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Preparation and chelation adsorption property of composite chelating material poly(amidoxime)/SiO_2 towards heavy metal ions

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ABSTRACT

Micron-sized silica gel particles were first surface-modified with coupling agent, γ-methacryloylpropyl trimethoxysilane (MPS), introducing polymerizable double bonds into the surfaces of silica gel particles, and then acrylonitrile (AN) was graft-polymerized in the manner of "grafting from", resulting in the grafted particles PAN/SiO_2. In succession, the grafted PAN was transformed into the grafted poly(amidoxime) (PAO) via amidoximation transformation reaction with hydroxylamine hydrochloride as reaction reagent, and the composite chelating particles PAO/SiO_2 were obtained. In this work, the chelating adsorption property and mechanism of PAO/SiO_2 particles towards heavy metal ions were mainly investigated, and the adsorption thermodynamics was also researched. The experiment results show that PAO/SiO_2 particles possess strong chelating adsorption ability for heavy metal ions, for example, the saturated adsorption amounts of Pb^{2+} and Cu^{2+} ions on PAO/SiO_2 particles can get up to 12 and 10 g/100 g, respectively. The adsorption of PAO/SiO_2 towards heavy metal ions is an endothermic chemical adsorption process driven by entropy, and the adsorption capacity increases with raising temperature. The adsorption property of PAO/SiO_2 is dependent on the pH value of the medium, and in a certain pH range, the adsorption ability is strengthened with increasing pH value. The adsorption of PAO/SiO_2 for heavy metal ions is selective, and the adsorption capacity is in the order of $Cu^{2+} \gg Ni^{2+} > Pb^{2+} > Cd^{2+}$.

1. Introduction

Heavy metal pollution has become more serious with the rapid increase in global industrial activities. Heavy metal pollution has accumulating characteristics in nature and cannot be biodegraded, and this environmental issue is threatening the health of human beings seriously. There is a continuous need for new separation techniques which selectively extract metal ions from dilute wastewaters and industrial process streams. Among various methods of the heavy metal removal such as precipitation, reduction, electrochemical treatment, reverse osmosis, solvent extraction, membrane filtration, ion exchange and adsorption, the last is generally preferred because of its high efficiency, ease of handling, and availability of different sorbents. Nowadays, among various solid adsorbents, chelating resins are increasingly used in the removal of metal ions due to their high adsorption capacities and selectivity [1–5]. Except chelating resins, recently, composite chelating materials, which consist of the chelating agent and inorganic particle matrix, such as silica gel, attapulgite, smectite, bentonite and hydroxyapatite [6–9], have been developed greatly because of a good combination of chelating functionality of the chelating agent and excellent mechanical strength of the inorganic matrix. Among such materials, a kind of novel composite chelating materials, which consist of the polymer with chelating function and inorganic matrix particles, has attracted much attention for the applications in the removal of heavy metals from different industrial wastewaters [10–12]. The novel composite materials combine well with the strong chelating property of the polymer, which is coming from high density of chelating ligands, with the high specific area, excellent mechanical property and thermal and chemical stability as well as low cost of inorganic particles. For preparing these composite chelating materials, two methods can be adopted. One is coating or impregnating the inorganic particles with the solutions of chelating polymers [13–15], and this is a conventional and simple method; another method is to try to chemically bond the polymer with chelating function onto the surfaces of the inorganic particles (chemically anchoring or grafting) [16]. This method is more effective due to the combining stability of the polymers and inorganic particles, and should be developed vigorously.

There are many types of chelation group, such as iminoacetate, Schiff base, aminophosphonate, 8-hydroxyquinoline and amidoxime. Among these chelation groups, amidoxime group has very strong chelation action towards many rare earth and heavy metal ions, so the chelating materials carrying amidoxime groups

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attract much attention in the enrichment, recovery and removal of rare earth and heavy metal ions [17–19]. Especially, in uranium recovery from seawater, the amidoxime-type chelating materials play a unique role [20–23]. Most of amidoxime-type chelating adsorption materials are derived from the chemical transform of polyacrylonitrile [24–26]. In this work, we prepared an amidoxime-type composite chelating material PAO/SiO_2, in whose structure poly (amidoxime) (PAO) macromolecules were grafted on the surfaces of silica gel particles, and the chelating adsorption properties of PAO/SiO_2 for some heavy metal ions as well as adsorption thermodynamics were mainly investigated. The investigation result indicates that the composite chelating material PAO/SiO_2 have strong adsorption ability for some heavy metal ions by right of strong chelation. The composite material PAO/SiO_2 combines well the strong chelating adsorption ability of PAO for some heavy metal ions with the excellent physicochemical properties of silica gel particles, and such material is significant and promising in environmental protection.

2. Experimental

2.1. Materials and equipments

Silica (120–160 mesh, about 125 μm of diameter, Ocean Chemical Limited Company, Qingdao city, Province Shandong, China) was of agent grade. γ-Methacryloylpropyl trimethoxysilane (MPS, Nanking Chuangshi Chemical Aux Ltd., Province Jiangsu, China) was of analytical grade. Acrylonitrile (AN, Fuchen Chemical Reagent Plant, Tianjin city, China) was of analytical grade, and was purified by vacuum distillation before use. Hydroxylamine hydrochloride (HAHC, Chengyuan Trade Ltd., Tianjin city, China) was of analytical grade. Azobisisobutyronitrile (ABIN, Guanfu Fine Chemical Institute, Tianjin city, China) was of analytical grade, and was purified by recrystallizing from ethanol. The other chemicals used were all of commercial analytical grade, and were purchased from Chinese companies.

The used instruments in this study were as follows: Perkin-Elmer 1700 infrared spectrometer (FTIR, Perkin-Elmer Company, American); LEO-438VP scanning electronic microscope (SEM, LEO Company, UK), PHS-3C pH meter (Shanghai Precision Scientific Apparatus Inc., Shanghai city, China); STA449 thermogravimetric analyzer (TGA, Netzsch Company, Germany); THZ-92C constant temperature shaker equipped with gas bath (Shanghai Boxun Medical Treatment Equipment Factory, Shanghai city, China).

2.2. Preparation and characterization of grafted particles PAN/SiO_2

According to the procedures described in Ref. [27], silica gel particles were surface-modified with coupling agent MPS, and the polymerizable double bonds were introduced on the surfaces of silica gel particles, resulting in modified silica gel particles MPS-SiO_2. The double bond content was determined with KBr-$KBrO_3$ method, and was 2.11 mmol/g.

1.23 g of the modified particles MPS-SiO_2 was added into a four-necked flask equipped with a mechanical agitator, a reflux condenser, a thermometer and a N_2 inlet, followed by adding 100 mL of *N*,*N*-dimethylformamide (DMF) solution in which 11.79 mL of monomer AN was dissolved. The content was stirred and the modified particles MPS-SiO_2 were made to be dispersed fully. N_2 was bubbled for 30 min to exclude air. The content was heated to 75 °C, and 0.143 g of initiator ABIN was added. The graft polymerization was performed under N_2 atmosphere at 75 °C for 5 h. The resultant particles were extracted with acetone in a Soxhlet for 24 h to remove the polymer attaching physically to the particles, dried under vacuum, and finally the grafted particles PAN/SiO_2 were obtained. The IR spectrum of PAN/SiO_2 particles was determined with KBr pellet method. The grafting degree (GD, g/100 g) of PAN/SiO_2 particles was determined with TGA method, and the used PAN/SiO_2 particles in this study have a grafting degree of about 14 g/100 g.

2.3. Preparation and characterization of composite particles PAO/SiO_2

20 mL of aqueous hydroxylamine hydrochloride solution with a concentration of 1.0 M and 20 mL of aqueous Na_2CO_3 solution of 1.0 M were mixed (the pH value of the mixed solution was 6.5). The mixed solution was added into a four-necked flask, followed by adding 1 g of grafted particles PAN/SiO_2. The amidoximation transform reaction of the nitrile groups of the grafted PAN was conducted with stirring under N_2 atmosphere at 70 °C for 4 h. The product particles were washed with distilled water repeatedly until the cleaning liquid was neutral. After vacuum drying, the functional composite particles PAO/SiO_2 were obtained.

The IR spectrum of particles PAO/SiO_2 was determined with KBr pellet method to characterize the chemical structure. Weighing method was used to measure the amount of the AN unit of the grafted PAN that has converted into amidoxime unit, and the conversion (Conv., mol%) of nitrile groups was further calculated. The used functional particles PAO/SiO_2 in this work have a nitrile group conversion of about 78%.

2.4. Examining the adsorption properties of composite particles PAO/SiO_2 for several heavy metal ions

2.4.1. Adsorption kinetics experiment

Numbers of 25 mL of $Pb(NO_3)_2$ solution of 0.005 M were placed into numerous conical flasks with plug, and 0.1 g of PAO/SiO_2 particles was added into these solutions. These conical flasks were placed in a constant temperature oscillator and were shaken. At different time intervals, the mixtures were taken out, respectively, and after centrifugal separation, the Pb^{2+} concentrations in the supernatants were determined by EDTA complexometric titration. The corresponding adsorption amounts were calculated, and the adsorption kinetics curve was plotted, obtaining the equilibrium adsorption time.

2.4.2. Isothermal adsorption experiments

Based on the adsorption kinetics experiments, the isothermic adsorption experiments of PAO/SiO_2 particles towards Pb^{2+} ion were conducted. $Pb(NO_3)_2$ solutions with different concentrations were prepared in a concentration range of 2.5×10^{-3} to 3.5×10^{-2} M. Numbers of 25 mL of $Pb(NO_3)_2$ solutions with different concentrations were placed into numerous conical flasks with plug, and about 0.1 g of particles weighted accurately was added into these solutions. These mixtures were shaken on a constant temperature oscillator for 3.5 h, and the adsorptions were allowed to reach equilibrium. After centrifugal separation, the Pb^{2+} concentrations in the supernatants were determined, and the equilibrium adsorption amount was calculated according to Eq. (1). The relationship curve between the equilibrium adsorption amount and the equilibrium concentration of Pb^{2+} ion was plotted, namely, the adsorption isotherm of PAO/SiO_2 for Pb^{2+} ion was obtained.

$$Q_e = \frac{V(C_0 - C_e) \times 207}{m \times 10} \tag{1}$$

where Q_e (g/100 g) is the equilibrium adsorption amount; V (mL) is the volume of the solution; C_0 (mol/L) is the Pb^{2+} ion concentration in the initial solution; C_e (mol/L) is the equilibrium concentration of

Pb^{2+} ion in the supernatant; *m* (g) is the mass of PAO/SiO_2 particles; relative molar mass of Pb atom is equal to 207.

2.4.3. Examining effects of main factors on the chelating adsorption property of PAO/SiO$_2$

(1) *Examining the effect of pH value on the chelating adsorption properties of PAO/SiO$_2$*: By varying the pH value of the Pb^{2+} ion solutions, the isothermal adsorption experiments were performed at different pH values to examine the effect of pH value on the chelating adsorption property of PAO/SiO_2, and to investigate the chelating adsorption mechanism of PAO/SiO_2 particles towards heavy metal ions.

(2) *Examining the chelating adsorption abilities of PAO/SiO$_2$ towards different heavy metal ions*: The heavy metal ion solutions with different concentrations for the four kinds of ions, Pb^{2+}, Cu^{2+}, Cd^{2+} and Ni^{2+} ions, were prepared (the used compounds were all nitrates, i.e. $Pb(NO_3)_2$, $Cu(NO_3)_2$, $Cd(NO_3)_2$ and $Ni(NO_3)_2$) and the isothermal adsorption experiments of PAO/SiO_2 particles towards the four ions were carried out, respectively, obtaining the corresponding adsorption isotherms. During determining the concentrations of the four ions by EDTA complexometric titration, the different indicators were used. Chrome black T is used for Pb^{2+} and Cd^{2+} ions, xylenol is used for Cu^{2+} ion and murexide is used for Ni^{2+} ion, respectively.

(3) *Examining the effect of temperature on the chelating adsorption property of PAO/SiO$_2$*: The isothermal adsorption experiments were carried out at different temperatures to evaluate the effect of the temperature on the chelating adsorption property of PAO/SiO_2 and to investigate in depth the chelating adsorption thermodynamics.

3. Results and discussions

3.1. Reaction process to prepare functional composite particles PAO/SiO$_2$

Silica gel particles were first surface-modified with couple reagent MPS so as to introduce polymerizable double bonds onto the surfaces of silica gel particles, resulting in modified particles MPS-SiO_2. Then the graft polymerization of acrylonitrile (AN) was allowed to be conducted in the manner of "grafting from" and on the surfaces of MPS-SiO_2 particles by initiating of ABIN, forming grafted particles PAN/SiO_2. Finally, by the action of hydroxylamine which is released from the reaction of hydroxylamine hydrochloride and sodium carbonate, the nitrile groups of the grafted PAN were gradually transformed into amidoxime (AO) groups, resulting in the functional composite particles PAO/SiO_2 on which poly (amidoxime) (PAO) macromolecules were grafted. The entire chemical process to prepare the composite particles PAO/SiO_2 is expressed schematically in Scheme 1.

3.2. Characteristic of PAN/SiO$_2$ and PAO/SiO$_2$ particles

3.2.1. Infrared spectra

Fig. 1 presents the infrared spectra of three kinds of particles, silica gel particles SiO_2, grafted particles PAN/SiO_2 and functional particles PAO/SiO_2. In comparison to the spectrum of SiO_2, in the spectrum of PAN/SiO_2, the characteristic vibration absorption band of nitrile group C≡N appears at 2240 cm^{-1} (the vibration absorption of nitrile group is very weak), and the absorption band of silanol group at 3440 cm^{-1} becomes obviously weak because of the surface modification of silica gel as well as the graft polymerization. These changes indicate the formation of the grafted particles PAN/SiO_2. In the spectrum of PAO/SiO_2, the absorption band of nitrile group C≡N at 2240 cm^{-1} has disappeared. There appear two new bands at 1660 cm^{-1} and 950 cm^{-1}. The former should be ascribed to the vibration absorption of C=N bond in amidoxime group, and the latter should be attributed to the vibration absorption of N–O bond in amidoxime group. Furthermore, the stretching vibration absorption band of –NH_2 group of amidoxime group appears at 3300 cm^{-1}. The above changes demonstrates that the amidoximation transform of the grafted PAN has been realized, and the functional composite particles PAO/SiO_2 on which poly(amidoxime) macromolecules are grafted have been prepared. It needs to be pointed out that all of the above various absorption bands of PAO/SiO_2 as well as that of PAN/SiO_2 look very weak because of the affect of the strong absorption background of SiO_2.

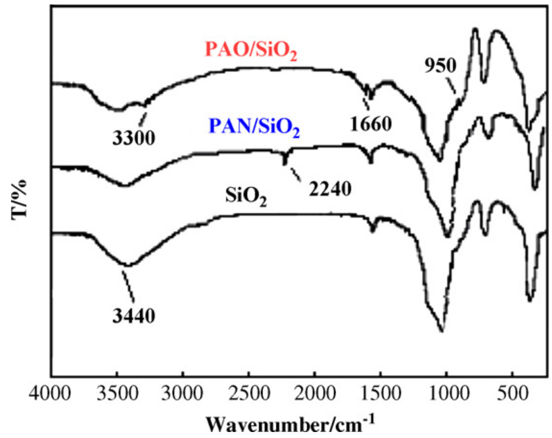


Fig. 1. Infrared spectrum of three kinds of particles.

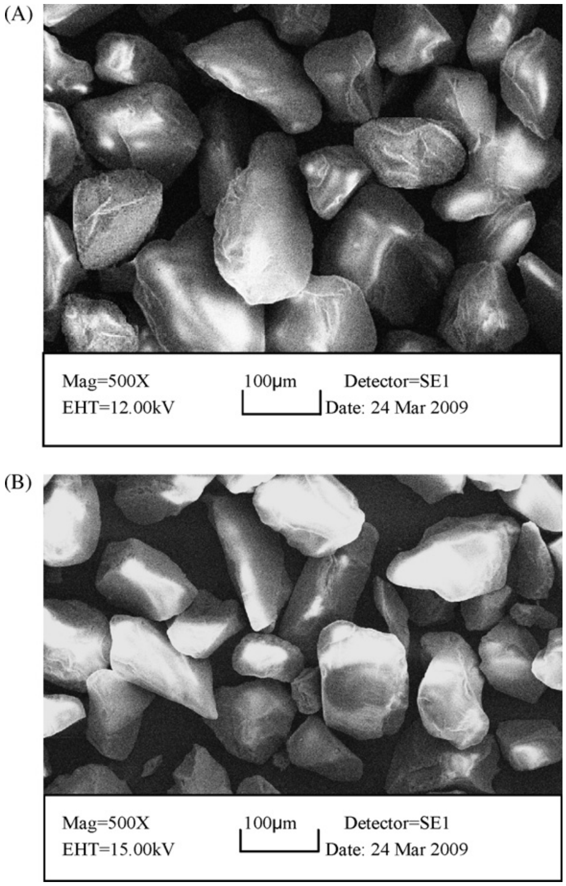
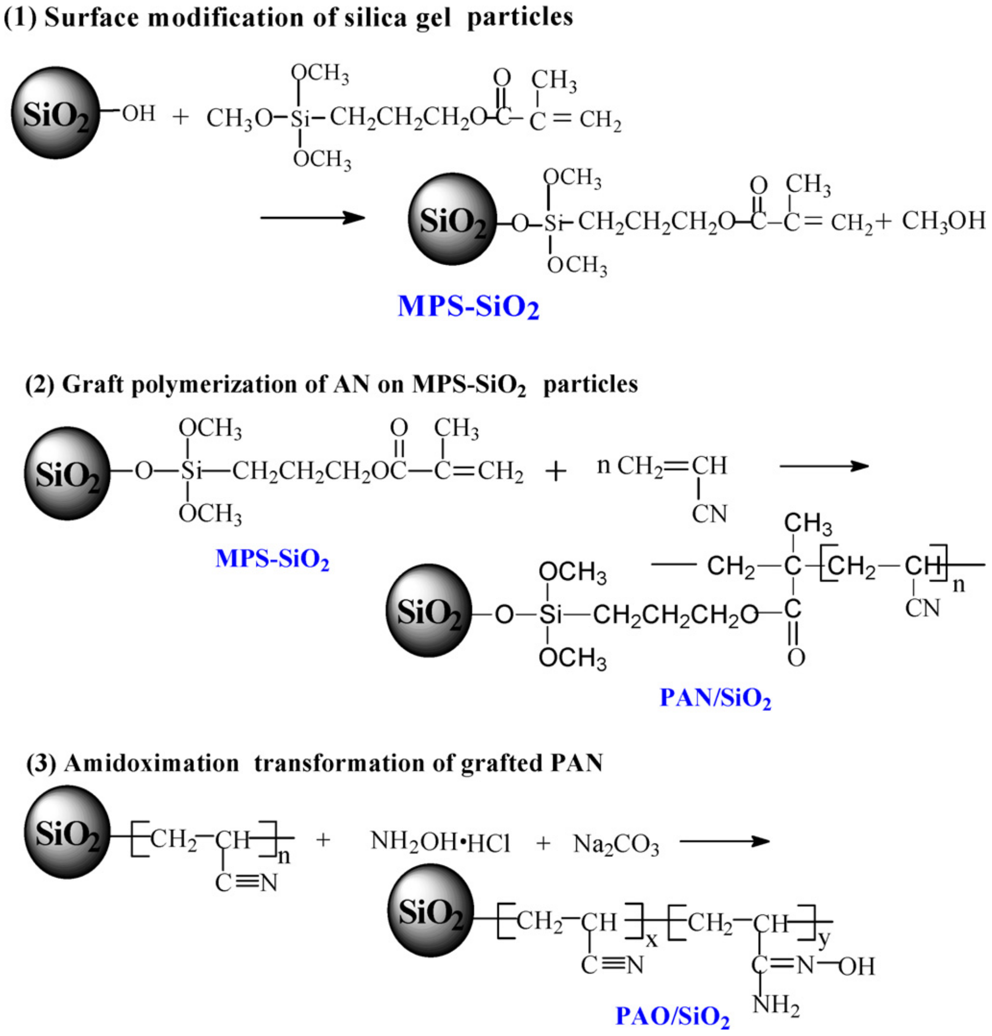


Fig. 2. SEM images of SiO_2 and PAN/SiO_2 particles. A: SiO_2; B: PAN/SiO_2.



Scheme 1. Schematic illustration of preparation process of composite particles PAO/SiO_2.

3.2.2. SEM image

Fig. 2(A) and (B) presents the SEM images of raw silica gel particles and the grafted particles PAN/SiO_2. It can be found that before the grafting of PAN, the surfaces of raw silica gel particles are rough and scraggy. After the grafting of PAN, the surfaces of the grafted particles PAN/SiO_2 become smoother, and this is caused by the coating and filling up action of the grafted PAN macromolecules. The surface condition of PAO/SiO_2 particles is similar to that of PAN/SiO_2 particles.

3.3. Isothermal adsorption behavior and mechanism of PAO/SiO_2 towards heavy metal ions

3.3.1. Adsorption kinetics curve

Fig. 3 gives the adsorption kinetics curve of the functional particles PAO/SiO_2 towards Pb^{2+} ion. It can be seen from Fig. 3 that in 3.5 h, the adsorption of PAO/SiO_2 can reach equilibrium, displaying a faster adsorption rate. This is mainly due to that there are a mass of hydrophilic amidoxime groups on PAO/SiO_2 particles, and it makes the polymeric layer on PAO/SiO_2 particles to have excellent swelling property in water resulting in the smaller diffusion resistance of Pb^{2+} ions, so that Pb^{2+} ions are easy to diffuse within the polymeric layer, and a faster adsorption kinetics behavior of PAO/SiO_2 is displayed.

3.3.2. Adsorption isotherms

By using the three particles, silica gel particles SiO_2, the grafting particles PAN/SiO_2 and the functional particles PAO/SiO_2, the isothermal adsorption experiments were carried out for Pb^{2+} ion at 30 °C, respectively, and the adsorption isotherms are presented in Fig. 4.

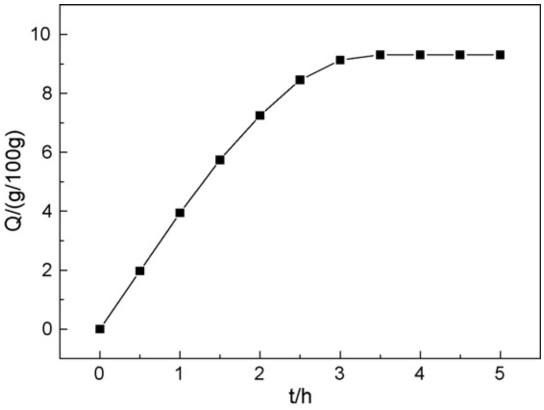


Fig. 3. Adsorption kinetics curve of PAO/SiO_2 particles towards Pb^{2+} ions. $T = 30\,^{\circ}C$; pH = 4.

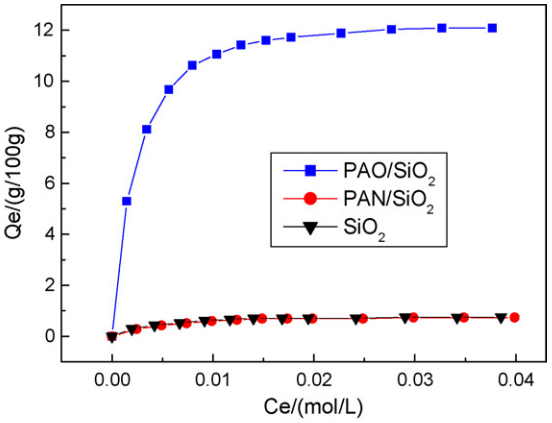
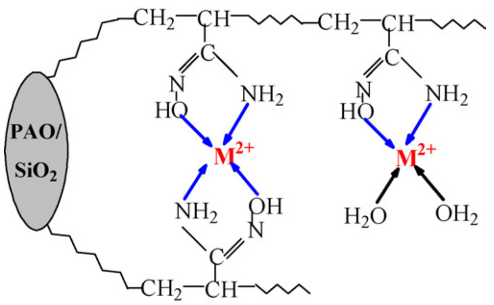


Fig. 4. Adsorption isotherm of PAO/SiO_2 for Pb^{2+} ion. $T = 30\,^{\circ}C$; pH = 5.

It can be seen that the adsorption ability of SiO_2 particles for Pb^{2+} ions is very weak because there are no functional groups that can interact with Pb^{2+} ions. Similarly, it also can be found that the adsorption ability of PAN/SiO_2 particles for Pb^{2+} ions is also very weak, or rather PAN/SiO_2 particles do not adsorb Pb^{2+} ions basically due to that there is no interaction between the nitrile groups of PAN and Pb^{2+} ions. However, after amidoximation transform of the grafted PAN, the functional particles PAO/SiO_2 exhibit strong adsorption ability for Pb^{2+} ion, and the saturated adsorption amount gets up to 12 g/100 g. The adsorption behavior of PAO/SiO_2 for Pb^{2+} ion apparently belongs to Langmuir mode, namely, a monomolecular layer adsorption mode. The adsorption action of PAO/SiO_2 for Pb^{2+} ion is originated from the strong chelation of amidoxime groups towards Pb^{2+} ion. Amidoxime group is a bidentate ligand, and a stable five-membered chelating ring can form between one amidoxime group and one Pb^{2+} ion. The possible combining mode of PAO/SiO_2 with Pb^{2+} ion is shown in Scheme 2, indicating the possible ortho-effect of PAO/SiO_2, namely, the co-chelation of the adjacent amodoxime units of PAO macromolecules on PAO/SiO_2 for Pb^{2+} ion. Just the chelation of amodoxime group towards Pb^{2+} ion enables PAO/SiO_2 particles to have strong chelating adsorption ability for Pb^{2+} ions.

3.3.3. *Effect of pH value of medium on adsorption property of PAO/SiO_2 and adsorption mechanism*

By varying the pH value of the medium, the isothermal adsorption experiments of PAO/SiO_2 for Pb^{2+} and Cu^{2+} ions at different pH values were carried out, respectively, and Fig. 5 presents the adsorption isotherms of PAO/SiO_2 for Pb^{2+} ion at different pH values. In order to display more clearly the effect of pH value, by taking the saturated adsorption data in Fig. 5, the saturated adsorption amount as a function of pH value is shown in Fig. 6.



Scheme 2. Possible model of chelation adsorption of PAO/SiO_2 for Pb^{2+}ion.

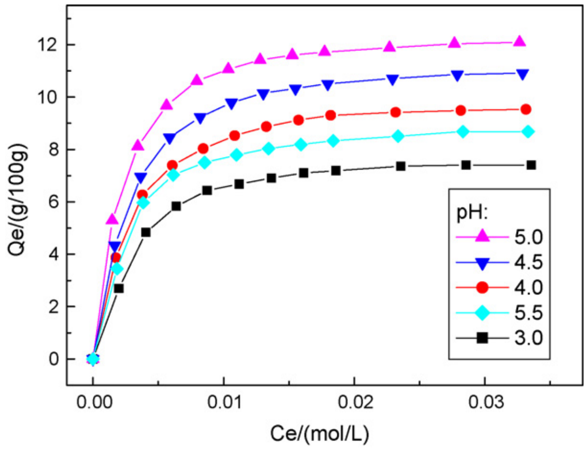


Fig. 5. Adsorption isotherm of PAO/SiO_2 for Pb^{2+} ions at different pH values. $T = 30\,^{\circ}C$.

The following facts can be found from Figs. 5 and 6. As pH < 5, the adsorption capacity of PAO/SiO_2 for Pb^{2+} ion increases with increasing pH value; as pH = 5, the adsorption capacity gets up to a maximum; over pH 5, the adsorption capacity turns to decline with the increase of pH value (in the experiment, here the system became turbid). The above facts reflect the interaction mechanism between PAO/SiO_2 particles and Pb^{2+} ions, and it can be explained as follows. The amidoxime group has amphiprotic property [28], so the amidoxime groups of the grafted PAO will exhibit this property. At lower pH, the basic amino groups of amidoxime groups of PAO/SiO_2 will be highly protonized, displaying the cationic character, whereas at higher pH, the acidic hydroxyl groups of oxime groups will dissociate, exhibiting the anionic character. As pH is lower, the amino groups of amidoxime groups will lose the complex ability towards Pb^{2+} ions due to protonation, leading to the low adsorption ability of PAO/SiO_2 particles for Pb^{2+} ions. Along with the increase of pH value, the protonation degree of the amino groups of amidoxime groups will be weakened, and the coordination and chelating ability of these amino groups towards Pb^{2+} ions will be strengthened. In addition, here the dissociation degree of oxime hydroxyl groups will increase, and negative oxygen-ion of oxime hydroxyl groups will be produced, resulting in the electrostatic interaction between PAO/SiO_2 particles and Pb^{2+} ions. By the synergism of the electrostatic interaction and the chelating action, a mass of Pb^{2+} ions will be attracted to the surfaces of PAO/SiO_2 particles and then is chelated, leading to the high adsorption capacity. However, the heavy metal ions are easy to be hydrolyzed. As pH > 5, the hydrolysis of Pb^{2+} ions has become obvious (the first

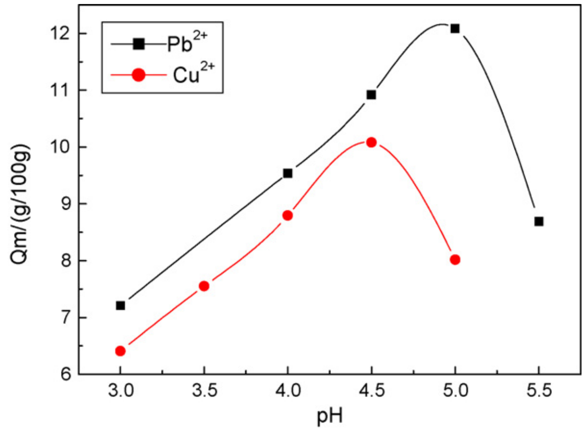


Fig. 6. Effect of pH value on adsorption property of PAO/SiO_2.

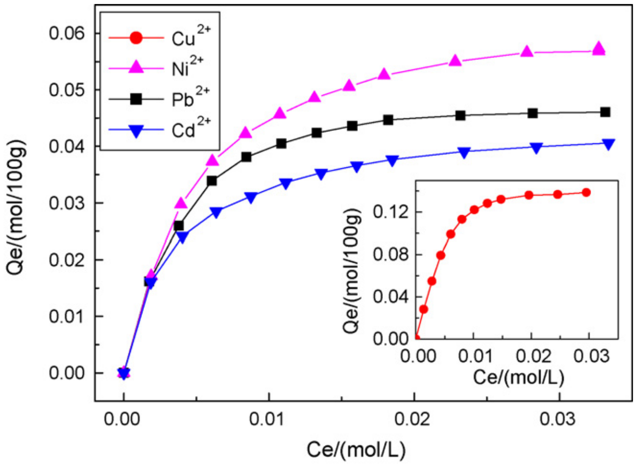


Fig. 7. Adsorption isotherm of PAO/SiO_2 for different metal ions. T = 30 °C; pH = 4.

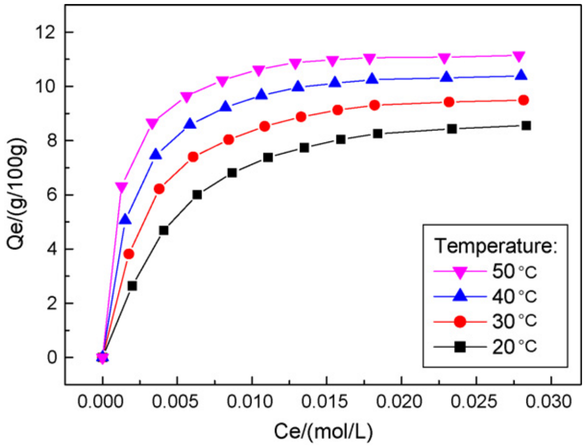


Fig. 8. Adsorption isotherm of PAO/SiO_2 for Pb^{2+} ions at different temperatures. pH = 4.

order hydrolysis constant of Pb^{2+} ion is $K_1 = 6.3 \times 10^{-8}$), and the surfaces of PAO/SiO_2 particles will be covered with the hydrolysis product. This will badly affect the adsorption property of the solid adsorbent [24] and lead to the decline of the adsorption capacity.

The saturated adsorption amount of Cu^{2+} ion on PAO/SiO_2 particles as a function of pH value is also displayed in Fig. 6, and the similar variation trend is also displayed (the maximum saturated adsorption amount of Cu^{2+} ion can get up to 10 g/100 g). Because the hydrolysis resistance of Cu^{2+} ion is weaker than that of Pb^{2+} ion (the first order hydrolysis constant of Cu^{2+} ion is $K_1 = 3.16 \times 10^{-7}$), the maximum adsorption capacity of Cu^{2+} ion appears at a lower pH value, pH 4.5.

In a word, for the strong chelating adsorption action of PAO/SiO_2 particles towards heavy metal ions, the driving force comes from the cooperation of electrostatic interaction and coordination chelating action.

3.4. Adsorption properties of PAO/SiO_2 particles towards various heavy metal ions

The isothermal adsorption experiments of PAO/SiO_2 particles towards four kinds of heavy metal ions, Pb^{2+}, Cu^{2+}, Cd^{2+} and Ni^{2+} ions, were conducted at the same temperature, respectively, and Fig. 7 gives the corresponding adsorption isotherms. It needs to be pointed out that in order to substantively display the adsorption abilities of PAO/SiO_2 particles towards various heavy metal ions, for the adsorption isotherms of Fig. 7, the equilibrium adsorption amount is expressed as mol/100 g.

It is displayed in Fig. 7 that the adsorption capacities of the four ions on PAO/SiO_2 particles are in the order: $Cu^{2+} \gg Ni^{2+} > Pb^{2+} > Cd^{2+}$. It is obvious that PAO/SiO_2 particles exhibit the strongest chelating adsorption affinity for Cu^{2+} ions among the four heavy metal ions, and the saturated adsorption amounts get up to 0.14 mol/100 g. The different adsorption abilities of the identical chelating adsorbent towards various heavy metal ions are dependent on the ionic structures of these heavy metal ions probably, namely, are dependent on the structures of the valence electron orbits of these heavy metal ions.

3.5. Effect of temperature on adsorption property of PAO/SiO_2 and chelating adsorption thermodynamics

The isothermal adsorption experiments of PAO/SiO_2 for Pb^{2+} ion at different temperatures were carried out, and the adsorption isotherms at different temperatures are presented in Fig. 8. It can be seen that the adsorption capacity of Pb^{2+} ion increases with raising temperatures. The physical adsorption is an exothermic process, and the adsorption capacity of the adsorbate always decreases with raising temperatures. It is apparent that the adsorption of Pb^{2+} ions on PAO/SiO_2 particles is an endothermic process implying a chemical adsorption process [26], and for this, the further explanation will be described below. This chemical adsorption is originated from the coordination and chelating action of the amidoxime groups of PAO/SiO_2 towards Pb^{2+} ions.

The straight line form of Langmuir adsorption isotherm is presented in Eq. (2), and the figure of C_e/Q_e versus C_e should be a straight line.

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \quad (2)$$

where C_e (mol/L) is the equilibrium concentration of Pb^{2+} ion; Q_e (g/100 g) is the equilibrium adsorption amount of Pb^{2+} ion; Q_m (g/100 g) is the saturated adsorption amount of Pb^{2+} ion; b is Langmuir constant. According to Eq. (2), for the adsorptions data of Pb^{2+} ion at different temperatures as shown in Fig. 8, four straight lines are obtained and they are presented in Fig. 9. It can be seen from Fig. 9 that for the four straight lines, the linear dependences are all fine. The Langmuir constants at different temperatures can be obtained by the slopes and intercepts of the four lines.

In the strict sense, for the solid–liquid (solid–water solution) adsorption, when the adsorption of the solute on the solid adsorbent is investigated, at the same time, the adsorption of the solvent (water) on the solid adsorbent should also be considered. Here, there is a relationship between the Langmuir constant b and the adsorption equilibrium constant K as shown in Eq. (3) [5,29,30].

$$b = (K - 1) \times \frac{M}{\rho} \quad (3)$$

where M and ρ are the molar mass and density of the solvent (water), respectively. For the adsorption system of PAO/SiO_2–Pb^{2+} ion, the Langmuir constants at different temperatures can be obtained from Fig. 9, and then according to Eq. (3), the adsorption equilibrium constants at different temperatures can be resulted in.

Van't Hoff equation shown in Eq. (4) indicates the relationship between the adsorption equilibrium constant K and the temperature T [29], in which ΔH is the adsorption enthalpy change.

$$\ln K = -\frac{\Delta H}{R} \times \frac{1}{T} + C \quad (4)$$

For the adsorption system of PAO/SiO_2–Pb^{2+} ion, the straight line of $\ln K$ versus $1/T$ is plotted and is presented in Fig. 10. The adsorption enthalpy change ΔH is obtained from the slope of this straight line, and it is equal to 41.32 kJ/mol.

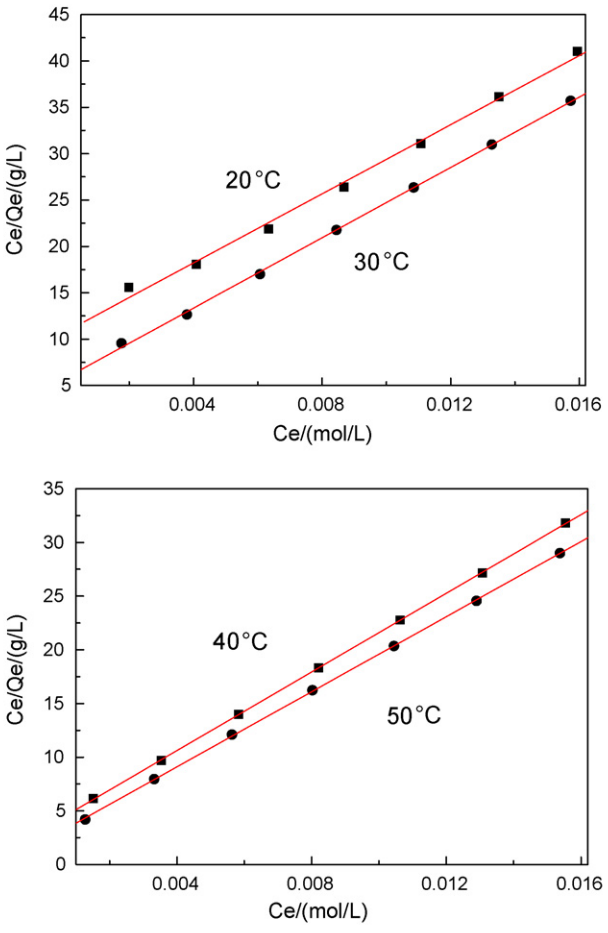


Fig. 9. Linearized Langmuir isotherm plots at different temperatures.

Eq. (5) presents the relationship between the adsorption Gibbs free energy change ΔG and the equilibrium constant K, whereas Eq. (6) indicates the mutual relationship of ΔG, ΔH and ΔS (adsorption entropy change) [5,30]. From Eq. (5), the data of ΔG at different temperatures can be obtained, and according to Eq. (6), the data of ΔS can be easily calculated. The data of ΔG, ΔH and ΔS are together summarized in Table 1.

$$\Delta G = -RT \ln K \tag{5}$$

$$\Delta G = \Delta H - T\,\Delta S \tag{6}$$

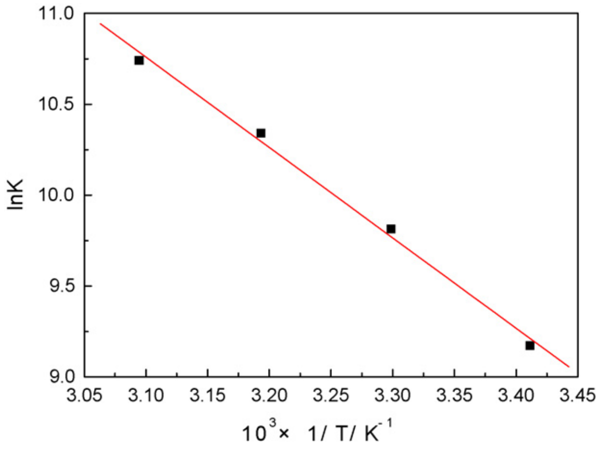


Fig. 10. Relationship curve between ln K and $1/T$.

Table 1
Thermodynamics parameters for adsorption of Pb^{2+} ions on particles PAO/SiO_2.

T (K)	$-\Delta G$ (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
293.15	22.35	41.32	217.19
303.15	24.73	41.32	217.88
313.15	26.92	41.32	217.91
323.15	28.86	41.32	217.17

The following facts are displayed from the data in Table 1. (1) The Gibbs free energy change ΔG is negative, demonstrating the chelating adsorption process of PAO/SiO_2 particles towards heavy metal ions is spontaneous; (2) the adsorption enthalpy change ΔH is greater than zero, indicating that the chelating adsorption is an endothermic process and suggesting that the chelating adsorption is a chemical adsorption process [31]; (3) the adsorption entropy ΔS is greater than zero, displaying the chelating adsorption is a process of entropy increase.

It can be deduced by combining the above data and Eq. (6) that the adsorption of the chelating material PAO/SiO_2 towards heavy metal ions is a spontaneous process driven by entropy, and raising temperature is of great advantage to the adsorption process. The entropy increase is caused by the release of free water molecules from the hydration ions. Before adsorption, Pb^{2+} ion in the solution exists as hydration ion, and one Pb^{2+} ion combines with four water molecules. After Pb^{2+} ion is chelated by the amidoxime group of PAO/SiO_2, these water molecules originally combined with Pb^{2+} ion will be replaced partially or completely by the amino groups and hydroxyl groups of amidoxime groups, and are released as free molecule. As a result, the number of the particle in the system increases greatly, leading to the increase of entropy. In general, the adsorption processes are driven by enthalpy, namely enthalpy change is a larger negative value resulting in a negative Gibbs free energy change. The adsorption process, in which the entropy factor plays a dominant role, is unusual, but such case can be found in the chelation adsorption systems [32,33].

4. Conclusions

By using a three-step chemical process, surface modification of silica gel particles, graft polymerization and polymer reaction (aminoximation transform), composite chelating material PAO/SiO_2 on which poly(amidoxime) macromolecules were grafted was successfully prepared. PAO/SiO_2 particles have strong chelating adsorption ability for heavy metal ions, especially for Cu^{2+} ion. The adsorption of PAO/SiO_2 for heavy metal ions is a chemical adsorption process driven by entropy, and to raise temperature can accelerate the adsorption process. The adsorption of PAO/SiO_2 for heavy metal ions is dependent on pH value of the medium, and in a range of lower pH, the adsorption ability of PAO/SiO_2 for heavy metal ions is strengthened with the increase of pH value. PAO/SiO_2 particles have definite adsorption selectivity for heavy metal ions, and the adsorption capacities towards various metal ions are in the order: $Cu^{2+} \gg Ni^{2+} > Pb^{2+} > Cd^{2+}$.

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