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Removal of transition metal ions from aqueous solutions by adsorption using a novel hybrid material silica gel chemically modified by triethylenetetraminomethylenephosphonic acid

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ABSTRACT

A novel inorganic–organic hybrid material silica gel chemically modified by triethylenetetraminomethylenephosphonic acid (denoted as GH-T-P) has been synthesized and characterized. Its adsorption properties GH-T-P for Au(III), Hg(II), Cu(II), Pb(II), Co(II), Zn(II), Ni(II), Cr(III) and Cd(II) have been investigated, and the research results revealed that GH-T-P has the best adsorption capacity for Au(III). Furthermore, the adsorption selectivity results of GH-T-P for Au(III) displayed that GH-T-P had excellent adsorption for Au(III) in binary ions systems, especially in the systems of Au(III)–Zn(II), Au(III)–Ni(II) and Au(III)–Cr(III). Langmuir and Freundlich isotherm models were applied to analyze the experimental data, and the best interpretation for the experimental data was given by the Langmuir isotherm equation. GH-T-P could reach to the saturation adsorption capacity within 2 h, and its excellent adsorption capacity for Au(III) was 266.49 mg/g when the initial solution concentration was 2.0 mmol/L at 35 °C. Moreover, the research revealed that its adsorption kinetics can be modeled by pseudo-second-order rate equation wonderfully, and the thermodynamic parameters ΔG, ΔH and ΔS were $-20.79\,\mathrm{kJ\,mol^{-1}}$, $5.17\,\mathrm{kJ\,mol^{-1}}$, and $84.37\,\mathrm{J\,K^{-1}\,mol^{-1}}$, respectively. Thus, this novel hybrid material silica gel chemically modified by triethylenetetraminomethylenephosphonic acid GH-T-P is favorable and useful for the uptake of Au(III), and the high adsorption capacity and good reproducibility make it a good promising candidate material for the precious metal uptake.

1. Introduction

The removal and recovery of heavy metal ions from industrial wastewater has been a significant concern in most industrial branches due to economic and environmental factors. Many treatment processes, such as chemical precipitation, electrodialysis, adsorption, are currently used. Among these methods, adsorption is highly effective and economical, and is a promising and widely applied method [1,2].

On the other side, inorganic–organic hybrids offer very interesting actual and potential applications, and may have prominent properties in areas such as adsorbents [3]. Due to the excellent thermal and mechanical stability, unique large surface area and well-modified surface properties, silica gel was widely used as inorganic solid matrix in inorganic–organic composite materials. Such kinds of materials have received a great deal of attention recently because of their excellent performance in the field of chromatography, adsorption, and catalysis [4–6]. Chemical modification of the skeleton of silica gel via the covalent coupling of an organic moiety is a promising approach to obtain such kind of silica gel-based materials [7], therefore, many chemically modified silica gel have been synthesized during the past three decades, and it has been found that the behavior of these solids used as adsorbent are mainly dependent on the presence of active donor atoms such as O, S and N of the incorporated organic moieties [8–10]. In the previous work in our group, we have introduced polyamine to the surface of silica gel through amido bond to obtain some novel adsorbents [11]. The objective of the present work was to explore a novel adsorbent silica gel chemically modified by triethylenetetraminomethylenephosphonic acid GH-T-P in extension of our earlier work and study the adsorption behavior for transition metal ions from aqueous solutions by GH-T-P.

2. Experimental details

2.1. Materials and methods

Silica gel (GH) of chromatographic grade (60–80 mesh size) was obtained from Yantai Chemical Institute, Shandong Province of China. Organic solvents methyl acrylate (MA) and toluene were

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redistilled just before use. 3-Aminopropyltrimethoxysilane (APTS) (Jianghan Chemicals Factory, Jinzhou, China), triethylenetetramine (TETA) (Shanghai Chemical Factory of China) and the other reagents were used without further purification. The pH of solution of Au(III) was adjusted with hydrochloric acid aqueous solution (1 mol/L) and sodium hydroxide aqueous (1 mol/L). However, those pH values of solution of the other metal ions were adjusted with ammonium acetate/nitric acid solutions. Distilled water was used to prepare all the solutions. Infrared spectra (FT-IR) of samples were reported in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}, by accumulating 32 scans using a Nicolet MAGNA-IR 550 (series II) spectrophotometer, and KBr pellets were used for solid samples. Porous structure parameters were characterized using an automatic physisorption analyzer ASAP 2020 (Micromeritics Instruments Corporation, USA) by BET and BJH methods through N_2 adsorption at 77 K. The N analysis of products was analyzed by elemental analyzer Vario EL III. The concentration of metal ions was determined using a 932-model atomic absorption spectrometer (GBC-932A, made in Australia), equipped with air–acetylene flame.

2.2. Synthesis of the hybrid adsorbent GH-T-P

Silica gels were activated with nitric acid aqueous solution (HNO_3:H_2O = 1:1) at refluxing temperature for 3 h, then dipped in the hydrochloric acid aqueous solution (HCl:H_2O = 1:1) at room temperature for 6 h, finally washed with distilled water and dried in muffle at 160 °C for 12 h.

A suspension of 145.0 g of activated silica gel and APTS were stirred at 70 °C in the 437 mL of toluene solution for 8 h, and then the product was filtered off and transferred to a Soxhlet extraction apparatus for reflux-extraction in toluene and methanol for 6 h, respectively. The solid product was dried in vacuum at 50 °C over 48 h, and it was referred to as GH-APTS.

Under a nitrogen atmosphere, a mixture of 166 g of GH-APTS and 129 mL MA was added into a 1000 mL flask with 600 mL methanol as solvent. The mixture was stirred at 50 °C for 3 days, and then the solid was filtered off and transferred to a Soxhlet extraction apparatus for reflux-extraction in methanol and tetrahydrofuran for 12 h, respectively. The solid product was dried in vacuum at 50 °C over 48 h, and it was referred to as GH-MA.

Under a nitrogen atmosphere, a suspension of 10 g GH-MA and 224 mL TETA was stirred at 50 °C for 5 days using 180 mL methanol as solvent. Then the solid was filtered off and transferred to a Soxhlet extraction apparatus for reflux-extraction in methanol and tetrahydrofuran for 12 h, respectively. The solid product was dried in vacuum at 50 °C over 48 h, and it was referred to as GH-TETA.

7.2 g of GH-TETA were added to 60 mL ethanol at room temperature for 12 h, then 2.0 g of paragormaldehyde, 5.0 g of phosphorous acid and 2.0 mL of hydrochloric acid were added. After being refluxed at 90 °C for 12 h refluxed for 8 h, the product (GH-T-P) was filtered off, then washed thoroughly with distilled water and finally dried under vacuum over 48 h at 50 °C. It was referred to GH-T-P.

2.3. Adsorption experiments for transition metal ions

Static adsorption experiment was employed to determine the adsorption capacities of GH-T-P for different kinds of metal ions. The static adsorption experiments were carried out with shaking 0.02 g of resins with 10 mL of metal ion solution (2 mmol/L). The mixture was equilibrated for 24 h on a thermostat-cum-shaking assembly at 25 °C.

The adsorption amount was calculated according to the Eq. (1):

$$q = \frac{(C_0 - C_e)V}{W} \tag{1}$$

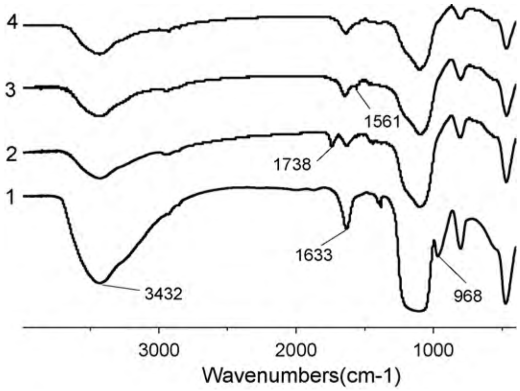

Fig. 1. FT-IR spectra of silica gel (1), GH-MA (2), GH-TETA (3) and GH-T-P (4).

where q is the adsorption amount (mmol/g); C_0 and C_e are the initial and equilibrium concentrations of metal ions (mmol/ml) in solution, respectively; V is the volume of the solution (mL); W is the weight of GH-T-P (g).

2.4. Competitive adsorption

In order to investigate the adsorption selectivity of the adsorbent for Au(III), 0.02 g of adsorbents were added into 10 mL solutions(binary system which containing equal initial concentrations (2.5 mmol/L) of Au(III) ion and other coexisting metal ions) and the mixture were shaken for 12 h. The initial pH was adjusted to 2.0 with the temperature at 25 °C.

2.5. Adsorption isotherms

The adsorption isotherms were investigated using 0.02 g of the adsorbent with various Au(III) ion concentrations (1.0–5.0 mmol/L) and a contact time of 12 h at pH 2.0 and 5–35 °C.

2.6. Adsorption kinetics

The adsorption kinetics on the uptake of Au(III) ion by the adsorbent was studied by placing 0.02 g of adsorbents with 10 mL of metal ion solution in a series of flasks at pH 2.0 and 5–35 °C with the concentration of the metal ion being 2 mmol/L. At a certain time interval, the adsorbent was filtrated and the concentrations of Au(III) ion in solutions were determined.

3. Results and discussion

3.1. Synthesis and characterization of the hybrid adsorbent GH-T-P

The synthetic route of GH-T-P included the steps of activation of silica gel, syntheses of GH-APTS, GH-MA, GH-TETA and the final product GH-T-P. The introduction of the organic groups onto the hybrid material can make the material form the stable chelating compounds with precious metal ions. The aim of chemical modification with amino methylene phosphonic acid, which has both N donor atoms and O donor atoms, is to make the material have excellent coordination properties with precious metal ions and to obtain a novel adsorbent with high loading of metal ions. The FT-IR analysis is a very useful technology in identifying the immobilization process by comparing the precursor and modified surfaces. The infrared spectra of silica gel, GH-MA, GH-TETA and GH-T-P (Fig. 1) displayed that a large broad band at 3432 cm^{-1} and a weak band at about 1633 cm^{-1} in the IR spectrum of silica gel were attributed to the presence of the O–H bond stretching vibration

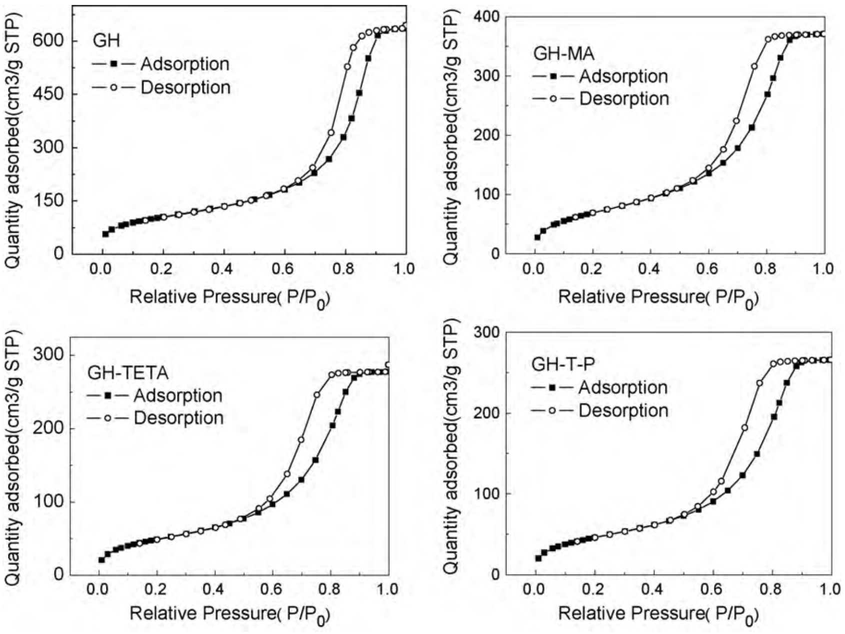

Fig. 2. Nitrogen adsorption–desorption isotherms of silica gel (GH), GH-MA, GH-TETA and GH-T-P.

of Si–OH group and the adsorbed water. The intense band related to Si–O–Si stretching vibration was at 1105 cm^{-1}, and the peaks around 806 cm^{-1} and 474 cm^{-1} were due to Si–O–Si symmetric stretching and Si–O–Si bending vibrations, respectively. Moreover, a characteristic stretching band of the free silanol groups centered at 968 cm^{-1}. As to that of GH-MA, two new bands appeared at 2933 cm^{-1} and 2855 cm^{-1} corresponded to the typical asymmetric and symmetric stretching vibration of –CH$_2$–, followed by a new and distinct peak at 1738 cm^{-1} assigned to the symmetric stretching vibrations of C=O, suggesting the successful anchoring reaction between MA and silica gel with the silylant agent. The band around 968 cm^{-1} of the free silanol groups disappeared, due to the reaction with the alkoxide groups of the silylant agent. After reaction with polyamines, the band at 1738 cm^{-1} of C=O disappeared, and a new absorption appeared at 1561 cm^{-1}, which was characteristic of primary amino group, due to the reaction with the ester groups of the GH-MA functionalized with polyamines. The stretching vibrations of N–H were overlapped in the range of 3731–2998 cm^{-1}. In the spectrum of GH-T-P, the band at 1561 cm^{-1} of primary amino group were disappeared and the strong peak centered at 3432 cm^{-1} containing the stretching vibration of N–H were decreased, confirming the methylene phosphonic acid were successfully introduced onto the amino-terminated chelating resin silica gel. Both of the bond P=O at 1175 cm^{-1} and the characteristic sorption peak of P–OH around 930 cm^{-1} were overlapped in the broad band between 1346 cm^{-1} and 876 cm^{-1}.

Fig. 2 shows the nitrogen adsorption–desorption isotherms for silica gel and its derivatives. It can be seen that silica gel and its derivatives were type IV according to the acknowledged BDDT classification and each had a hysteresis loop that was representative of mesoporous. The volume adsorbed for silica gel steeply increases at a relative pressure (P/P_0) of approximately 0.7, representing capillary condensation of nitrogen within the uniform mesoporous structure. The inflection position shifted toward lower relative pressures and the volume of nitrogen adsorbed decreased with functionalization. Fig. 3 shows the BJH desorption pore size distributions of silica gel and its derivatives. As illustrated in Fig. 3, the pores between 3 nm and 12 nm were dominant for all products. With the proceeding of the reaction, the amount of the pores between 3 nm and 12 nm became smaller gradually and the pore size distribution moved to the smaller pore size. In the present case, the values of BET surface area, BJH desorption average pore radius and BJH desorption cumulative volume of pores for silica gel decreased gradually with the functionalization reactions, due to the formation of the pendant organic chains, which made the pore size of silica gel become smaller and even some pores disappeared, which blocks the adsorption of nitrogen molecules.

3.2. Static adsorption of the hybrid adsorbent GH-T-P for transition metal ions

Fig. 4 showed the static adsorption capacities of GH-T-P for Au(III), Hg(II),Cu(II), Pb(II), Co(II), Zn(II), Ni(II), Cr(III) and Cd(II) metal ions. The research result displayed the static adsorption capacities for Au(III), Hg(II) and Cu(II) were 0.965 mmol/g, 0.606 mmol/g, and 0.311 mmol/g, respectively. However, those for Pb(II), Co(II), Zn(II), Ni(II), Cr(II) and Cd(II) metal ions were 0.0811 mmol/g, 0.0735 mmol/g, 0.0341 mmol/g, 0.0964 mmol/g, 0.00425 mmol/g and 0.0766 mmol/g, respectively. Obviously, the as-synthesized adsorbent had good adsorption capability for Au(III), Hg(II) and Cu(II) metal ions, especially for Au(III) ion.

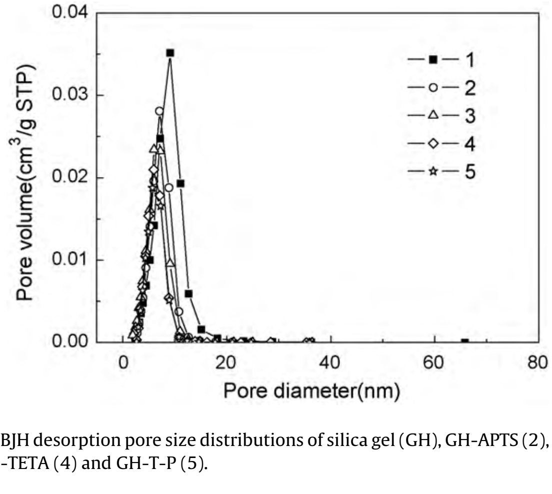

Fig. 3. BJH desorption pore size distributions of silica gel (GH), GH-APTS (2), GH-MA (3), GH-TETA (4) and GH-T-P (5).

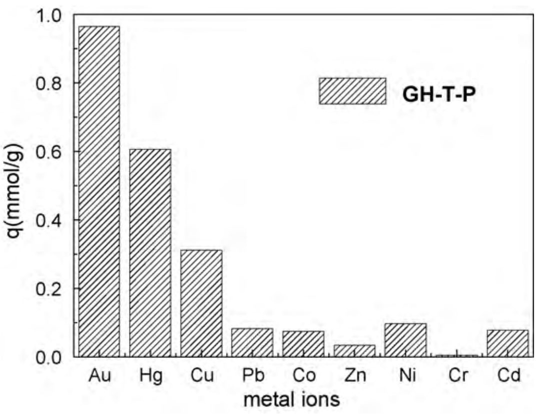

Fig. 4. The static adsorption capacities of GH-T-P for metal ions (the initial solution concentration: 2 mmol/L; pH = 5.0 (except pH_{Au} = 2.0); 25 °C).

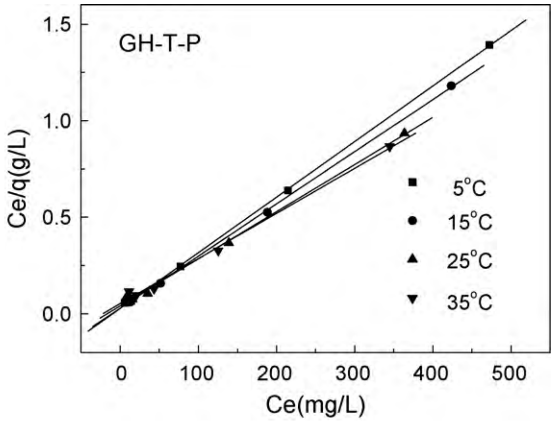

Fig. 5. The Langmuir isotherms of the sample GH-T-P for Au(III) at different temperatures.

Through the amino phosphonic acid groups, GH-T-P can form the stable chelating compounds with many transition metal ions, especially with Au(III). According to the theory of hard and soft acids and bases (HSAB) defined by Pearson, metal ions will have a preference for coordinating with ligands that have more or less same electronegative donor atoms. Chelating agents with N and O donor atoms are highly efficient for the selective sorption of precious metal ions.

3.3. Competitive adsorption

The competitive adsorption experiments by GH-T-P were carried out from Au(III)–Hg(II), Au(III)–Cu(II), Au(III)–Cd(II), Au(III)–Pb(II), Au(III)–Ni(II), Au(III)–Zn(II), Au(III)–Cr(III), and Au(III)–Co(II) binary systems. The initial gold(III) concentration as well as other transition metal ions such as Zn(II), Ni(II), Pb(II) and Cu(II) was 2.5 mmol/L. The obtained results for gold(III) adsorption at 25 °C are presented in Table 1.

The selective coefficients were the ratio of adsorption capacities of metal ions in binary mixture:

The selective coefficient $t = q'/q''$, where q' is adsorption capacities of Au(III)ion in binary mixture and q'' is adsorption capacities of the other metal ion in binary mixture. The results displayed that GH-T-P had excellent adsorption for Au(III) in binary ions systems, especially in the systems of Au(III)–Zn(II), Au(III)–Ni(II) and Au(III)–Cr(III). Thus, this novel inorganic–organic hybrid material silica gel chemically modified by triethylenetetraminomethylenephosphonic acid GH-T-P has good adsorption properties and high capacity for Au(III), which can be applied for removing this precious metal element from aqueous solutions.

3.4. Adsorption isotherms

The adsorption isotherm were studied the relationship between equilibrium adsorption capacity and equilibrium concentration at a certain temperature. The absorption capacities of Au(III) onto GH-T-P increased with the increase of temperature. At a certain temperature, it is clear that the adsorption capacities of Au(III) rises with the increase of the equilibrium concentration. As we compared the adsorption capacity of different types of adsorbents using for Au(III) adsorption (Table S1, available online in the supplemental materials), It was clear that the adsorption capacity of GH-T-P was relatively high when compared to several other adsorbents such as L-lysine modified crosslinked chitosan resin, thiol cotton fiber, Alfalfa biomass, poly(vinylbenzylchloride–acrylonitryle–divinylbenzene) modified with tris(2-aminoethyl)amine [12–17]. The above-mentioned research results show that the novel inorganic–organic hybrid material silica gel chemically modified by diethylenetriamine methylene phosphonic acid GH-T-P is favorable and useful for the removal of precious metal ions, and the high adsorption capacity make it a good promising candidate material for Au(III) uptake.

The adsorption isotherms were studied and the data were analyzed with Langmuir equation (2) and Freundlich equation (3) (see Figs. 5 and 6). The Langmuir model, which interpreted homoge-

Table 1
The adsorption selectivity of the hybrid adsorbent GH-T-P for Au(III).

Adsorbent	System	Metal ions	Adsorbents capacity (mmol/g)	Selective coefficient
GH-T-P	Au(III)–Hg(II)	Au(III)	1.51	$\alpha_{Au(III)/Hg(II)} = 4.3$
		Hg(II)	0.35	
	Au(III)–Cu(II)	Au(III)	1.5	$\alpha_{Au(III)/Cu(II)} = 16$
		Cu(II)	0.09	
	Au(III)–Cd(II)	Au(III)	1.42	$\alpha_{Au(III)/Cd(II)} = 46$
		Cd(II)	0.31	
	Au(III)–Pb(II)	Au(III)	1.39	$\alpha_{Au(III)/Pb(II)} = \infty$
		Pb(II)	0	
	Au(III)–Ni(II)	Au(III)	1.4	$\alpha_{Au(III)/Ni(II)} = \infty$
		Ni(II)	0	
	Au(III)–Zn(II)	Au(III)	1.44	$\alpha_{Au(III)/Zn(II)} = \infty$
		Zn(II)	0	
	Au(III)–Cr(III)	Au(III)	1.51	$\alpha_{Au(III)/Cr(III)} = \infty$
		Cr(II)	0	
	Au(III)–Co(II)	Au(III)	1.38	$\alpha_{Au(III)/Co(II)} = \infty$
		Co(II)	0	

Au(III) concentration: 2.5 mmol/L; concentration of coexisting metal ions: 2.5 mmol/L; pH = 2.0; T = 25 °C.

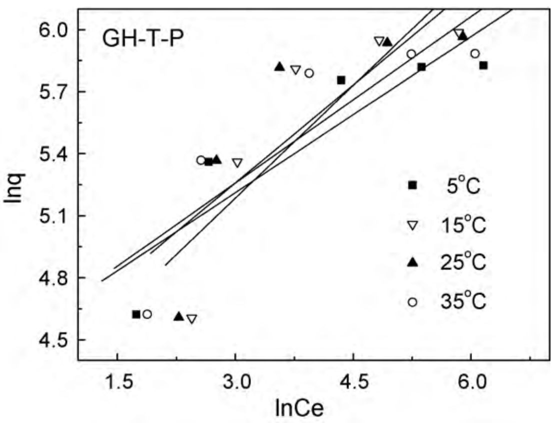

Fig. 6. The Freundich isotherms of the sample GH-T-P for Au(III) at different temperatures.

neous adsorption systems, is represented as:

$$\frac{C_e}{q_e} = \frac{C_e}{q} + \frac{1}{qK_L} \tag{2}$$

where q_e is the adsorption capacity, mg/g; C_e is the equilibrium concentration of Au(III), mg/L; q is the saturated adsorption capacity, mg/g and K_L is the Langmuir adsorption constant, L/mg.

The Freundich isotherm model, which describe heterogeneous adsorption systems, can be expressed as follows:

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \tag{3}$$

where q_e is the adsorption capacity, mg/g; C_e is the equilibrium concentration of Au(III), mg/L; n is Freundlich constant and K_F is the binding energy constant reflecting the affinity of the adsorbents to metal ions, mg/g.

The isotherm parameters of Langmuir and Frendlich for the sorption of Au(III) obtained using least square method showed that the regression coefficients R^2 obtained from Langmuir model were very close to 1, suggesting the Langmuir model could well interpret the studied adsorption procedure. From the comparison of correlation coefficients, it can be concluded that the data were fitted better by Langmuir equation than by Freundlich equation, indicating the adsorption of GH-T-P for Au(III) ion obeyed the Langmuir adsorption isotherm. It is well known that the Langmuir equation is applicable to homogeneous adsorption, where the adsorption of each adsorbate molecule onto the surface had equal adsorption activation energy. The fact shows that the adsorption of the hybrid adsorbent is attributed to monolayer adsorption.

Table S2 (available online in the supplemental materials) gives the N concentrations of the adsorb materials determined by elemental analysis. Furthermore, it is possible to calculate the amount of attached functional groups onto the surface of silica gel (*F*, mmol/g) from the percentage of nitrogen in the functionalized silica gel. The amount of the F of GH-T-P was 0.712 mmol/g. Table S3 (available online in the supplemental materials) gives the results of energy spectrum analysis of GH-T-P. As can be observed from Table S3, the mass percentage of phosphor of GH-T-P was 2.99% confirming the phosphonic acid groups were successfully introduced onto the amino-terminated chelating resin silica gel. Furthermore, it is possible to calculate the amount of attached functional groups onto the surface of silica gel (*F*′, mmol/g) from the percentage of phosphor in the functionalized silica gel. The amount of the *F*′ of GH-T-P was 0.84 mmol/g. Comparing the amount of the *F* with *F*′, it was easy to conclude that the amount of attached functional groups from elemental analysis is consistent with that from energy spectrum analysis. Moreover, the adsorption capacity of resin GH-T-P for Au(III) was 0.97 mmol/g, which was close to the ligand content (about 0.78 mmol/g). Thus, most of the functional groups of resin GH-T-P seemed to form 1:1 complex with Au(III).

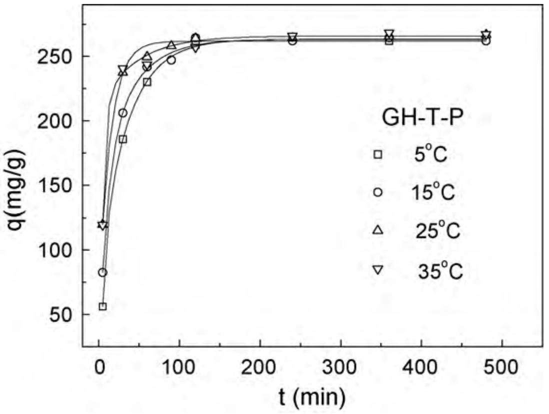

Fig. 7. Adsorption kinetics of Au(III) on GH-T-P at different temperatures (the initial concentration of Au(III): 2.0 mmol/L; pH = 2.0).

FT-IR analysis is a useful technology in exploring the adsorption behaviors of metal ions on adsorbents. In order to further confirm the adsorption mechanism of GH-T-P for Au(III), the changes of characteristic absorption peaks in adsorbents before and after adsorption were investigated by FT-IR. Fig. S1 shows FT-IR spectra of GH-T-P before and after loading with Au(III) ions solution. The band at 1401 cm^{-1} and the broadening peak centered at 3432 cm^{-1}, which can be assigned to the stretching vibration and bending vibration (N–H), were transferred to lower frequencies. It is also observed that a new peak at 972 cm^{-1} occurred in the FT-IR spectrum of GH-T-P after adsorption in Fig. S1 (1). The peak at 972 cm^{-1} is a characteristic peak for the stretching vibration of P–O in the $-PO_3^{2-}$ ions. The results of FT-IR analysis further demonstrated that the adsorption of GH-T-P for Au(III) were carried out through chemical adsorption mechanism, which means N and O atoms of the functional groups of adsorbent GH-T-P seemed to complex with Au(III).

3.5. *Adsorption kinetics*

In order to determine the uptake rate of Au(III) on the as-synthesized adsorbent and get access to the equilibrium time, studies on adsorption kinetics were carried out. The adsorption kinetics of silica gel functionalized by triethylenetetraminomethylenephosphonic acid GH-T-P for Au(III) ions at different temperature was investigated. Fig. 7 showed the adsorption kinetics of GH-T-P for Au(III) at 5–35 °C. As shown in Fig. 7, the adsorption capacities of GH-T-P for Au(III) increased with the extension of contact time, it was obvious that in the first 30 min, the adsorption was rapid, and then slowed considerably. The reason perhaps is that in initial fast adsorption step, Au(III) ions might enter easily the accessible pore sites and bind with the chelating ligands. While in the slow adsorption step, some Au(III) ions might be hampered to diffusion into the deeper pores. As a significant practical importance, the rapid kinetics will facilitate smaller reactor volumes ensuring efficiency and economy. Fig. 7 also displayed that the effect of temperature on the adsorption of Au(III) by the chelating resin GH-T-P, and it was demonstrated that temperature generally has only a slight positive effect on the adsorption capacity. From these experimental data, it was obvious that about 90% of the equilibrium adsorption capacity could be achieved after 1 h. The adsorption equilibrium was completely achieved within 2 h under the given test conditions, and its excellent adsorption capacity for

Table 2
The Bt versus time linear equations and coefficients R^2.

Adsorbent	T (°C)	Linear equation	R^2
GH-T-P	5	$\mathrm{Bt} = 0.0168t + 0.2608$	0.9752
	15	$\mathrm{Bt} = 0.0327t - 0.0672$	0.9763
	25	$\mathrm{Bt} = 0.0311t + 0.3503$	0.9668
	35	$\mathrm{Bt} = 0.0148t + 0.6642$	0.9516

Table 4
The thermodynamic parameters of GH-T-P for Au(III).

Adsorbent	T (K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/K mol)
GH-T-P	278	−18.27	5.17	84.37
	288	−19.11		
	298	−19.98		
	308	−20.79		

Au(III) was 266.49 mg/g when the initial solution concentration was 2.0 mmol/L at 35 °C.

The adsorption procedure of adsorbents for metal ions is generally considered to take place through two mechanisms of film diffusion and particle diffusion. The kinetics experimental results were usually analyzed by Boyd equation and Reichenberg equation in order to distinguish film diffusion from particle diffusion controlled adsorption [12,16]. The relevant equations were given as follows:

$$F = 1 - \frac{6}{\pi^2}\sum\nolimits_{n-1}^{\infty}\frac{1}{n^2}\left[\frac{-D_i t\pi^2 n^2}{r_0^2}\right] \tag{4}$$

or

$$F = 1 - \frac{6}{\pi^2}\sum_{n-1}^{\infty}\frac{1}{n^2}\exp[-n^2 \mathrm{Bt}] \tag{5}$$

and

$$B = \frac{\pi^2 D_i}{r_0^2} = \text{time constant} \tag{6}$$

where n is an integer that defines the infinite series solution; D_i is the effective diffusion coefficient of metal ions in the adsorbent phase; r_o is the radius of the adsorbent particle, assumed to be spherical; F is the fractional attainment of equilibrium at time t, and it is obtained by the expression:

$$F = \frac{q_t}{q_0} \tag{7}$$

where q_t is the amount of adsorbate taken up at time t and q_o is the maximum equilibrium uptake.

Values of Bt can be obtained from corresponding values of F, and Bt–F fitting results were shown in Table 2. Plots of Bt versus time of Au(III) onto GH-T-P at 5–35 °C were used to distinguish between the film diffusion and particle diffusion controlled adsorption. If the plots were straight line passing through the origin, the adsorption process should be dominated by the particle diffusion mechanism, otherwise, it might be governed by the film diffusion. The lines of Bt versus time plots did not pass through the origin in the cases studied, indicating the film diffusion, not the particle diffusion, dominated the adsorption processes of GH-T-P for Au(III).

Moreover, both pseudo-first-order equation and pseudo-second-order equation [12,16] were used to express the adsorption process of the chelating resin GH-T-P for Au(III), and they can be expressed by Eqs. (8) and (9), respectively:

$$\ln\,(q_\mathrm{e} - q_t) = \ln q_\mathrm{e} - k_1 t \tag{8}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_\mathrm{e}^2} + \frac{t}{q_\mathrm{e}} \tag{9}$$

where q_e is the amount of metal adsorbed at equilibrium per unit weight of adsorbent, mg/g, q_t is the amount of metal ion adsorbed at t time, k_1(min^{-1}) and k_2 (g/mg min) are the rate constants of pseudo-first-order and pseudo-second-order adsorption. The experimental and calculated q_e values, k_1, k_2 and regression coefficient (R^2) values were presented in Table 3. Pseudo-first-order kinetic and pseudo-second-order kinetic plots and kinetic parameters for the sorption of Au(III) onto GH-T-P at different temperatures were shown in Figs. S2 and S3 (available online in the supplemental materials), respectively. As seen from Table 3, the obtained coefficients values of the pseudo-second-order model (>0.9993) were better than those of the pseudo-first-order model for the adsorbent (0.8876–0.9941), suggesting the pseudo-second-order model was more suitable to describe the adsorption kinetics of GH-T-P for Au(III). Moreover, the calculated q_e values depending on the pseudo-second-order model were much closer to the experimental values q_e(exp). Therefore, the adsorption kinetics could well be approximated more favorably by pseudo-second-order kinetic model for Au(III) onto GH-T-P.

3.6. Determination of the thermodynamics parameters

From the kinetics adsorption experiments, the thermodynamic parameters such as ΔG, ΔH and ΔS, were obtained from the following equations [12,16]:

$$K_\mathrm{c} = \frac{C_\mathrm{Ae}}{C_\mathrm{e}} \tag{10}$$

$$\log\,K_\mathrm{c} = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \tag{11}$$

$$\Delta G = -RT\,\ln K_\mathrm{c} \tag{12}$$

where C_e and C_Ae are the equilibrium concentration in solution (mg/L) and the solid phase concentration at equilibrium (mg/L), respectively. K_c is the partition coefficients of each temperature. R is the gas constant (8.314 J/mol K), and T is the temperature in Kelvin. From the slope and y-intercept of the linear plot of $\ln K_\mathrm{c}$ versus $1/T$ (shown in Fig. S4, available online in the supplemental materials), the changes of enthalpy and entropy could be obtained. The thermodynamic parameters were listed in Table 4. The positive values of ΔH (5.17 kJ mol^{-1}) indicated that Au(III) ion adsorption on GH-T-P were endothermic. This result was consistent with the above-mentioned case that the adsorption capacities of Au(III) ion increased with the increasing of temperature. The negative value of ΔG (−20.79 kJ mol^{-1} at 35 °C) for Au(III) adsorption on GH-T-P indicated that the adsorption process was spontaneous, and the

Table 3
The adsorption kinetic parameters of GH-T-P for Au(III) at different temperatures.

Adsorbent	T (°C)	$q_\mathrm{e,exp}$ (mg/g)	Pseudo-first-order kinetics			Pseudo-second-order kinetics		
			k_1 (min^{-1})	$q_\mathrm{e,cal}$ (mg/g)	R_1^2	$k_2 \times 10^3$ (g/mg min)	$q_\mathrm{e,cal}$ (mg/g)	R_2^2
GH-T-P	5	264.0	0.0375	288.36	0.9941	0.3049	270.27	0.9993
	15	264.6	0.0264	174.97	0.9547	0.5127	270.27	0.9996
	25	266.8	0.0315	121.36	0.9548	0.8348	270.27	1.0000
	35	268.4	0.0148	75.95	0.8876	0.6678	270.27	0.9999

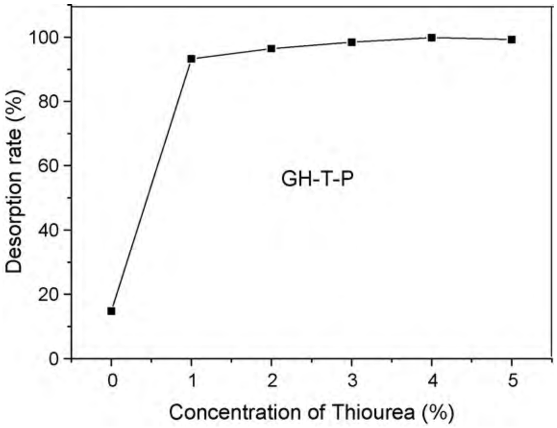

Fig. 8. Effects of different concentrations of thiourea on the desorption rate.

positive values of ΔS (84.37 J K^{-1} mol^{-1}) suggest an increase in the randomness at the solid/solution interface during the adsorption process.

3.7. The recycling properties of GH-T-P

To test the reusability of GH-T-P adsorbents, the Au(III) ion loaded GH-T-P sample were treated with 0.1 mol/L hydrochloric acid and different concentrations of thiourea, respectively, for12 h to remove the Au(III) ions and then neutralized and followed with a second round of metal ion adsorption testing. The results of elution from Fig. 8 show that the system of 2% thiourea + 0.1 mol/L HCl is very efficient, and the elution rate is both up to 99.7%. The results for Au(III) ion adsorption using the regenerated adsorbents are summarized in Table S4 (available online in the supplemental materials). Only a little decrease of the adsorption efficiency was seen in the second use, and the samples retain their Au(III) uptake capacities of 96.7% after twice use cycles. Then the Au(III) uptake capacities decreased gradually in the next successive uses. Therefore, the high adsorption capacity and good reproducibility make this hybrid material had a significant potential for removing Au(III) from aqueous solutions using adsorption method.

4. Conclusions

A novel hybrid material silica gel chemically modified by triethylenetetraminomethylenephosphonic acid GH-T-P has been synthesized and characterized. The results of the adsorption of various metal ions Au(III), Hg(II), Cu(II), Pb(II), Co(II), Zn(II), Ni(II), Cr(II) and Cd(II) from aqueous solution on the as-synthesized GH-T-P showed that this high efficient inorganic–organic hybrid adsorbent had good adsorption capacity for Au(III), Hg(II) and Cu(II) metal ions, especially for Au(III). Moreover, the study indicated the best interpretation for the experimental data was given by the Langmuir isotherm equation, and the adsorption kinetics of GH-T-P can be modeled by pseudo-second-order rate equation wonderfully, and the adsorption thermodynamic parameters ΔG, ΔH and ΔS were -20.79 kJ mol^{-1}, 5.17 kJ mol^{-1}, and 84.37 J K^{-1} mol^{-1}, respectively. Thus, the high adsorption capacity and good reproducibility make this hybrid material have a significant potential for uptaking Au(III) from aqueous solutions using adsorption method.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.05.065.

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