Synthesis of Chemically Modified Chitosan with 2,5-Dimercapto-1,3,4-thiodiazole and Its Adsorption Abilities for Au(III), Pd(II), and Pt(IV)

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ABSTRACT: A new chemically modified chitosan hydrogel with 2,5-dimercapto-1,3,4-thiodiazole (CTS-DMTD) has been synthesized. The structure of CTS-DMTD was confirmed by elemental analysis and FTIR. It was found that adsorption capacities were significantly affected by the pH of solution, with optimum pH values of 3.0 for Au(III), 2.0 for Pd(II) and Pt(IV). The saturated adsorption capacities were 198.5 mg/g for Au(III), 16.2 and 13.8 mg/g for Pd(II) and Pt(IV), respectively. Langmuir and Freundlich isotherm adsorption models were applied to analyze the experimental data. The results showed that adsorption isotherms of Pd(II) and Pt(IV) could be well described by the Langmuir equation. The adsorption kinetic investigations indicated that the kinetic data correlated well with the pseudo-second-order model. The recovery experimental data showed that CTS-DMTD had a higher affinity toward Au(III), Pd(II), and Pt(IV) in the coexistence system containing Cu(II), Fe(III), Cd(II), Ni(II), Mg(II), and Zn(II). The studies of desorption were carried out using various reagents and the optimum effect was obtained using thiourea. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1604–1610, 2009

Key words: heteroatom-containing polymers; chitosan; synthesis; adsorption

INTRODUCTION

Precious metals find varied applications in many different fields such as jewelry, electronics, glass-making equipment, electrode coatings, temperature sensors, dental alloys and especially automobile industry for some unique physical and chemical characteristics. Thus, in recent years there is a growing demand for them. Accordingly, recent research has been focused on analytical techniques toward precious metals recovery from industrial wastewaters as alternative. The conventional methods for the removal of metal ions from aqueous solution included oxidation, reduction, precipitation, membrane filtration, ion-exchange and adsorption. Among all the above methods adsorption was highly effective and economical.[1]

Chitosan, (1→4)-2-amino-2-acetamido-2-deoxy-β-D-glucan is obtained from partial N-deacetylation of chitin with a strong alkali solution such as sodium hydroxide. Useful features of chitosan include its abundance, nontoxicity, hydrophilicity, and biodegradability.[2] In recent years, chitosan has already been described as a suitable natural polymer for the collection of metal ions and precious ones[3–6] since the amine and hydroxyl function groups on the chitosan chain can act as chelation sites for metal ions. Besides inherent sorption, the adsorption capacity and selectivity of chitosan also could be enhanced by chemical modification.[7–9]

According to Pearson's hard and soft acid–base theory, polymers containing functional groups with N or S donor atoms should be promising as sorbents of precious metal ions. Some of previous literatures[1,10–12] have been demonstrated this viewpoint. But, so far, there have been no reports for the adsorption of precious metal ions onto chitosan using thiadiazole as functional group. Because there are three sulfur atoms and two nitrogen atoms in the structure of 2,5-dimercapto-1,3,4-thiodiazole, it would be expected such a functional group would have promising adsorption property toward precious metal ions.

In this study, a new chitosan derivative, chitosan crosslinking 2,5-dimercapto-1,3,4-thiodiazole (CTS-DMTD) was synthesized by elimination reaction of DMTD with halogenated chitosan. The adsorption of Au(III), Pd(II), and Pt(IV) onto CTS-DMTD was investigated in details.

EXPERIMENTAL

Reagents

Chitosan powder, with a deacetylation degree of about 90%, was purchased from Boao Biological
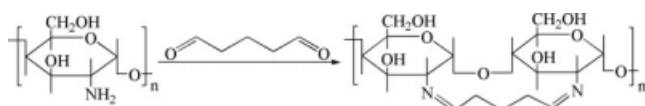
Scheme 1 Chitosan crosslinked with glutaraldehyde.

Scheme 2 Synthesis of CTS-Cl.

Tech. Co. Ltd., Shanghai, China. DMTD and epichlorohydrine were obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Acetic acid, sodium hydroxide, glutaraldehyde, and isopropyl alcohol were supplied by Beijing Chemical Reagent Factory, China. HAuCl$_4$, PdCl$_2$, and H$_2$PtCl$_6$ were purchased from Fisher Scientific Company Chemical Manufacturing Division, USA. All the other reagents were of analytical grade and were used without further purification.

Measurements

Infrared spectra were recorded on a Nicolet AVATAR-IR 360 spectrophotometer (test conditions: potassium bromide pellets, scanning 32 times, resolution 4 cm^{-1}). Elemental analysis was performed by a Leco CS-230 (USA) to determine the sulfur content. A TAS-990 flame atomic absorption spectrophotometer (FAAS) was used for the determination of the metal ions in aqueous solutions before and after adsorption or desorption.
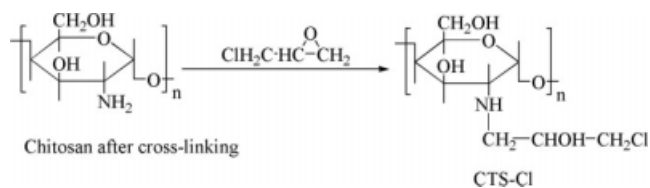
Preparation of chitosan beads

Chitosan powder 2.5 g was dissolved in a 1.0% (v/v) aqueous acetic acid, stirred for 24 h. Then the solution was dropped into a precipitation bath containing 3.0% (w/v) aqueous sodium hydroxide solution, by using a 0.05-mm diameter hypodermic needle, and stirred using a magnetic stirrer. The injection speed was controlled at about 60 drops per minute. A few hours later, the transparent nascent beads became opaque and solidified. The resultant beads were left resting for 24 h in the NaOH solution, washed several times with distilled water until pH of the water became neutral. Finally, the wet beads were stored in double distilled water until use.

Preparation of CTS-DMTD

Schemes 1–3 showed a representation of the preparation of CTS-DMTD. The wet chitosan beads obtained in the previous step was suspended in 50 mL methanol. A 1.19 mL 50% aqueous solution of glutaraldehyde was added and then stirred at room temperature for 3 h followed by heating at 70°C for 4 h. Finally, the crosslinked spheres was isolated by filtration and washed with ethanol followed by distilled water.[13]

The crosslinked chitosan beads obtained in the previous step were suspended in a solution of iso-

propyl alcohol (35 mL) while a solution of epichlorohydrine (5 mL) dissolved in 50 mL acetone/water mixture (1 : 1 v/v) was added. The resulting mixture was stirred at 60°C for 24 h. The mixture was filtered, the beads were washed several times with ethanol followed by distilled water, and the products were denoted by CTS-Cl.

To a three-necked round-bottom flask equipped with a mechanical stirrer and a thermometer was added 2.0 g DMTD followed by 100 mL of NaOH 2% (w/v) solution and 100 mL of methanol. Then, the CTS-Cl obtained in the previous step was added. After complete addition, the mixture was refluxed at 70°C for 40 h. Finally, the products were filtered and washed several times with ethanol followed by distilled water until neutral.

Adsorption studies

To 10 mL of an aqueous solution of Au(III), Pd(II), and Pt(IV), metal ions that was adjusted to the desired pH with hydrochloric acid was added to 5 mg of the CTS-DMTD. Stirring at room temperature (15°C ± 1°C) for 6 h, the mixture was filtrated. The concentration of metal ions was analyzed by FAAS. The effect of metal ions concentration (1–50 mg/L), contact time (0.1–4 h), and solution pH (0–5) were studied. Blank solutions were treated similarly (without adsorbent) at the recorded concentration by the end of each operation. Adsorption capacity (Q) was calculated according to eq. (1):

$$Q(mg/g) = \frac{(C_0 - C)}{W} V \qquad (1)$$

Adsorption isotherm models

Langmuir adsorption isotherm is one of the most well known and applied adsorption isotherms and described by the eq. (2):
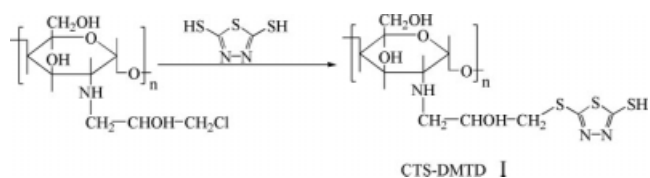
Scheme 3 Synthesis of CTS-DMTD.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{bq_{\max}} \qquad (2)$$

A plot of C_e/q_e versus C_e shows linearity. Hence, Langmuir constants $q_{\max}$ and b can be calculated from the gradient and intercept of the plot.

We also analyzed the adsorption data of Pd(II) and Pt(IV) in terms of Freundlich isotherm model. Freundlich isotherm equation $X/m = k_F C_e^{1/n}$ can be written in the linear form as given (3):

$$\log\frac{X}{m} = \log k_F + \frac{1}{n}\log C_e \qquad (3)$$

These constants can be calculated from the slope and intercept of the linear plot, with $\log(X/m)$ versus $\log Ce$.

Kinetics of adsorption

The kinetics of the adsorption process was studied by carrying out a set of adsorption experiments at constant temperature. The adsorption kinetic data of Pd(II) and Pt(IV) was analyzed in terms of pseudo-second-order kinetic eq. (4).

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (4)$$

Separating the variables in eq. (4) and integrating gives eq. (5):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (5)$$

The equilibrium adsorption capacity q_e and the pseudo-second-order rate constant k_2 can be experimentally determined from the slope and the intercept of the plot t/q_t against t.

RESULTS AND DISCUSSION

Elemental analysis

The elemental analysis was carried out on the synthesized CTS-DMTD to determine sulfur content. The obtained result was 4.67% in the compound of CTS-DMTD. It was proved that DMTD was successfully crosslinked onto chitosan.

Infrared spectral analysis

Figure 1 shows the FTIR spectra of the CTS, CTS-Cl, CTS-DMTD, Au(III), Pt(IV), and Pd(II) adsorbed onto CTS-DMTD. In all spectrums expect curve e, the adsorption band around 3420 cm^{-1} revealed the stretching vibration of N—H group bonded with O—H group in chitosan. The band around 2880 cm^{-1} indicated the C—H stretching vibration in
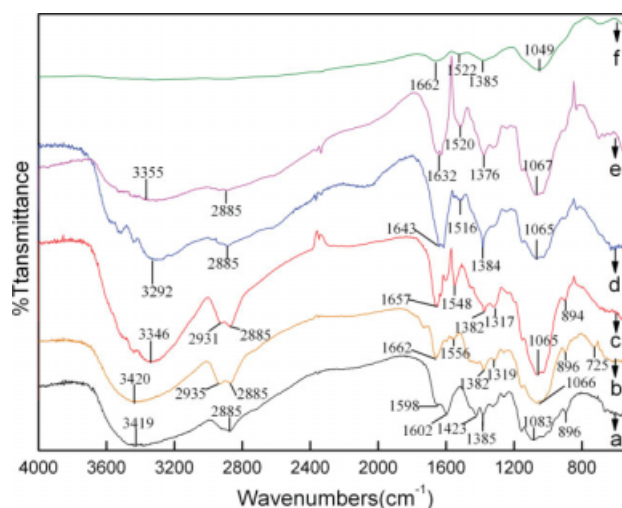

Figure 1 FTIR spectra: (a) CTS, (b) CTS-Cl, (c) CTS-DMTD, (d) Pd(II), (e) Pt(IV), (f) Au(III) adsorbed onto CTS-DMTD. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

methylenes of sugar residues.[14,15] The band around 1661 cm^{-1} confirmed the N—H scissoring from the primary amine, due to the free amino groups in the crosslinked chitosan.[16]

The new weak peak at 1156 cm^{-1} in the curve b demonstrated the N—H adsorption of secondary amine[17] resulting from the reaction of chitosan with epichlorohydrine. The new peak at 725 cm^{-1} revealing the stretching vibration of C—Cl bond also confirmed that chitosan has been halogenated.

It was observed that the increasing intensity at 1657 cm^{-1} and the new peak appeared at 1548 cm^{-1}, corresponding to the characteristic absorption of thiodiazole ring in DMTD.[18] These findings were confirmed that DMTD was successfully attached to chitosan.

The band around 1065 cm^{-1} was 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 decreasing intensity around 1065 cm^{-1} in curve d–f was observed indicating that the chemical interaction of Pd(II), Pt(IV), and Au(III) with CTS-DMTD. Also, the decreasing intensity around 1548 cm^{-1} and the increasing intensity around 1385 cm^{-1} in curve d–f indicated the chemical interaction of Pd(II), Pt(IV), and Au(III) with CTS-DMTD. The peak at 896 cm^{-1} demonstrated the β-glycoside bond of the chitosan,[19] and in curve d–f, the decreasing intensity of this peak also confirmed the chemical interaction of Pd(II), Pt(IV), and Au(III) with CTS-DMTD. It was predicted that sulfur and nitrogen atoms were the main adsorption cites for Pd(II), Pt(IV), and Au(III).

Effect of pH

Figure 2 shows the effect of pH on Au(III), Pd(II), and Pt(IV) adsorption by CTS-DMTD, respectively. The
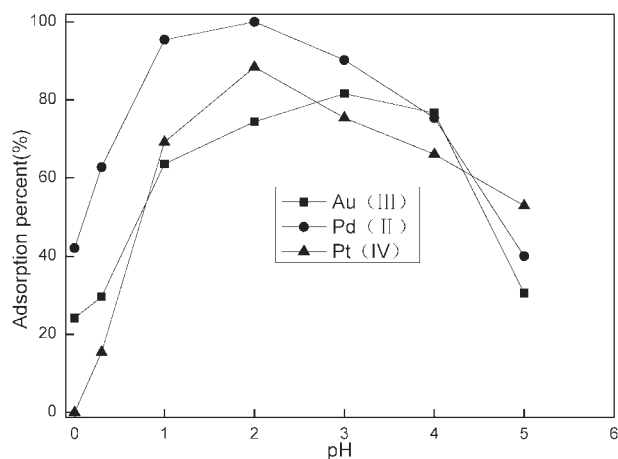
Figure 2 Effect of pH on Au(III), Pd(II), and Pt(IV) adsorption by CTS-DMTD (initial metal ions concentration 15 mg/L, contact time 4 h, adsorbent mass 5 mg).

results indicated that the adsorption capacity of the metal ions increased significantly with an increase in pH and adsorption amounts reached to maximum when pH was 3.0 for Au(III), and 2.0 for Pd(II) and Pt(IV). Then, the adsorption amount decreased obviously. This was probably because, at low pH, in the presence of HCl, the amount of chloride was high enough to favor the formation of chloro-anioinc spices, which was easily adsorbed on protonated amine groups of CTS-DMTD.[20] At higher pH, the decreasing sorption capacity may be explained by the presence of less-adsorbable Au(III), Pd(II), and Pt(IV) species because of the lower availability of chloride anions. The adsorption mechanism of Au(III), Pd(II), and Pt(IV) on CTS-DMTD was assumed to be electrostatic attraction and ion exchange. The probable interactions were shown below.
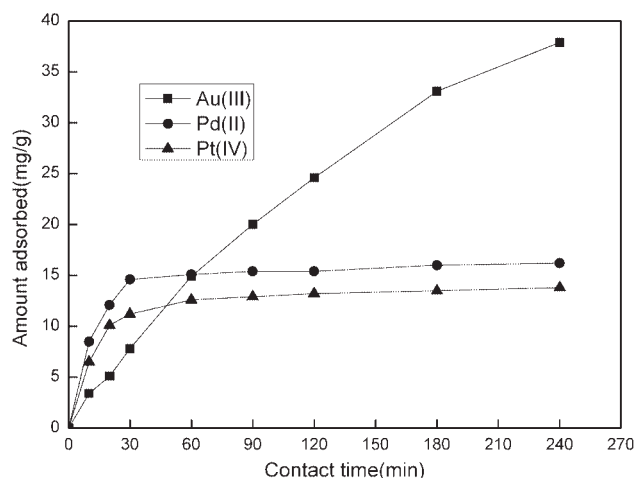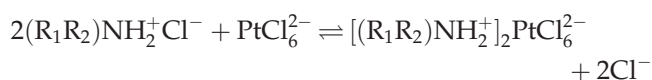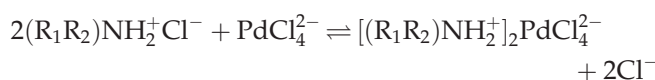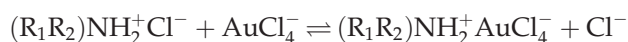

Figure 3 Effect of contact time on Au(III), Pd(II), and Pt(IV) adsorption by CTS-DMTD (initial metal ions concentration 30 mg/L, contact time 4 h, adsorbent mass 5 mg).

$$(R_1R_2)NH + HCl \rightleftharpoons (R_1R_2)NH_2^+Cl^-$$

$$(R_1R_2)NH_2^+Cl^- + AuCl_4^- \rightleftharpoons (R_1R_2)NH_2^+AuCl_4^- + Cl^-$$

$$2(R_1R_2)NH_2^+Cl^- + PdCl_4^{2-} \rightleftharpoons [(R_1R_2)NH_2^+]_2PdCl_4^{2-} + 2Cl^-$$

$$2(R_1R_2)NH_2^+Cl^- + PtCl_6^{2-} \rightleftharpoons [(R_1R_2)NH_2^+]_2PtCl_6^{2-} + 2Cl^-$$

Moreover, the lower pH values were really important for the precious metal ions recovery to eliminate the adsorption of other base metal ions[1]

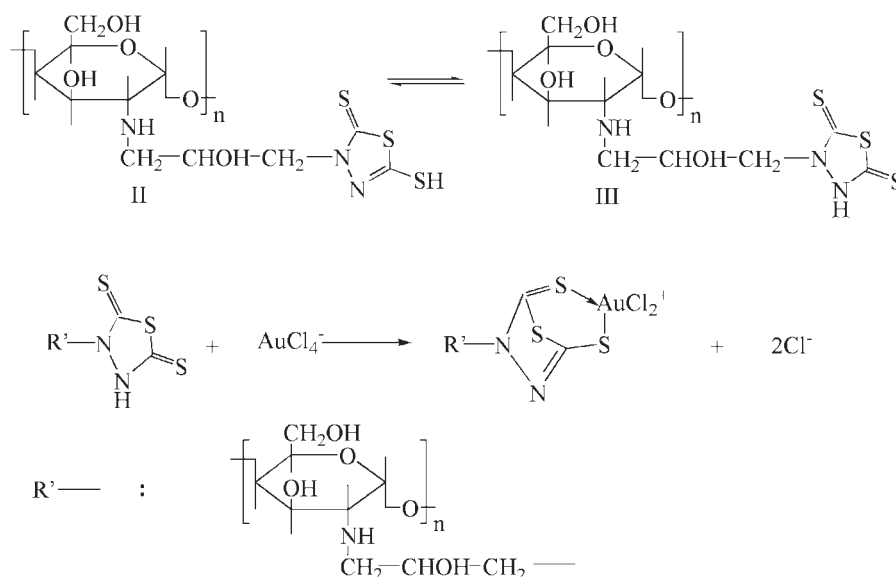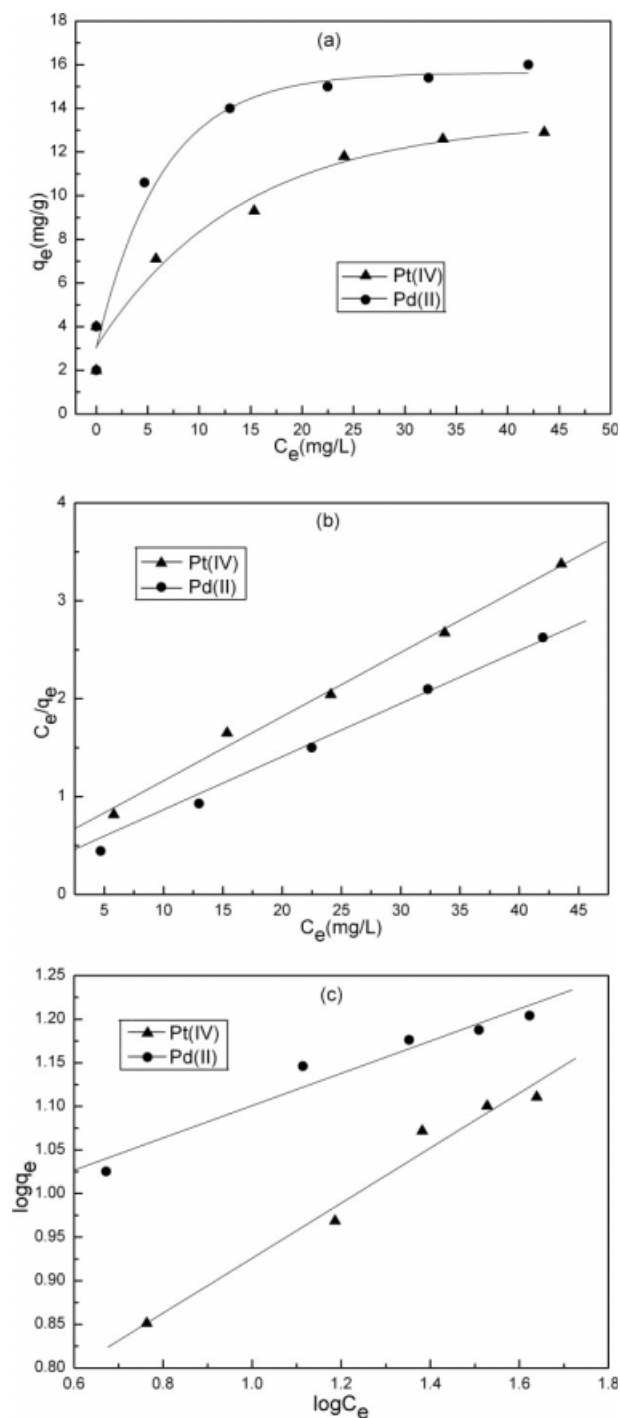**Figure 4** Mechanism of the Au(III) ions adsorption with CTS-DMTD.

Figure 5 Adsorption isotherms of Pd(II) and Pt(IV) on CTS-DMTD.

Effect of contact time

Figure 3 shows the effect of contact time on Au(III), Pd(II), and Pt(IV) adsorption by CTS-DMTD. The results demonstrated that the adsorption increased with increasing in agitation time and attained the equilibrium at around 240 min for Pd(II) and Pt(IV), whereas the capacity to adsorb Au(III) continued to increase during the experiment, reaching 198.5 mg/

g after 6 days. The process of adsorption for Au(III) was irregular after 4 h. This phenomenon probable because the Au(III) ions could be forming six-membered rings with DMTD besides ion exchange. The three forms of the structure of DMTD (I, II, and III in the Scheme 3 and Fig. 4) resulted from the complexity of the organic reaction and ketone-enol tautomerism. The complex reaction of Au(III) and DMTD was described as shown in Figure 4. Figure 3 also shows that the saturated capacity of Pt(IV) was lower than Pd(II). A possible explanation for this is that Pd(II) and Pt(IV) ions are in the form of $PdCl_4^{2-}$ and $PtCl_6^{2-}$, respectively. $PdCl_4^{2-}$ has a planar configuration, whereas $PtCl_6^{2-}$ has a octahedron configuration. Although the two kinds of chloro-coordinated anions both contained two negative charges, the planar-configured anion was more easily adsorbed by CTS-DMTD than the octahedron-configured anion.[21]

Adsorption isotherm models

Because the adsorption mechanism for Au(III) was different from Pd(II) and Pt(IV), it was hard to describe the adsorption process according to the isotherm of Langmuir or Freundlich. Figure 5 shows Langmuir and Freundlich adsorption isotherms of Pd(II) and Pt(IV) on CTS-DMTD. As can be seen from Figure 6(b,c), the fit was better with Langmuir model than with Freundlich model. The isotherm constants are presented in Table I. Based on the highest regression coefficient value of Langmuir isotherm, it was suggested that the adsorption process probably should be dominated by a monolayer adsorption process rather than a mutiple adsorption one.
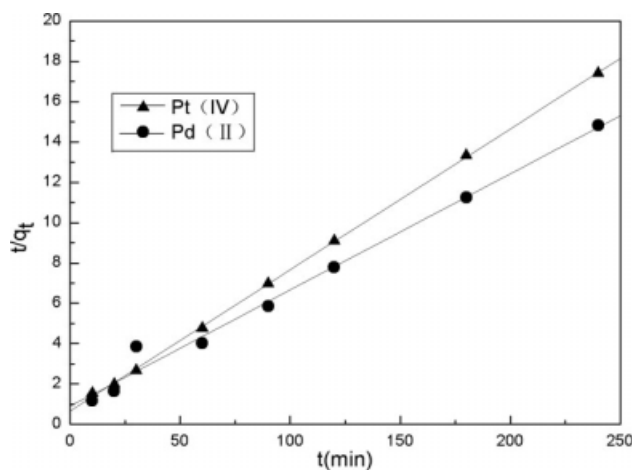

Figure 6 Pseudo-second-order kinetic model for the adsorption of Pd(II) and Pt(II).

TABLE I
Langmuir and Freundlich Isotherm Constants

	Pd(II)	Pt(IV)
Langmuir		
q_{max} (mg/g)L	16.9750	15.2648
b (L/mg)	0.3466	0.1292
R^2	0.9909	0.9927
Freundlich		
k_F (mg/g)	8.2421	4.0780
n	5.4107	3.1693
R^2	0.9460	0.9741

Kinetics of adsorption

The experimental data in Figure 6 indicated that the adsorption rates of Pd(II) and Pt(IV) on the CTS-DMTD were fast at the beginning and then slowed as equilibrium approached. The adsorption equilibrium of Pt(IV) and Pd(II) was attained in 2000 min. It was found that the adsorption kinetics of Pd(II) and Pt(IV) on CTS-DMTD could be well described by the pseudo-second-order rate model. As displayed in Table II, the calculated q_e values from pseudo-second-order model were very close to experimental q_e values.

Recovery of Au(III), Pd(II), and Pt(IV) from mixture solution of metal ions

Figure 7 illustrated that the equilibrium adsorption capacities of Au(III), Pd(II), and Pt(IV) on the CTS-DMTD were remarkably higher than those of the base metal ions in the mixture solution containing Cu(II), Fe(III), Cd(II), Ni(II), Mg(II), and Zn(II). This fact strongly suggests that the CTS-DMTD is capable of selectively adsorption for Au(III), Pd(II), and Pt(IV) under proper conditions, which could be valuable in practical uses.

Desorption studies

Desorption studies were performed using various concentrations of HCl, NaOH, and thiourea. As displayed in Table III, the results showed that desorption percent was low by HCl and NaOH, but only

TABLE II
Adsorption Kinetics Model Parameters of Au(III), Pd(II), and Pt(II) on CTS-DMTD

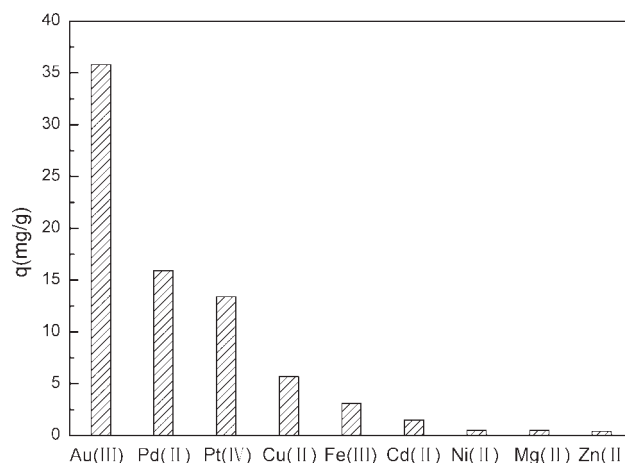|	Pd(II)	Pt(IV)
k_2 (g/mg min)	3.6860×10^{-3}	7.3715×10^{-3}
q_e (mg/g) calcd.	17.3611	14.3000
q_e (mg/g) exp.	16.2023	13.7998

Figure 7 Recovery of Au(III), Pd(II), and Pt(IV) from mixture solution of metal ions.

0.1 mol/L thiourea solution without adding HCl can effectively desorbed the Au(III), Pd(II), and Pt(IV) metal ions from CTS-DMTD, more than 95%. So, in this study, thiourea was choosed as the eluent. The low recoveries caused by HCl and NaOH also demonstrated the chelating mechanism involved in the metal ions adsorption process.

CONCLUSIONS

This study demonstrated that CTS-DMTD hydrogel were efficient in removing Au(III), Pd(II), and Pt(IV) from dilute solutions. A range of static sorption studies were performed on this adsorbent, which showed the selectivity towards cations of the precious metals over other transition metal cations. The sorption studies also revealed a considerable capacity for Au(III) ions, which might be useful in the removal of gold from ores. However, the CTS-DMTD was a little bit more difficult to reuse. Therefore, the future work of the present study will mainly include how to overcome this deficiency.

TABLE III
Effect of eleunt on Desorption Efficiency of Pd(II)

Eluent (mol/L)		Desorption percent (%)		
		Au(III)	Pd(II)	Pt(IV)
HCl	3.0	8.65	10.15	13.24
	4.0	10.09	15.96	15.62
	5.0	11.23	19.15	13.79
NaOH	0.5	28.65	42.81	37.56
	1.0	23.79	47.23	38.21
	2.0	24.33	47.18	38.97
Thiourea	0.1	96.78	98.92	95.87
	0.2	97.65	98.79	96.28
	1.0	97.02	99.91	95.67

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