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Adsorption and Determination of Pd(II) and Pt(IV) onto 3′-Nitro-4-amino Azobenzene Modified Chitosan

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ABSTRACT: 3′-Nitro-4-amino azobenzene modified chitosan has been prepared and characterized by FT-IR. The adsorption data have been investigated including the effects of pH, initial concentration, and contact time by batch method. The adsorption of Pd(II) and Pt(IV) was best in the pH range of 4.0−6.0 for Pd(II) and at pH 3.0 for Pt(IV), where the maximum mass adsorption were (29.33 and 43.10) $\text{mg}\cdot\text{g}^{-1}$, respectively. The adsorption isotherms obeyed the Langmuir equation for the adsorption of Pd(II) and Pt(IV). The adsorption kinetic data were fitted with a pseudosecond-order model and an intraparticle diffusion model. The results indicated that the adsorption of Pd(II) and Pt(IV) followed a pseudosecond-order model. The adsorbent shows high affinity for Pd(II) and Pt(IV) in binary systems containing each noble metal ion and other base metal ions. The optimal desorption reagent was 0.20 $\text{mol}\cdot\text{L}^{-1}$ thiourea + 0.50 $\text{mol}\cdot\text{L}^{-1}$ HCl solution for both Pd(II) and Pt(IV). The method was successfully applied for the determination and separation of Pd(II) and Pt(IV) in ore samples.

1. INTRODUCTION

Because noble metals are useful in a multitude of fields, including industry, mining, environmental technology, and so on, the extraction of noble metal ions has become particularly important. Among a wide variety of conventional separation methods, including solvent extraction,[1] ion-exchange,[2,3] adsorption,[4−6] etc., adsorption is a relatively effective and convenient method.

Chitosan is an abundant biopolymer obtained after deacetylation of chitin, which is poisonless, has many biofunctionalities, and possesses a high adsorption capacity. These excellent properties make chitosan a promising material for a large number of applications, such as biomedicine, commercial production, and adsorption of metal ions.[7,8] The amino and hydroxyl groups in chitosan are propitious for modifying chitosan in order to optimize its adsorption behavior. These active groups make chitosan efficient in the adsorption of metal ions through coordination or ion-exchange. However, the solubility of chitosan in acidic solutions limits its application. Over the past few years, there have been great acheivements in the chemical modification of chitosan. Chitosan modified with *N*-(2-pyridylmethyl),[9] 1,2-ethylenedisulfide,[10] 2,5-dimercapto-1,3,4-thiodiazole,[11] tripolyphosphate,[12] epichlorohydrin,[13,14] crown ether,[15] and cyclodextrin[16] has been prepared by researchers. Cross-linking agents not only stabilize chitosan in acid solutions so that it becomes insoluble but also enhance the adsorption capacity and selectivity of chitosan.

The known ability of compounds with a N atom to establish a lone-pair electron can facilitate the selective adsorption of previous metal ions. In our previous work, we have reported an azobenzene modified chitosan where nitro and amino are at the contrapuntal position.[17] The compounds containing a single azo group have shown good adsorption toward noble metal ions. Furthermore, to the best of our knowledge, no such study about the adsorption of Pd(II) and Pt(IV) with 3′-nitro-4-amino azobenzene modified chitosan has been reported until now.

In the present study, the adsorption toward Pd(II) and Pt(IV) was studied by the adsorbent of 3′-nitro-4-amino azobenzene modified chitosan (abbreviated as CS-MANAB). The effects of various parameters such as pH, initial concentration, and contact time on adsorption were investigated. The Pd(II) and Pt(IV) desorption from adsorbent were also discussed using various eluents. The standard ore samples were employed to evaluate the feasibility of this adsorbent. FT-IR was used to note the functional groups on the modified chitosan before and after adsorption.

2. EXPERIMENTAL SECTION

2.1. Chemicals. All chemicals used in the experiments were of analytical reagent grade. Chitosan with a deacetylation degree of about 90% was purchased from Boao Biological Tech. Co. Ltd., China. *m*-Nitroaniline was supplied by Shanghai Chemical Reagent Company of China Pharmaceutical Group. Aniline, glutaraldehyde, and isopropyl alcohol were supplied by Beijing Chemical Reagent Factory, China. Epichlorohydrin was provided by Tianjin North Joint Development of Fine Chemicals Co., Ltd., China. The Pd(II) and Pt(IV) working solutions supplied by Beijing NCS Analytical Instruments Co., Ltd. were prepared to the required levels by progressive dilutions of standard solutions using distilled water.

2.2. Apparatus and Methods. An Affinity-1 Fourier transform infrared spectrophotometer (KBr pellet, resolution 4 cm^{-1} for 32-time scanning, Shimadzu, Japan) was used to analyze the functional groups of the adsorbent. The concentrations of the metal ions in aqueous solutions were detected by a TAS-990 flame atomic absorption spectrophotometer (PGeneral, Beijing, China). The operating parameters for working elements were set as recommended by the manufacturer. A digital pH meter

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(pHS-25C, Shanghai, China) was employed for pH measurements, and a water-bathing constant temperature vibrator (SHA-BA, Shanghai, China) was employed for the constant shaking rate. The experimental data were investigated by batch method and various kinds of adsorption models.

2.3. Synthesis of CS-MANAB. 3′-Nitro-4-amino azobenzene was synthesized based on the theory of diazo coupling reaction. $NaHSO_3$ was added into a mixture of formaldehyde and distilled water and reacted for 30 min at (60−65) °C. Next the aniline was added and reacted for another 1 h, and the phenylamino-methanesulfonate was obtained. An aqueous solution $NaNO_2$ was added dropwise under ice water bath to *m*-nitroaniline which was dissolved by a 6 $mol \cdot L^{-1}$ HCl solution. The mixture was stirred for 30 min and vacuum-filtrated, and the filtrate was dropped into the obtained phenylamino-methanesulfonate solution under a controlled temperature of (0−5) °C. The solution acidity was adjusted with saturated sodium acetate solution. After reaction for 5 h, NaOH was added and hydrolyzed at (70−75) °C for 2 h, followed by stationary placement for 24 h. The product of 3′-nitro-4-amino azobenzene was collected and washed several times with distilled water, 50 % ethanol, and 95 % ethanol successively.

CS-MANAB was prepared by adding epichlorohydrin cross-linked chitosan to the mixture of methanol solution of 3′-nitro-4-amino azobenzene, NaOH, and ethanol. Epichlorohydrin cross-linked chitosan was synthesized according previous literature.[18] The product was stirred at 40 °C for 24 h, filtered, washed with ethanol and distilled water, and dried at 50 °C.

2.4. Adsorption Studies. Batch adsorptions of Pd(II) and Pt(IV) were carried out by placing a certain amount of dry adsorbent in metal ion solutions with different concentrations at room temperature. The solution with a volume of 10 mL was adjusted to the desired pH value with HCl. All of the experiments were agitated at a constant shaking rate of 150 rpm in a vibrator. The concentration of precious metal ions was determined by FAAS. The adsorption capacity was calculated through the mass balance equation listed as below:

$$Q = \frac{(C_0 - C)}{m} V \qquad (1)$$

where Q ($mg \cdot g^{-1}$) is the adsorption amount of metal ion, m (g) is the adsorbent dose, and V (L) is the volume of solution. C_0 and C ($mg \cdot L^{-1}$) are the concentrations of metal ion in the beginning and at time *t*, respectively.

2.5. Sample Analysis. The standard ore sample of GBW07293 containing 0.568 $\mu g \cdot g^{-1}$ Pd and 0.440 $\mu g \cdot g^{-1}$ Pt was used in the sample analysis. The sample was pretreated with aqua regia after being calcined at 650 °C for 2.5 h in a high temperature furnace. The solutions were evaporated to moist salt state, adding 4 $mol \cdot L^{-1}$ HCl to dissolve the residue. After filtration, the filter liquor was transferred to a volume flask and adjusted to the scale using distilled water.

3. RESULTS AND DISCUSSION

3.1. Characterization of CS-MANAB. Chitosan, CS-MANAB, and noble metals adsorbed on CS-MANAB were characterized by FT-IR, and the results were shown in Figure 1. The bands around 898 cm^{-1} in all infrared spectra were observed for the β-glycoside bond of the chitosan. In Figure 1b, the (3478 and 3383) cm^{-1} peaks represented the characteristic absorption peak of $-NH_2$. A new peak appearing at 1398 cm^{-1} was the characteristic band of −N=N−, and the peak at 1350 cm^{-1} represented the $-NO_2$ stretching vibration. These peaks confirmed the modification of 3′-nitro-4-amino azobenzene on chitosan. Compared with the peak at 1398 cm^{-1}, the intensity decreased a lot or disappeared in Figure 1c,d, which implied the chemical reaction between the precious metal ions and the −N=N− group. Additionally, the disappearance of the peak at 3478 cm^{-1} and the broad peak at 3400 cm^{-1} reflected the chemical adsorption appearing in −NH groups.

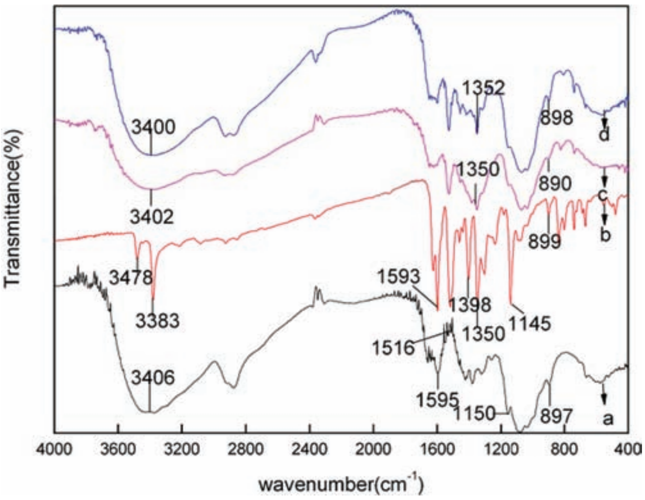

Figure 1. FT-IR spectra of (a) chitosan, (b) CS-MANAB, (c) Pd(II), and (d) Pt(IV) adsorbed onto CS-MANAB, respectively.

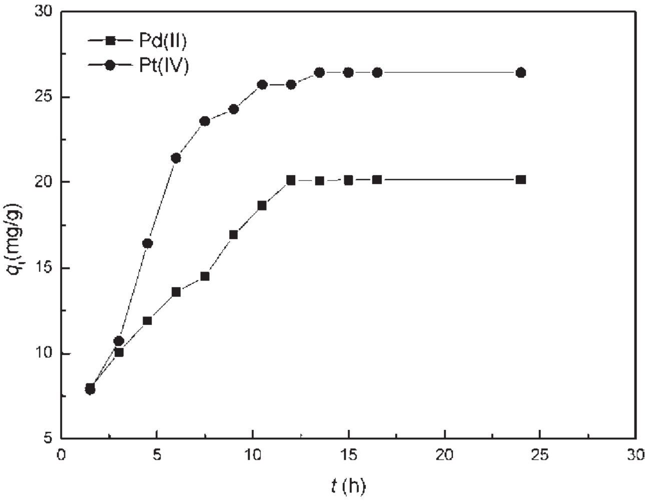

Figure 2. Effect of contact time on the adsorption of Pd(II) and Pt(IV) by CS-MANAB (adsorbent dose 5 mg; contact time (1.5−24) h; initial metal ions concentration 15 mg/L).

3.2. Effect of pH. Adsorption experiments under controlled pH ranging from 1.0 to 6.0 were carried out to study the effect of solution pH on the precious metal ion adsorptions in an initial concentration of 12 $mg \cdot L^{-1}$. A total of 5 mg adsorbant was added. The desired pH was adjusted using HCl. The mixture was shaken for 20 h at room temperature. The results indicated that the maximum adsorption amounts, about 38 mg/g for Pt(IV) and 30 mg/g for Pd(II), were obtained at pH 3.0 in the case of Pt(IV) and in the range of 4.0−6.0 in the case of Pd(II).

The adsorption mechanism was related with adsorbent and the existing form of metal ions in solution. In acidic solutions, the adsorption was processed through electrostatic attraction and ion exchange between protonated amine groups and chloride anion of Pd(II) and Pt(IV).

3.3. Effect of Contact Time and Initial Concentration. The influences of contact time on the adsorption of Pd(II) and Pt(IV) by CS-MANAB were shown in Figure 2. As seen from Figure 2, the adsorption amounts increased with the increasing adsorption time, and reached the equilibrium around 14.5 h. The adsorption process was slow-paced, it was suggested that the adsorption process might probably dominated by chelating adsorption. The effects of initial metal ion concentrations in the range of (5−30) mg·L^{-1} on adsorptions were also investigated. The results indicated that the adsorption of Pd(II) and Pt(IV) increased when the initial concentrations were increasing in the first instance and stayed stable with the increasing concentration. This was due to the fixed total active sites in the adsorbent, and the adsorption amounts would reach a state of saturation eventually.

3.4. Adsorption Isotherms. The experimental data were analyzed with Freundlich isotherm about multiple layer adsorption with uniform energy and Langmuir isotherm models based on the monolayer adsorption on the active sites of the adsorbent to evaluate the adsorption system. The Freundlich isotherm equation can be expressed in the linear form as follows:

$$\log \frac{X}{m} = \log k_F + \frac{1}{n} \log C_e \tag{2}$$

where X/m (mg·g^{-1}) is the equilibrium adsorption and C_e (mg·L^{-1}) is the equilibrium concentration of metal ion in solutions. k_F is the Freundlich constant related to adsorption capacity and n is the Freundlich constant related to adsorption intensity. The Langmuir isotherm equation is written on linearization as

$$\frac{C_e}{X/m} = \frac{C_e}{Q_m} + \frac{1}{Q_m k_L} \tag{3}$$

where Q_m (mg·g^{-1}) represents the maximum adsorption amount and k_L is the Langmuir constant concerning the adsorption energy. Moreover, the equilibrium parameter R_L, calculated as $R_L = 1/(k_L C_0)$, can be used to testify whether an adsorption system is favorable or unfavorable.

The above two isotherm fitting lines were shown in Figures 3 and 4 and the corresponding parameters were stated in Table 1. The Q_m values listed in Table 1 are 29.33 mg·g^{-1} for Pd(II) and 43.10 mg·g^{-1} for Pt(IV). However, the maximum adsorptions using nonmodified chitosan were (19.62 and 17.33) mg·g^{-1} for Pd(II) and Pt(IV), respectively. The increasing adsorption capacities were ascribed to the increasing adsorption sites by the grafting of the −N═N− group. As seen from Figures 3 and 4, the data were better fitted with the Langmuir model than with the Freundlich model. Additionally, the regression coefficients in Table 1 indicated that the adsorption process might be mainly influenced by a monolayer adsorption. The R_L values in Table 1 were within the range of 0−1, indicating that this is a favorable adsorption system.

3.5. Adsorption Kinetics. The pseudosecond-order[19,20] and intraparticle diffusion[21,22] models were used to evaluate the kinetic process. The pseudosecond-order kinetic equation can be written as

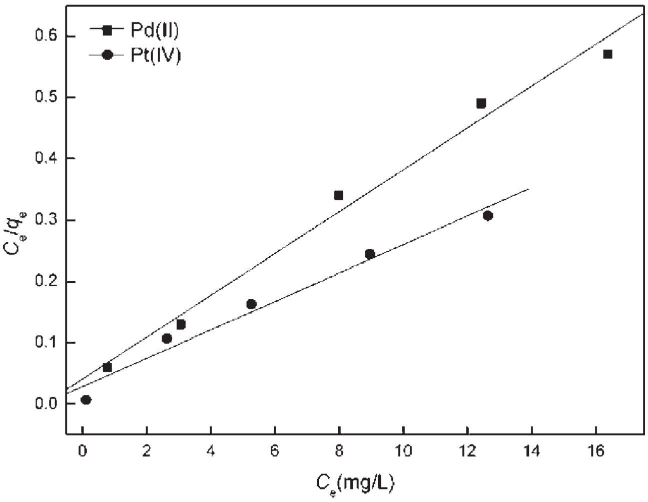

Figure 3. Langmuir isotherm of Pd(II) and Pt(IV) on CS-MANAB at room temperature (adsorbent dose 3 mg; contact time 20 h; initial metal ions concentration (5−25) mg/L).

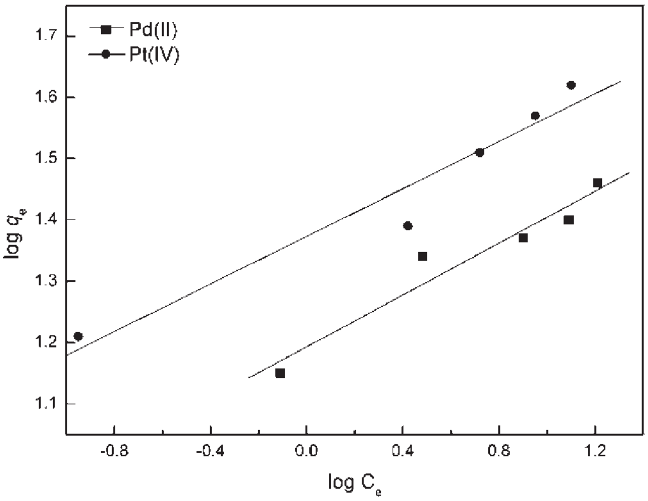

Figure 4. Freundlich isotherm of Pd(II) and Pt(IV) on CS-MANAB at room temperature (adsorbent dose 3 mg; contact time 20 h; initial metal ions concentration (5−25) mg/L).

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{4}$$

where k_2 is the pseudosecond-order rate constant. q_e and q_t are the adsorption amounts (mg/g) at equilibrium and time t, respectively. h stands for original adsorption rate[23] which can be defined as $h = k_2 {q_e}^2$. The intraparticle diffusion model which was introduced to testify if the intraparticle diffusion was the rate limiting step can be represented as

$$q_t = k_{id} t^{0.5} \tag{5}$$

where k_{id} is the intraparticle diffusion rate constant.

The kinetic models were presented in Figures 5 and 6 and the corresponding kinetic parameters were listed in Table 2. As shown in Table 2, the regression coefficients (R^2) were higher

Table 1. Constants of Langmuir and Freundlich Isotherms for Adsorption of Pd(II) and Pt(IV) on CS-MANAB

	Langmuir isotherm				Freundlich isotherm		
metal	Q_m ($mg \cdot g^{-1}$)	k_L (mg^{-1})	R^2	R_L	k_F	n	R^2
Pd(II)	29.33	0.83	0.99	$4.59 \times 10^{-2} < R_L < 0.19$	15.60	4.73	0.94
Pt(IV)	43.10	0.81	0.98	$4.71 \times 10^{-2} < R_L < 0.20$	23.62	5.16	0.95

Table 2. Pseudosecond-Order Kinetic Parameters and Intrapracticle Diffusion Rate Constant for the Adsorption of Pd(II) and Pt(IV) on CS-MANAB

		pseudosecond-order kinetic				intraparticle difusion	
metal	$q_{e(exp)}$ ($mg \cdot g^{-1}$)	$k_2 \cdot 10^3$ ($g \cdot mg^{-1} \cdot h^{-1}$)	h ($mg \cdot g^{-1} \cdot h^{-1}$)	$q_{e(cal)}$ ($mg \cdot g^{-1}$)	R^2	k_{id} ($mg \cdot g^{-1} \cdot h^{-0.5}$)	R^2
Pd(II)	20.16	8.73	5.53	25.19	0.98	4.54	0.93
Pt(IV)	27.53	5.06	6.83	36.81	0.97	6.20	0.87

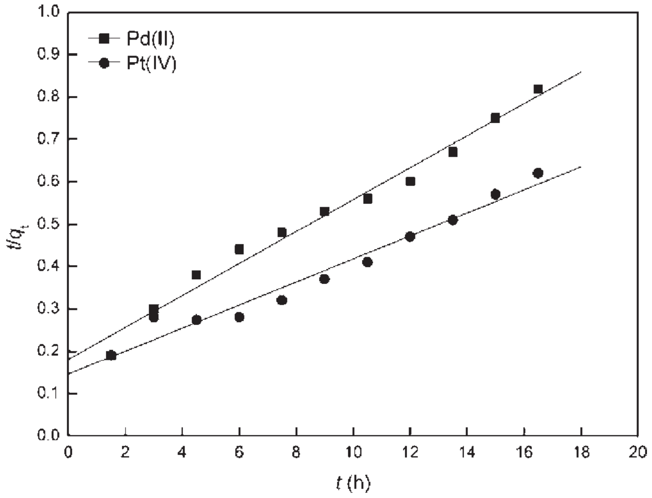

Figure 5. Pseudosecond-order kinetic model for the adsorption of Pd(II) and Pt(IV) on CS-MANAB (adsorbent dose 5 mg; contact time (0−16.5) h; initial metal ions concentration 15 mg/L).

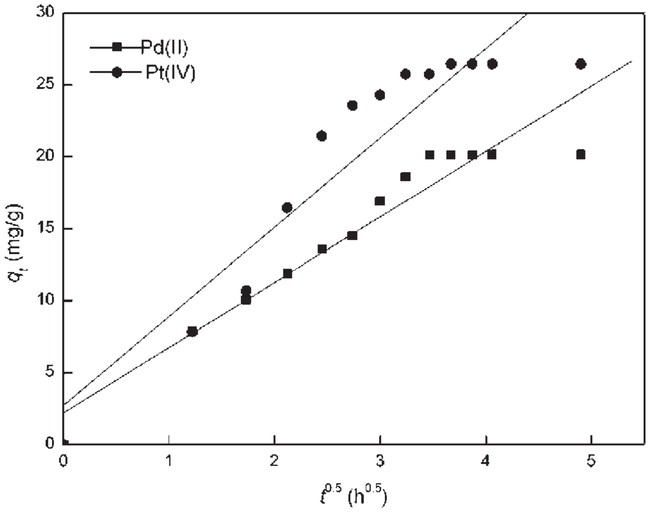

Figure 6. Intrapracticle diffusion model for the adsorption of Pd(II) and Pt(IV) on CS-MANAB (adsorbent dose 5 mg; contact time (0−24) h; initial metal ions concentration 15 mg/L).

than 0.96. Additionally, the calculated q_e values from pseudosecond-order kinetic equation were close to the experimental values. So the kinetic could be well-described by this model. The intraparticle diffusion plots obtained in Figure 6 showed multilinearity with three different adsorption phases. As shown, the line did not pass through the origin. The results implied that the intraparticle diffusion may not be the sole rate limiting step.[24]

3.6. Adsorption Selectivity. The selectivity of common coexisting ions on the adsorption of Pd(II) and Pt(IV) in binary systems containing one noble metal and the other base metal ion, i.e., Co(II), Ni(II), Cu(II), Zn(II), K(I), Na(I), Ca(II), and Mg(II), were studied. The selectivity was judged by the separation factor[25] which was expressed as

$$K_{A/B} = \frac{(C_{A1} - C_{A2})C_{B2}}{(C_{B1} - C_{B2})C_{A2}} \qquad (6)$$

where C_{A1} and C_{A2} (mg/L) were the concentrations of noble metal ions before and after adsorption and C_{B1} and C_{B2} were the concentrations of the other base metal ions in binary system before and after adsorption. The results indicated that the adsorbent showed high affinity for Pd(II) and Pt(IV), the separation factors are 993 in the case of K(I)/Pd(II) and 1567 in the case of Ca(II)/Pd(II) binary solutions, whereas there was nonadsorbing of the other metal ion in both Pd(II) and Pt(IV) binary systems. It could be concluded that various base metal ions had no obvious effect on the adsorption of tested noble metal ions. The mutual effects of Pd(II) and Pt(IV) on each other had also been examined from their binary solutions. Under each optimum condition, the adsorption influences of Pd(II) and Pt(IV) on each other were weak.

3.7. Elution and Reuse. The desorption of Pd(II) and Pt(IV) from CS-MANAB was studied using various concentrations of thiourea and thiourea + HCl solutions under different temperatures of 25 °C, 40 and 50 °C. Five mg CS-MANAB adsorbed with Pd(II) and Pt(IV) was washed with distilled water and transferred into test tubes. Ten mL of elution agent was added. The tubes were shaken at room temperature for 2 h, and the released Pd(II) or Pt(IV) concentrations were determined by FAAS. The results indicated that the 0.20 mol/L thiourea +0.50 mol/L HCl were the optimal eluent and the highest desorption ratios were obtained at 40 °C, the relevant desorption ratios were 90.40%

for Pd(II) and 93.38% for Pt(IV), respectively. After three adsorption−desorption cycles of Pd(II) and Pt(IV), the desorption ratios were still above 90% and the adsorptions were relatively stable.

3.8. Sample Analysis. The obtained amounts of Pd(II) and Pt(IV) were determined as (0.516 and 0.411) $\mu g \cdot g^{-1}$, whereas the standard contents were (0.568 and 0.440) $\mu g \cdot g^{-1}$ in the ore sample of GBW07293, respectively. The relative standard deviation (n = 6) values were 5.10 % and 3.76 %, respectively. Additionally, the limits of detection (LOD) of Pd(II) and Pt(IV) which were calculated basing on three times the standard deviation of the peak height were (0.015 and 0.024) $\mu g \cdot mL^{-1}$ respectively. The results demonstrated that CS-MANAB was an efficient adsorption for the removal of Pd(II) and Pt(IV) from ore samples getting rid of interferences.

4. CONCLUSIONS

Azobenzene modified chitosan was prepared and studied against the adsorption of Pd(II) and Pt(IV). The results suggested that the adsorption was dependent on pH values, contact time and initial concentration. The desorption was influenced by the eluent concentration and desorption temperature. It was concluded that CS-MANAB with high selectivity, excellent ability to resist interferences could be an efficient adsorbent for the separation and extraction of Pd(II) and Pt(IV) in practical samples. The relative standard deviations were 5.10 % and 3.76 % for palladium and platinum, respectively. The limits of detection of this method were 0.015 $\mu g \cdot mL^{-1}$ for Pd(II) and 0.024 $\mu g \cdot mL^{-1}$ for Pt(IV). It is of profound theoretical and practical significance for the removal of the noble metal ions.

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