou.com (L. Zhou).

wastewater, Banerjee et al. [14] also utilized gum Arabic modified magnetic nano-adsorbent to do that. And Ngomsik et al. [15] reported the removal of nickel ions from aqueous solution by magnetic alginate microcapsules. 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. Several chelating ligands such as thiourea [7], thiocarbonyl [16], crown ethers [17], and L-lysine [18] were used to functionalize the crosslinked chitosan for adsorption of metal ions. Although there are reports on the effectiveness of the magnetic chitosan on the removal of metal ions [11,12,19], the ethylenediamine-modified magnetic chitosan nano-adsorbent and the potential effectiveness of the adsorbent for the adsorption of Pt(IV) and Pd(II) have not been discussed.

In the present work, the magnetic cross-linking chitosan nanoparticles were prepared and then modified with ethylenediamine (EMCN). The high content of amine groups makes possible chemical modification in chitosan with the purpose of improving its features as an adsorbent, such as selectivity and adsorption capacity. The adsorption behavior of the EMCN toward Pt(IV) and Pd(II) was studied. Sorption isotherms were established for both single-component and bicomponent metal solutions with different initial mass ratios Pd/Pt in batch systems. This study also focuses on the study of Pt(IV) and Pd(II) desorption by various eluants.

2. Experimental

2.1. Chemicals and reagents

Chitosan (CTS) with 40 mesh, 90% degree of deacetylation and molecular weight of 1.3×10^5 was purchased from Yuhuan Ocean Biology Company (Zhejiang, China). Glutaraldehyde, epichlorohydrin, and ethylenediamine were Aldrich products and were used as received. All the other reagents used in this work were of analytical grade. 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 magnetic chitosan nanoparticles (MCN)

Firstly, chitosan solution was prepared by dissolving 1.5 g of chitosan powder in 100 mL of 0.5 mol/L hydrochloric acid. Cyclohexane (82.5 mL), *n*-hexanol (45 mL), hydrochloric acid (HCl) solution containing chitosan (12 mL), and 0.1 mol/L ferrous salt solutions (12 mL) were mixed in a flask. The microemulsion was formed by adding Triton X-100 into the mixture while stirring until the mixed emulsion became transparent or semi-transparent. Secondly, under the protection of nitrogen and controlled flow of oxygen (0.5%, v/v), 10 mL of 5 mol/L NaOH solution was quickly added into the W/O microemulsion with chitosan and ferrous salt under stirring to react with HCl, $Fe(OH)_2$ and the chitosan were precipitated with the increase of pH. Then the magnetization process demands the presence of an extremely low concentration of dissolved oxygen which oxidize $Fe(OH)_2$ to Fe_3O_4 without forming essentially magnetic $Fe(OH)_3$. To activate Fe_3O_4 to get better magnetic properties, the reaction systems were kept at 333 K for 2 h in a water bath. The cross-linked magnetic chitosan nanoparticles were formed by adding 2 mL of microemulsion containing glutaraldehyde and by keeping the same condition for 2 h. After reaction, the magnetic nanoparticles was precipitated with centrifugation (4000 rpm for 20 min) at room temperature, and rinsed with ethanol and deionized water for three times. Finally, the

prepared nanoparticles were dried in a vacuum oven for about 24 h.

2.3. Modification of magnetic chitosan nanoparticles with ethylenediamine

Grafting of ethylenediamine using epichlorohydrin as a crosslinking agent was carried out similar to the procedure described by Atia [20] with chitosan resin. The magnetic chitosan nanoparticles (2.5 g) were suspended in 35 mL isopropyl alcohol to which 2.5 mL epichlorohydrin (31.25 mmol) dissolved in 50 mL acetone/water mixture (1:1, v/v) was added. The contents were stirred for 24 h at 333 K. The solid (labeled as MCN1) was isolated, and washed several times with ethanol followed by water.

MCN1 obtained were suspended in 50 mL ethanol/water mixture (1:1, v/v), then ethylenediamine (2.5 mL) was added. The reaction mixture was stirred at 333 K for 12 h, then the solid products (ethylenediamine-modified magnetic chitosan nanoparticles, EMCN) were isolated and washed with ethanol followed by water, and finally dried in a vacuum oven at 333 K.

2.4. Characterizations of the magnetic chitosan nanoparticles

The dimension and morphology of EMCN were observed by transmission electron microscopy (TEM) (Hitachi, H-800). X-ray diffraction (XRD) data were collected on a XRD-2000 X-ray diffractometer with $Cu K\alpha$ radiation. FTIR spectra was measured on a Nicolet, Magna-550 spectrometer. A background spectrum was measured on pure KBr. The concentration of the amine active sites in the obtained resins was estimated using the volumetric method [21]: 20 mL of HNO_3 (0.05 M) solution was added to 0.1 g resin and conditioned for 1 h on a shaker. The residual concentration of HNO_3 was measured through titration against 0.05 M NaOH. The number of moles of HNO_3 that interacted with the N atoms was determined and consequently the active sites concentration was calculated. Thermal gravimetric analysis of EMCN was conducted on Shimadzu TGA-50H with heating rate of 10 K/min in the nitrogen flow.

2.5. Metal adsorption–desorption experiments

2.5.1. Effect of pH

Uptake experiments were performed at controlled pH and 298 K by shaking 50 mg of EMCN with 100 mL (60 mg/L) metal ion solution for 1 h at 150 rpm. The solution pH was adjusted to the desired value by adding either nitric acid or sodium hydroxide standardized solutions. After mixing, the aqueous phase was separated from the solid phase by magnetic settlement and centrifugation at 12,000 rpm. The amount of metal ions in the supernatant was determined. And the concentration of Pt(IV) and Pd(II) in aqueous solutions were analyzed using Inductively Coupled Plasma (ICP, ARL-340, ICP-AES Fison Instruments).

2.5.2. Effect of contact time

The experiments were conducted by shaking 150 mg EMCN with 300 mL (60 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. Five 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.

2.5.3. Adsorption isotherms

The effect of initial concentration of the metal ion on the uptake by EMCN obtained was carried out by placing 50 mg EMCN in a series of flasks containing 100 mL of metal ions at definite concentrations and pH 2.0. The initial concentrations of metal ions for the

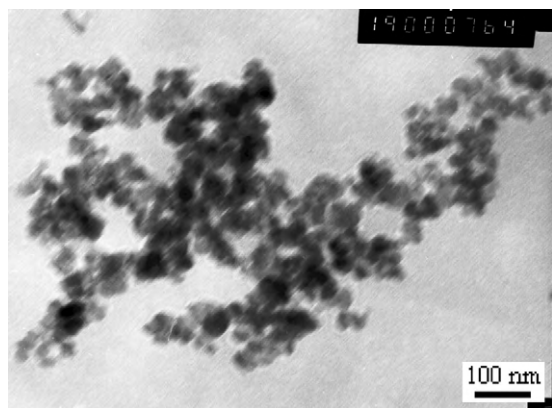


Fig. 1. TEM micrographs for EMCN, the bar is 100 nm.

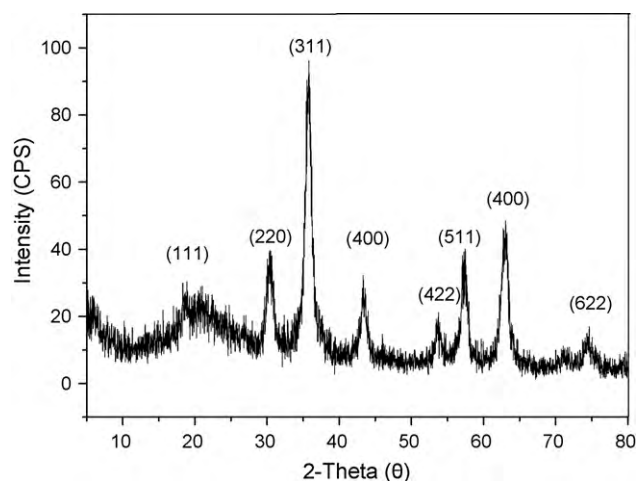


Fig. 2. XRD patterns for EMCN.

single-component experiments were 30–120 mg/L, while those for bicomponent experiments with different mass ratios (Pd/Pt) were: 10–40 Pd mg/L and 20–80 Pt mg/L (Pd/Pt = 1:2); 15–60 Pd mg/L and 15–60 Pt mg/L (Pd/Pt = 1:1); and 20–80 Pd mg/L and 10–40 Pt mg/L (Pd/Pt = 2:1). The flasks were agitated on a shaker at 150 rpm and 298 K for 1 h. After adsorption, the residual concentration of the metal ions in the solution was determined. The amount of metal adsorbed per unit of sorbent mass calculated by the mass balance equation.

2.5.4. Desorption of precious metals and reuse

Batch desorption experiments were carried out using 0.4 M HNO₃, 5 M NH₄OH, 1 M thiourea, and 0.4 M HNO₃–1.0 M thiourea. The adsorbed precious metal ions onto EMCN were washed with deionized water several times and transferred into stoppered reagent bottles. To these 30 mL of the desorption agent was added, and then the bottles were shaken at 298 K using mechanical shaker for 2 h. The concentration of precious metal ion released from the EMCN into aqueous phase was analyzed by ICP-AES. To investigate the reusability of the adsorbents, the EMCN after desorption was reused in adsorption experiment and the process was repeated for five times. In this process, the metal-loaded EMCN was desorbed by 0.4 M HNO₃–1.0 M thiourea for the single-component experiments (initial metal concentration for adsorption: 120 mg/L); and by the combination of successive treatments of 5 M ammonia and 0.4 M HNO₃–1.0 M thiourea for the bicomponent experiments (initial metal concentration for adsorption: 60 Pd mg/L and 60 Pt mg/L).

3. Results and discussion

3.1. Characterization of EMCN

The TEM micrograph for EMCN is shown in Fig. 1. It can be observed that EMCN were essentially monodispersed and had a particle size distribution of 15–40 nm. It is found that when a magnet with a surface magnetization of 3000 G was near the bottle, the chitosan nanoparticles suspended in the solution was aggregate within 1–2 min, which indicated that the nanoparticles have good magnetic properties and were easily and quickly separated from the solution by a magnetic field.

Fig. 2 shows the XRD patterns for EMCN. Eight characteristic peaks for Fe₃O₄ marked by their indices ((111), (220), (311), (400), (422), (511), (440), and (622)) were observed for the sample. These peaks are consistent with the database in JCPDS file (PDF No. 65-3107) and reveal that the resultant nanoparticles are pure Fe₃O₄ with a spinel structure.

Fig. 3 shows the FTIR spectra of EMCN and MCN, The peaks at 560–660 cm⁻¹ were assigned to Fe–O bond vibration of Fe₃O₄. The

carbonyl bands at around 1630 cm⁻¹ indicate that chitosan reacts with glutaraldehyde to form Schiff base. The absorption bands at 1598 cm⁻¹ and 1456 cm⁻¹ can be assigned to δNH and νCN, respectively. The increase of absorption intensity of peak at 2920 cm⁻¹ for EMCN compared to MCN should be attributed to the introduction of C–H in epichlorohydrine in synthesis of EMCN. The concentration of the amine active sites of MCN and EMCN was determined to be 2.4 and 3.8 mmol/g, respectively. These results indicated that the MCN was crosslinked and modified with ethylenediamine successfully.

The pyrolysis of chitosan occurred at high temperature, but Fe₃O₄ did not decompose under the N₂-protection atmosphere; therefore, the amount of Fe₃O₄ can be determined by thermogravimetric analysis (TGA). The average mass content of Fe₃O₄ in nanoparticles by TGA was about 33.5%, as calculated from the TGA data at 873 K.

3.2. The effect of pH

The influence of pH on the adsorption of Pt(IV) and Pd(II) by EMCN is shown in Fig. 4. The figure demonstrated that the maximum adsorption percentage occurred at around pH 2.0 for both Pt(IV) and Pd(II). With increasing pH, the adsorption percentage of metal ions increases at pH < 2.0 but decreases at pH > 3.0.

Metal ion sorption on chitosan is assumed to occur through several single or mixed mechanisms including: (a) coordination on amino groups in a pendant fashion or in combination with vici-

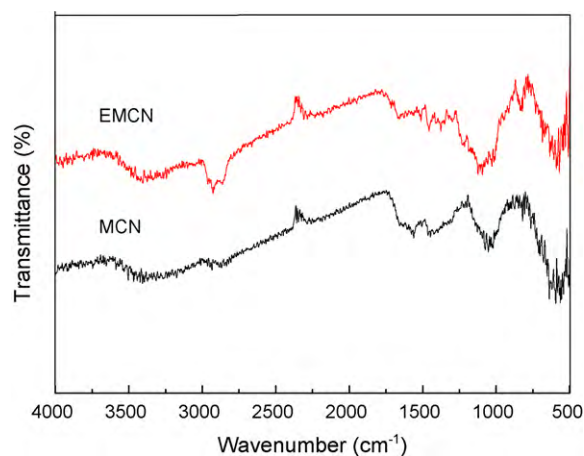


Fig. 3. FTIR spectra of magnetic chitosan nanoparticles before (MCN) and after (EMCN) modification with ethylenediamine.

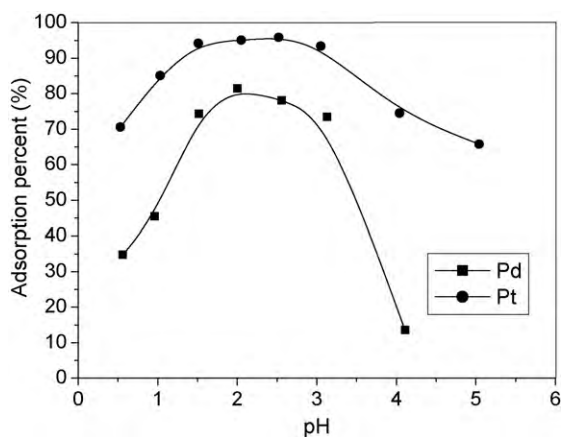
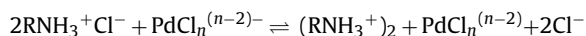
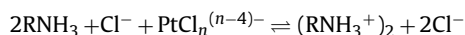
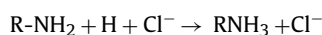


Fig. 4. Effect of pH on the uptake of Pt(IV) and Pd(II) by EMCN (initial concentration 60 mg/L, EMCN 0.5 g/L, contact time 1 h, shaking rate 150 rpm, 298 K).

nal hydroxyl groups, (b) electrostatic attraction (in acidic media), and (c) ion exchange with protonated amino groups through proton exchange or anion exchange, the counter ion being exchanged with the metal anion [6]. The nature of the reaction depends on several parameters related to the sorbent (ionic charge), to the solution (pH) and the chemistry of the metal ion: ionic charge, ability to be hydrolyzed and to form polynuclear species. The point of zero charge for EMCN was found to be 4.8 using standard potentiometric method. Therefore, the surface charge of EMCN was positively charged at $\text{pH} < 4.8$. It appears that around $\text{pH} 2\text{--}3$, most of the amino groups are protonated.

The speciation of Pt(IV) and Pd(II) depends on both pH and chloride concentrations. At low pH, platinum and palladium are usually present in solution in its most stable form, i.e., Pt(IV) and Pd(II). They can form stable complexes especially with amino group chelation sites of EMCN, due to their characteristics of soft acid. Moreover, with Pt(IV) and Pd(II) being provided as K_2PtCl_6 and PdCl_2 in this study, the amount of chloride in the solution is high enough to favor the formation of chloro-anionic species ($\text{PtCl}_n^{(n-4)-}$ or $\text{PdCl}_n^{(n-2)-}$) that will be adsorbed on protonated amine groups of EMCN [18]. The protonation of amine groups on the EMCN induced an electrostatic attraction of anionic metal complexes and increased the number of available binding sites for precious metal ions uptake. In the presence of chloride ions, the interaction between metal anions and active sites of the EMCN are shown as follows:



At lower pH, the excess of NO_3^- anions from HNO_3 (used for adjusting pH) involves competition between the PGMs chlorocomplexes and the counter anions for the sorption on protonated sites. Increasing the pH results in a decrease of this competition and the predominance of species more favorable for sorption around pH 2.0. At higher pH values decrease the sorption percentage may be explained by the presence of less-adsorbable PGMs species such as hydroxyl complexes.

3.3. The effect of contact time

Fig. 5 shows the effect of contact time on the adsorption capacity (q_e , mg/g) of Pt(IV) and Pd(II) by EMCN. The results demonstrate that the adsorption for both metal ions is rapid. In the case of Pt(IV), the maximum adsorption is attained in 20 min, while for Pd(II) it

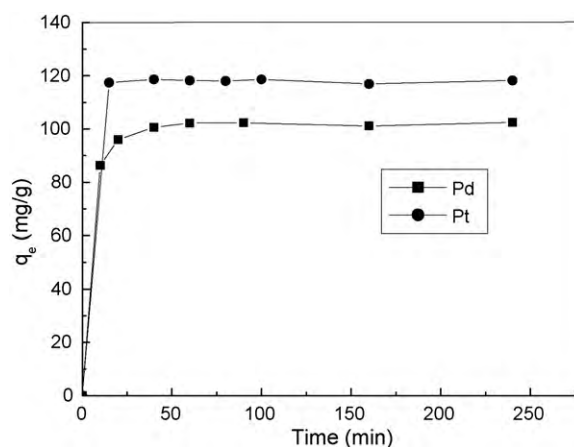


Fig. 5. Effect of adsorption time on the uptake of Pt(IV) and Pd(II) by EMCN (initial concentration 60 mg/L, solution pH 2.0, EMCN 0.5 g/L, shaking rate 150 rpm, 298 K).

takes 40 min, after which the change in the removal percentage is insignificant. The contact time of 1 h was found to be sufficient to reach equilibrium, and so it was selected in further experiments.

It was reported that a long time is needed to attain equilibrium for PGMs with several ion exchangers, such as crosslinked chitosan resin [18] and magnetic chelating resins [22]. Moreover, with metal oxides such as Al_2O_3 , the equilibrium time was reported to be several hours [23]. In contrast, in the present study, Pt(IV) and Pd(II) are extracted in a short time. This can be attributed to the large surface area and the high surface reactivity of the magnetic chitosan nanoparticles.

Furthermore, the effect of contact time on the adsorption of Pt(IV) and Pd(II) existing in a mixture was also studied under similar experimental conditions for individual metal ions (not shown). It was found that equilibrium is reached very fast (<1 h) for both metals within the mixture, as observed in individual studies. The results indicate that the adsorption capacity of Pt(IV) is the higher, while Pd(II) shows lower affinity toward EMCN. The decrease in adsorption of Pt(IV) and Pd(II) when contained in a mixture as compared to individual studies can be explained by the competence of the affinity of the two metal chlorocomplexes toward the active sites on the surface of the EMCN. It can be concluded that EMCN have greater affinity for Pt(IV) than for Pd(II).

3.4. Sorption isotherms

Experiments were performed using both single-component and bicomponent solutions with different mass ratios of Pd/Pt at pH 2.0, with the objective to determine if EMCN have a preference for one of the target metals. Fig. 6 shows that EMCN have a greater affinity for Pt(IV) than for Pd(II). With increasing Pd/Pt mass ratio, the sorption capacity for Pd(II) increases but that for Pt(IV) decreases. On the other hand, the isotherms of Pd(II) were more strongly effected by Pd/Pt mass ratio compared to those of Pt(IV). However, EMCN adsorbents are not able to selectively remove one of these metals (Fig. 6). The isotherms for both Pt(IV) and Pd(II) were characterized by the formation of a plateau of the typical shape of the Langmuir Type I model used for the description of sorption isotherms.

The maximum loading capacity (q_m) of Pt(IV) and Pd(II) for the single-component adsorption was determined to be 171 and 138 mg/g. The q_m values of the unmodified chitosan magnetic nanoparticles (MCN) obtained at 298 K and in the same other conditions as in EMCN for Pt(IV) and Pd(II) are 128 and 112 mg/g, respectively, which are lower than those of EMCN. The higher maximum adsorption capacity obtained for EMCN is because of the fact that the incorporation of ethylenediamine in MCN produces

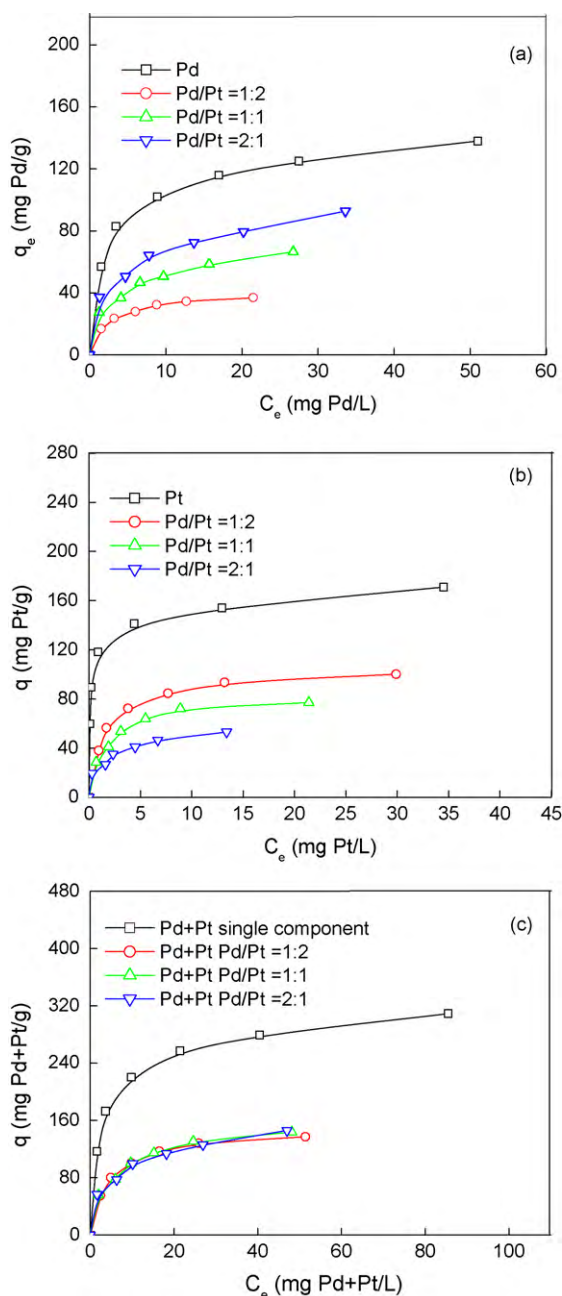


Fig. 6. (a) Pd, (b) Pt sorption isotherms, and (c) combined sorption isotherms for Pd and Pt (total Pd+Pt sorption capacity versus residual combined Pd and Pt residual concentrations) in the single-metal and bicomponent solutions with different initial mass Pd/Pt ratios for EMCN (solution pH 2, EMCN 0.5 g/L, shaking rate 150 rpm, 298 K).

more amine groups to interact with Pt(IV) and Pd(II) ions, which enhances the adsorption capacity.

The differences observed in the case of Pt(IV) and Pd(II) sorption may be explained by the difference in the affinity of the sorbents toward them and the speciation of the metals. Related to the differences in Pt(IV) and Pd(II) chemistries, the distribution of palladium species may be affected by the excess of platinum. The formation of chloro-platinum species diminished the number of chloride ions available for the formation of palladate chloro-anionic species, resulting in a decrease of Pd(II) sorption (Fig. 6(a)). This mechanism explains the decrease in the sorption of palladium in the presence of platinum. The similar behavior were found for platinum adsorption

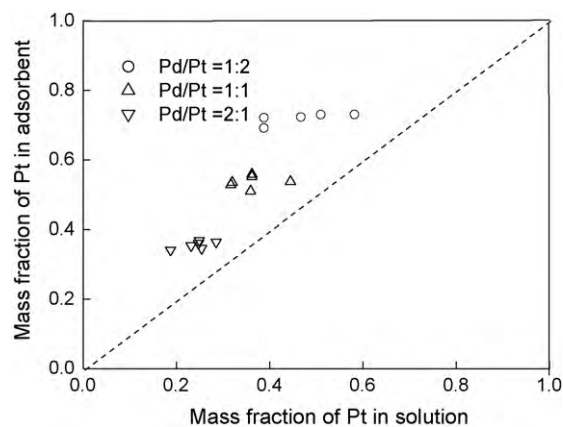


Fig. 7. Plots of mass fraction of Pt(IV) on the sorbent versus its mass fraction in the solution at equilibrium at pH 2 for EMCN.

from the bicomponent mixtures in the presence of palladium (Fig. 6(b)).

In competition tests, it was apparent that the sorption capacity for one metal was strongly decreased in the presence of the competitor metal. EMCN exhibited a greater sorption capacity and a marked preference for Pt(IV). Fig. 6(c) shows that the combined sorption capacity (addition of Pt(IV) and Pd(II) sorption capacities) was minimally affected by the composition of the initial solution (Pd/Pt mass ratio). Moreover, the combined sorption capacities were substantially lower (almost halved) compared to those obtained by the addition of sorption capacities using single-component solutions. These results indicate that Pt(IV) and Pd(II) compete for the same sorption sites. Decreasing the number of available sorption sites for one metal in presence of the other in the mixture solution may partly explain these results.

Fig. 7 shows the variation of platinum mass fraction in the sorbent in function of the mass ratio in solution at equilibrium, as an indication of the selective concentration effect of the sorbent. At low mass fraction of platinum in the solution, the mass fraction on the sorbent is about two times the equilibrium mass fraction in the liquid phase. At higher platinum fraction in the solution, the concentration effect is less apparent. This confirms the adsorption preference of the EMCN for Pt(IV) over Pd(II).

3.5. Desorption of precious metals, and reuse after desorption

Metal desorption was attempted using various eluants as shown in Table 1. Compared to Pt(IV), Pd(II) was rather easily desorbed from loaded sorbents using 0.4 M HNO₃ and 5 M NH₄OH: 23.2–84.2% of Pd(II) versus only 10.5–26.8% of Pt(IV). This finding indicates that pH has a more significant effect on the adsorption–desorption process for Pd(II) than that for Pt(IV). HCl could not be used as an eluent solution because it has a much higher rate of dissolution of Fe₃O₄, which is the magnetic component of the EMCN. Thiourea was known as a very strong chelating agent for many metals, and was proposed to replace the active groups on the EMCN and preferentially complex with PGMs. It can be seen from Table 1 that 1.0 M thiourea is efficient for desorption of both Pt(IV) and Pd(II) (desorption percent > 78%). However, 0.4 M HNO₃–1.0 M thiourea revealed to be the most efficient eluants, reaching metal desorption in the range 86.6–97.3%. The high percentage of desorption using 0.4 M HNO₃–1.0 M thiourea 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, which would weaken the interaction between the adsorbent and precious metal ions, promoting desorption.

Table 1
Recovery percentage of the metal ions obtained using different eluants.

	Single-component solution recovery (%)		Bicomponent solution recovery (%)					
	Pd	Pt	Pd–Pt (1:2) ^a		Pd–Pt (1:1) ^a		Pd–Pt (2:1) ^a	
			Pd	Pt	Pd	Pt	Pd	Pt
Metal concentrations (mg/L)	120	120	40	80	60	60	80	40
Eluants	Desorption efficiency (%)		Bicomponent solution recovery (%)					
	Pd	Pt	Pd–Pt (1:2) ^a		Pd–Pt (1:1) ^a		Pd–Pt (2:1) ^a	
			Pd	Pt	Pd	Pt	Pd	Pt
0.4 M HNO ₃	25.6	11.8	23.2	10.5	25.2	12.2	26.3	11.6
5 M NH ₄ OH	82.2	25.9	78.4	17.3	84.2	21.5	78.4	26.8
1.0 M thiourea	92.2	82.2	87.4	81.2	90.6	78.6	85.4	83.5
0.4 M HNO ₃ –1.0 M thiourea	97.3	90.5	94.5	87.1	96.3	86.6	93.8	89.6
5 M NH ₄ OH+0.4 M HNO ₃ –1.0 M thiourea ^b	–	–	–	–	98.6	91.5	–	–

^a Mass ratio of Pd/Pt.

^b The combination of successive treatments of 5 M ammonia and 0.4 M HNO₃–1.0 M thiourea.

As shown in Table 1, the highest selectivity was observed with 5 M ammonia. The separation of Pt(IV) and Pd(II) from each other could be accomplished by taking advantage of their different elution behavior and using a two-step elution sequence: the first step with 5 M ammonia to elute Pd(II), and the second one with 0.4 M HNO₃–1.0 M thiourea to elute the remaining metals, mostly Pt(IV). Table 1 showed that the efficient desorption of both Pt(IV) and Pd(II) (desorption percent >91%) was achieved by using this procedure.

The stability and the potential regeneration of the adsorbent were also investigated. The results showed that the adsorption capacities of the EMCN for both metals could still be maintained at over 90% level in the 5th adsorption/desorption cycle for both single-component and bicomponent experiments, indicating that no appreciable loss in activity over at least five cycles. It is noteworthy that an average of 0.8–1.0 wt.% of Fe₃O₄ on EMCN were dissolved after each cycle. The results of thermogravimetric tests showed that the average mass content of Fe₃O₄ on EMCN decreased from 33.5% before adsorption to 28.4–29.6% after five cycles. However, the EMCN after being used for five cycles could still be aggregated very fast from the solution by a 3000 G magnet. These results indicated that EMCN was stable and could be potentially applied for the recovery of Pt(IV) and Pd(II) from aqueous solution.

4. Conclusions

The present studies have demonstrated that EMCN can be used for the effective adsorption of Pt(IV) and Pd(II) from aqueous solution. The interest in using magnetic chitosan nanoparticles for removal or recovery of PGMs from aqueous solutions is related to their unique characteristics, such as very large surface area and high surface reactivity. In addition, magnetic chitosan nanoparticles offer added capability and selective adsorption properties with ease of phase separation. Therefore, the problem of phase separation associated with conventional separation techniques can be resolved.

Furthermore, the low particle-mass-to-solution ratio allows the process to compete with more traditional separation techniques, such as solvent extraction and ion exchange. EMCN nanoparticles exhibit good kinetic characteristics (equilibrium time < 1 h) and high adsorption loading capacities for Pt(IV) and Pd(II) at pH 2 (i.e., 171 and 138 mg/g, respectively). The ethylenediamine-modified chitosan magnetic nanoparticles showed good improvements in the uptake properties of Pt(IV) and Pd(II) compared to unmodified ones.

The EMCN exhibited the maximum adsorption capacity at around pH 2.0 for both Pt(IV) and Pd(II). Moreover, The EMCN have a greater affinity for Pt(IV) than for Pd(II), both in pure and bicomponent solutions. Pt(IV) and Pd(II) compete for the same sorption sites, thus the sorption capacity for one metal was strongly decreased in the presence of the competitor metal. The separation of Pt(IV) and Pd(II) from each other from loaded EMCN sorbent may be accomplished by using 5 M ammonia to elute Pd(II) and then 0.4 M HNO₃–1.0 M thiourea to elute the remaining metals. In addition, EMCN was found to be stable and have good resuability with no appreciable loss in activity over five cycles.

Acknowledgments

This work was supported by the Science & Technology Pillar Program of Jiangxi, China (No. 2009BSB08600), and the scientific research fund from the Education Bureau of Jiangxi, China (No. GJJ10494).

References

- [1] T. Kang, Y. Park, J.C. Park, Y.S. Cho, J. Yi, Functionalized mesoporous adsorbents for Pt(II) and Pd(II) adsorption from dilute aqueous solution, *Stud. Surf. Sci. Catal.* 146 (2003) 527–530.
- [2] E. Renbutsu, S. Okabe, Y. Omura, F. Nakatsubo, S. Minami, H. Saimoto, Y. Shigemasu, Synthesis of UV-curable chitosan derivatives and palladium (II) adsorption behavior on their UV-exposed films, *Carbohydr. Polym.* 69 (2007) 697–706.
- [3] 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.
- [4] A. Hulanicki, Ion exchange preconcentration and separation of trace amounts of platinum and palladium, *Anal. Lett.* 33 (2000) 2805–2820.
- [5] M. Ruiz, A.M. Sastre, E. Guibal, Palladium sorption on glutaraldehyde crosslinked chitosan, *React. Funct. Polym.* 45 (2000) 155–173.
- [6] E. Guibal, Interactions of metal ions with chitosan-based sorbents: a review, *Sep. Purif. Technol.* 38 (2004) 43–74.
- [7] L.M. Zhou, J.H. Liu, Z.R. Liu, Adsorption of platinum (IV) and palladium (II) from aqueous solution by thiourea-modified chitosan microspheres, *J. Hazard. Mater.* 172 (2009) 439–446.
- [8] P. Baroni, R.S. Vieira, E. Meneghetti, M.G. Silva, M.M. Beppu, Evaluation of batch adsorption of chromium ions on natural and crosslinked chitosan membranes, *J. Hazard. Mater.* 152 (2008) 1155–1163.
- [9] R.S. Vieira, M.M. Beppu, Dynamic and static adsorption and desorption of Hg (II) ions on chitosan membranes and spheres, *Water Res.* 40 (2006) 1726–1734.
- [10] P. Miretzky, A.F. Cirelli, Hg (II) removal from water by chitosan and chitosan derivatives: a review, *J. Hazard. Mater.* 167 (2009) 10–23.
- [11] Y.C. Chang, S.W. Chang, D.H. Chen, Magnetic chitosan nanoparticles: studies on chitosan binding and adsorption of Co (II) ions, *React. Funct. Polym.* 66 (2006) 335–341.
- [12] Y.C. Chang, D.H. Chen, Preparation and adsorption properties of monodisperse chitosan-bound Fe₃O₄ magnetic nanoparticles for removal of Cu (II) ions, *J. Colloid Interf. Sci.* 283 (2005) 446–451.

- [13] J. Hu, M.C. Lo, G.H. Chen, Performance and mechanism of chromate (VI) adsorption by δ -FeOOH-coated maghemite (γ -Fe₂O₃) nanoparticles, *Sep. Purif. Technol.* 58 (2007) 76–82.
- [14] S.S. Banerjee, D.H. Chen, Fast removal of copper ions by gum Arabic modified magnetic nano-adsorbent, *J. Hazard. Mater.* 147 (2007) 792–799.
- [15] A.F. Ngomsik, A. Bee, J.M. Siaugue, V. Cabuil, G. Cote, Nickel adsorption by magnetic alginate microcapsules containing an extractant, *Water Res.* 40 (2006) 1848–1856.
- [16] 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.
- [17] 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.
- [18] 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.
- [19] A.M. Donia, A.A. Atia, K.Z. Elwakeel, Selective separation of mercury (II) using magnetic chitosan resin modified with Schiff's base derived from thiourea and glutaraldehyde, *J. Hazard. Mater.* 151 (2008) 372–379.
- [20] A.A. Atia, Studies on the interaction of mercury (II) and uranyl (II) with modified chitosan resins, *Hydrometallurgy* 80 (2005) 13–22.
- [21] G.A. Latha, K.B. George, G.K. Kannan, N.K. Ninan, Synthesis of a polyacrylamide chelating resin and applications in metal ion extractions, *J. Appl. Polym. Sci.* 43 (1991) 1159–1163.
- [22] C. Zhang, X. Li, J. Pang, Synthesis and adsorption properties of magnetic resin microbeads with amine and mercaptan as chelating groups, *J. Appl. Polym. Sci.* 82 (2001) 1587–1592.
- [23] D. Spielbauer, H. Zeilinger, H. Knözinger, Adsorption of palladium-ammino-aquo-complexes on gamma-alumina and silica, *Langmuir* 9 (1993) 460–466.