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Selective adsorption of Pb(II) by a silica gel-immobilized Schiff base

Long Li, Yi Qian*, Haiming Zhang, Haoyue Han, Peng Qiao

College of Environment and Safety Engineering, Qingdao University of Science and Technology, Qingdao 266042, China, Tel. +86 84022020; Fax: +86 84022017; emails: lli@yic.ac.cn (L. Li), qianyi1962@126.com (Y. Qian), 651864511@qq.com (H.M. Zhang), 332886420@qq.com (H.Y. Han), 1192207563@qq.com (P. Qiao)

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ABSTRACT

A novel silica gel-based absorbent SG-GA, capable of selective adsorption of Pb(II) from an aqueous solution containing mixed metal ions of Cr(VI) and Cu(II), was prepared by grafting of a Schiff base glutaraldehyde (GA) ligand onto the surface of a modified silica gel. The functionalized silica gels were characterized by Fourier-transform infrared spectroscopy, thermogravimetric analysis, and porous structure analysis. The effect of pH, contact time, the concentration of Cr(VI) and Cu(II), and initial Pb(II) concentration parameters on the adsorption of Pb(II) ions were investigated. The effective pH range for selective Pb(II) adsorption was in the region 3~8. The adsorption study showed that SG-GA had good adsorption efficiency for Pb(II), and the maximum adsorption capacity was 19.96 mg g^{-1}. The adsorption kinetics of Pb(II) followed the pseudo-second-order kinetic models and the adsorption isotherms fitted well by Langmuir models, these results implied that the absorption selectivity may be tuned by modifying the structural conformation for the sites of metal ion binding through complexion. This study provides interesting material for selectively and effectively remove Pb(II) from water effluents containing mixed metal salts.

Keywords: Schiff base; Silica gel; Pb(II); Adsorption behavior

1. Introduction

Environmental contamination with heavy metal ions has been a significant concern in most industrial branches due to their tendency to accumulate in living organisms and their toxicities to aquatic lives, human beings, and ecosystems [1,2]. Among these existing heavy metals, Pb(II) emerges as one of the most troublesome metals due to its detrimental effects on human and animal health and obstructs the self-purification of water bodies [3,4]. Then the permissible limit has been set as 0.05 and 0.01 mg L^{-1} by U.S. Environmental Protection Agency (USEPA) and the World Health Organization, respectively [5,6]. A variety of technologies, including coagulation–flocculation, membrane separation, ions exchanges, liquid–liquid extraction and adsorption were implemented to remove Pb(II) from the wastewater [7–17]. Among these methods, adsorption has proven to be one of the most attractive options, owing to its flexibility and simplicity in design, convenience and ease of operation and, effective in removing heavy metal ions especially at low concentration [17]. Designing an appropriate and efficient material for the specific metal ion is necessary for successful Pb(II) adsorption.

Combining the excellent handling and flow characteristics of the porous adsorbent supports with the specific affinity of functional materials/groups toward targeted pollutants, inorganic-organic hybrids provide certain actual and potential applications properties, e.g., used as adsorbents [18–20]. Benefiting from its excellent thermal and mechanical stability, large surface area, and well-defined surface properties, modified silica gel was widely applied as an inorganic solid matrix in composite materials [21–23].

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* Corresponding author.

Being one of the most common methods in silica gel surface modification, the reaction of silanol groups with organosilane coupling reagents can contribute to a further immobilization of functional organic ligands [24,25]. The existence of terminal functional groups makes it possible to acquire special chelating properties. For this reason, large amount of silica gels were modified with oxygen-containing groups [26], nitrogen-containing groups [24,27,28], sulfur-containing groups [29,30] and phosphorus-containing groups [31,32]. For example, hydroxyl and amino terminated polyamines have been immobilized on silica gel, and the effects of functional groups on the adsorption capacities for four transition metal ions have been investigated [26]. Moreover, sulfur and amidoxime-containing bifunctional silica gel have also been developed and used as efficient Pb(II) adsorbent [29]. The polydentate nature makes Schiff bases excellent hosts for specific metal ions and immobilization of Schiff bases onto silica gel are especially attractive as an alternative absorbent to remove some metals ions from aqueous solutions [2,33]. However, the reported methods for developing Schiff base modified silica are rather tedious, a convenient and straight process is necessary.

We report herein the preparation of a novel silica gel-immobilized Schiff base inorganic-organic hybrid by grafting glutaraldehyde (GA) onto the surface of the silica gel. The structures and properties of the absorbent were characterized by Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TG) and porous structure analysis. The adsorption performance of the absorbent for Pb(II), Cu(II) and Cr(VI) were evaluated by adsorption studies, The influence of solution pH was also evaluated. The underlying adsorption mechanism was explored by fitting the results from the bath experiment to kinetic and equilibrium models.

2. Materials and methods

2.1. Reagents

Silica gel was of chromatographic grade (200–300 mesh), purchased from Shanghai Fine Silica Gel Chemistry Company (Shanghai). It was activated with 10% HCl at room temperature for 30 mins in a constant temperature oscillator. After 6 h of standing, the activated silica gel was washed thoroughly with distilled water to neutral pH and dried at 80°C for 12 h in a drying oven. 3-Aminopropyltriethoxysilane (APTES) (Aladdin Chemistry Co. Ltd., Shanghai) and 1,5-glutaraldehyde were both used without further purification. Organic solvents toluene, ethanol, and acetone were redistilled just before use. Other reagents were analytical grade and used as received.

2.2. Instruments

Infrared spectra were obtained in the 400–4,000 cm^{-1} region with a resolution of 4 cm^{-1} by accumulating 32 scans on an FTIR spectrometer (Shimazu IRAffinity-1, Japan). KBr pellets were used for the solid samples, the mass of the sample is 1% of the KBr. TG curves were recorded for modified silica gel structures on a DSC TG analyzer (Setaram Setsys, France), using 3.0–10.0 mg of the sample with a range of 100°C–900°C at a heating rate of 10 K min^{-1} under nitrogen flow. Porous structure parameters were measured at 77.350 K on the ASAP2020 instrument (Micromeritics Instrument Corp., USA).

2.3. Preparation of Schiff base-modified silica gel

The silica gel phase-bound amino derivative moiety was prepared from the reaction with (3-aminopropyl)triethoxysilane as a silylation agent. Silylant agent was used without purification. 10.0 g of the activated silica gel was suspended in 70–100 mL of toluene. 10.0 g of APTES was added to this suspension. The mixture was refluxed at 110°C for 6 h and the modified silica gel was filtered off. After washing with toluene, ethanol, and acetone, the product (SiO_2-NH_2) was dried under vacuum at 65°C.

8.0 g of SiO_2-NH_2 was suspended in 4 mL of 50% glutaraldehyde. 8 mL of Na_2HPO_4-NaH_2PO_4 as the buffering solution was added to this suspension at pH 7.5. The mixture was reacted at 50°C for 6 h in a water bath. The modified silica gel was filtered off with the buffering solution for repeated lavage. The silica gel immobilized with Schiff base (SiO_2-GA) was obtained. The preparation route is demonstrated in Fig. 1.

2.4. Adsorption properties for metal ions

2.4.1. Static adsorption for metal ions

Adsorption capacities of chemically modified silica were determined for variable kinds of metal ions at room temperature by static adsorption experiments. 0.1 g of dry modified silica structures were suspended in 20 mL aqueous solution containing Cr(VI), Pb(II), and Cu(II), respectively. For these measurements, the three solutions were kept at room temperature for 20 h in an orbital shaker thermostat, and the initial concentration of the metal ions is 100 mg L^{-1}. After standing for 20 h, the solid material was separated from the solutions by filtration. The amounts of metallic cations remaining in solution were determined by the atomic absorption spectrometer. The concentration of surplus metal ions was calculated as below.

$$Q = \frac{V\left(C_0 - C\right)}{m} \tag{1}$$

where Q is the amounts of metal ions adsorbed onto the unit amount of the adsorbent (mg g^{-1}). C_0 and C are the initial concentrations of metal ions and the concentrations of the metal ions after adsorption in the solution (mg L^{-1}). m is the mass of the adsorbent (g) and V is the volume of the aqueous phase (L).

2.4.2. Competitive adsorption

The adsorption selectivity of the adsorbent for Cr(VI), Pb(II), and Cu(II) was investigated. Modified silica (0.1 g) was added into 20 mL solutions containing Pb(II)-Cr(VI), Pb(II)-Cu(II), and Pb(II)-Cu(II)-Cr(VI), respectively. The initial concentrations of the heavy metals were all 100 mg L^{-1}. The mixtures were shaken at 25°C for 20 h.

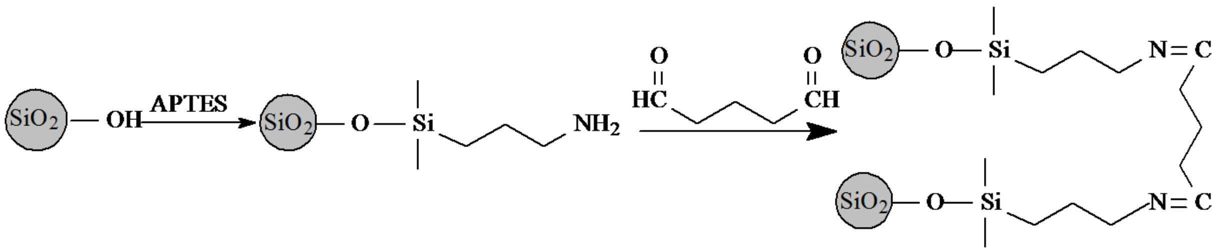

Fig. 1. Ideal synthetic route of the silica gel-immobilized Schiff base.

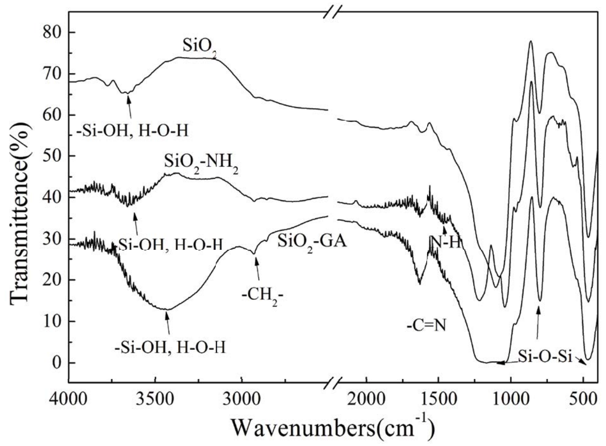

Fig. 2. FTIR spectra for SiO_2, SiO_2-NH_2, SiO_2-GA.

2.4.3. *pH influence*

The influence of pH value on adsorption was investigated. The developed sorbent (0.1 g) was added into 20 mL Pb(II), Cu(II) and Cr(VI) solutions (100 mg L^{-1}) at variable pH values (3–8), respectively. The mixed system oscillated at room temperature for 20 h.

2.4.4. *Adsorption kinetics*

0.1 g of the adsorbent was added into 20 mL of Pb(II) solution in a series of conical flasks at 15°C–35°C, the concentration of Pb(II) being 100 mg L^{-1}. At an interval of 2 h, the solid was filtrated and the concentrations of Pb(II) in the aqueous solution were determined.

2.4.5. *Adsorption isotherms*

The adsorption isotherms were obtained by shaking 0.1 g of the adsorbent with various concentrations of Pb(II) (25–200 mg L^{-1}) at 15°C–35°C for 20 h, kept at the best pH value level.

2.4.6. *Regeneration and reusability*

Solutions containing 5% thiourea (weight percentage) and 0.1 mol L^{-1} HCl were used to the regeneration of the adsorbent. After incubating for 30 min, the mixture was filtered and the solid was dried in an oven at 60°C. Then the adsorption performance of the regenerated adsorbent for Pb(II), Cu(II) and Cr(VI) was investigated.

3. Results and discussion

3.1. *FTIR spectroscopy analysis*

Immobilization of the Schiff base group onto the surface of the silica-gel follows a sequence of two steps as described in Fig. 1. The first one consisted of grafting APTES onto silica gel to yield the new surface with a functional group of amino (SiO_2-NH_2). In the next stage, glutaraldehyde was covalently bound onto silica gel to give the final product SiO_2-GA via the reaction between amino from SiO_2-NH_2 and aldehyde group of glutaraldehyde. The FTIR spectra of blank and functionalized silica gels are shown in Fig. 2. Several peaks were observed in the spectrum of silica gel, an intense band at 1,100 cm^{-1} could be attributed to the stretching of the siloxane group, the peaks at around 800 and 480 cm^{-1} can be attributed to the typical symmetric and bending vibrations of siloxane group in the mesoporous silica network, respectively, the large broadband around 3,500 cm^{-1} was assigned to the O–H stretching frequency of silanol groups and adsorbed water [33]. Comparing with the spectrum of silica gel, new absorption bands at 2,900 cm^{-1} in the spectra of SiO_2-GA can be related to the asymmetric and symmetric $-CH_2-$ bands, confirming the existence of organic groups in the products. The band around at 980 cm^{-1} related to free silanol groups was weakened after functionalization. In comparison with the silica gel, the band at 3,460 cm^{-1} is weaker and broader for SG-NH_2, which may be related to the relatively less hydrophilic character of the organ-functionalized surfaces of SG-NH_2 [2,33]. The band observed at 1,400 cm^{-1} can be assigned to the bending vibration of N–H, and its stretching vibration was overlapped with O–H stretching frequency in the range of 3,800–3,000 cm^{-1}. The peaks at 1,640 cm^{-1} were related to the C=N bond of Schiff bases, which may overlap with the angular H–O–H vibration of the water molecules. It can be observed that the band of C=N was not obvious, which can be explained by the strong background Si–O stretching vibration detected at 1,630 cm^{-1}, similar results have been reported previously [34]. The FTIR results clearly showed that APTES and glutaraldehyde were immobilized on the silica surface.

3.2. *TG analysis*

TG curves reflect the thermal stability of a material. Detected at a range of 0°C–900°C in Fig. 3, the curve of SiO_2

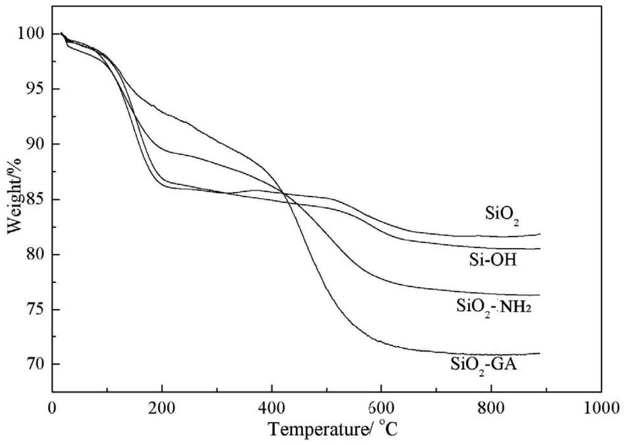

Fig. 3. Thermogravimetric curves for SiO_2, SiO_2-OH, SiO_2-NH_2, and SiO_2-GA.

presented a mass loss of 16%. Correspondingly, the mass loss of 19% in TG curves of the activated silica gel indicated the presence of a silanol group on the surface of silica gel, which is more hydrophilic than the SiO_2. Furthermore, the mass losses of the silica gel modified by APTES and glutaraldehyde were 23% and 30%, respectively. The samples presented two distinct stages of mass loss, a first mass loss below 200°C can be attributed to release of physically adsorbed water, a pronounced increase in the second mass loss from 290°C was related to the decomposition of the immobilized functional groups and further condensation of the remaining silanol groups. The second mass losses in these curves indicated the detaching of the organic groups from the silica surface, which is another evidence for the successful grafting of the amino and Schiff base groups. The thermal stability indicated that these composites satisfied the demand for leaching metal ions from the wastewater since the lowest decomposition temperature of organic groups was at 170°C.

3.3. Pore structure analysis

The porous structure parameters of the products were obtained by the nitrogen adsorption experiment, and the corresponding data are summarized in Table 1. The Brunauer–Emmett–Teller surface area and pore volumes of the silica-gel are 302.25 $m^2\ g^{-1}$ and 0.921 $cm^3\ g^{-1}$, which decreased to 178.101 $m^2\ g^{-1}$ and 0.740 $cm^3\ g^{-1}$ for SG-GA, respectively. The reason may be that functionalization has diminished pore sizes due to the pendant organic groups on the surface and inside the pores of the adsorbents. Interestingly, that the pore size increased from 11.52 nm for silica-gel to 12.99 nm for SG-GA. Fig. 4 shows the nitrogen adsorption-desorption isotherms of the silica-gel and its derivative, SG-GA.

Table 1
Parameters of the porous structure of SiO_2 and SiO_2-GA

Resins	BET surface area ($m^2\ g^{-1}$)	BJH desorption cumulative volume of pores ($cm^3\ g^{-1}$)	BJH desorption average pore diameter (nm)
SiO_2	302.25	0.92	11.52
SiO_2-GA	178.10	0.74	12.99

They both assumed a hysteresis loop which can be assigned to type IV adsorption behavior which can be related to mesoporous structures of the absorbent. It should also be noticed that the hysteresis loops results of the adsorption–desorption experiments are similar, indicating the pores of the silica gel were not changed significantly upon the functionalization. Moreover, there is almost no nitrogen adsorbed at lower P/P_0, indicating no or few microspores in all samples [2,3]. A steep increase in nitrogen adsorption at higher P/P_0 suggested a quite large distribution in the mesopore range in the functionalized silica gels. The volume adsorbed by the silica-gel hiked at a relative pressure (P/P_0) of 0.7, indicating the capillary condensation of nitrogen within the uniform mesoporous structure [2]. Fig. 5 shows the pore size distribution of the silica-gel and SG-GA. The pores between 12 and 16 nm were prominent on the products, and the quantity of adsorbed nitrogen increased with functionalization.

3.4. Absorption properties for metal ions

3.4.1. Saturated absorption of the modified silica gel for metal ions

The aim of grafting functional groups onto the surface of silica gel is to adjust the silica gel to the most excellent coordination properties. The saturated adsorption capacities

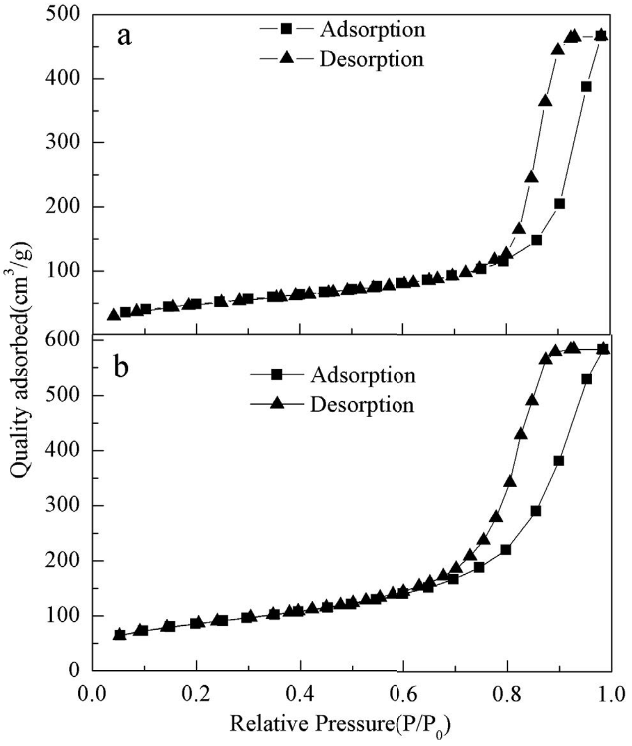

Fig. 4. Nitrogen adsorption–desorption isotherms (a) SiO_2 and (b) SiO_2-GA.

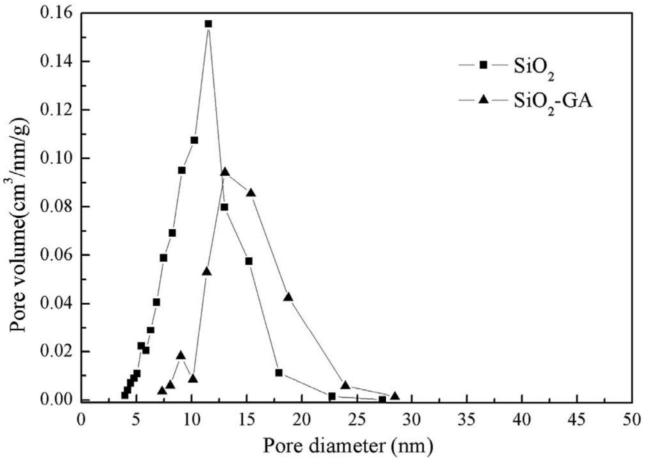

Fig. 5. Pore size distribution of SiO_2 and SiO_2-GA.

Table 2
Adsorption selectivity of the adsorbent for Pb(II) in binary ions systems

Solutions	Metal ions	Adsorption capacity (mg g^{-1})	Selective coefficient
Cr(VI)-Pb(II)	Pb(II)	19.89	2.43
	Cr(VI)	8.14	
Pb(II)-Cu(II)	Pb(II)	19.98	2.97
	Cu(II)	6.72	
Pb(II)-Cu(II)-Cr(VI)	Pb(II)	17.56	/
	Cu(II)	7.12	2.47
	Cr(VI)	7.67	2.29

Conditions: concentration = 100 mg L^{-1}; reaction time = 20 h; temperature = 25°C

of SG-GA for Cr(VI), Cu(II), and Pb(II) at pH 5.0 were studied at room temperature. They are important parameters in evaluating the ability of the modified silica gel to bind and extract different metal ions from aqueous solutions. The pH value of 5.0 was selected to avoid the decrease of adsorbent capacities at lower pH values and the formation of metal-ion precipitate at higher pH values. The exposure time of 20 h was chosen to ensure complete adsorption of the metal ions, though the equilibrium adsorption time of the functionalized silica gel for the metal ions was less than 10 h. The experiment results displayed that the static adsorption capacities of SG-GA for Cr(VI), Cu(II), and Pb(II) were 12, 11.6, and 19.96 mg g^{-1}, respectively. Moreover, it should be mentioned that there was no leaching or significant change in the surface of the developed adsorbent after the adsorptions (Fig. S1).

3.4.2. Competitive adsorption

The competitive adsorption experiments of SG-GA for metal ions were conducted in binary and triple systems, including Cr(VI)-Pb(II), Pb(II)-Cu(II) and Pb(II)-Cu(II)-Cr(VI). The initial concentration of the metal ions of Cr(VI), Pb(II), and Cu(II) was all 100 mg L^{-1}. The results for the competitive adsorption at 25°C are listed in Table 2. The selective coefficient was the ratio of the adsorption capacities of the metal ions in the binary system. It can be expressed as $t = Q_0/Q_1$, where Q_0 and Q_1 are the adsorption capacities of Pb(II) and the other metal ion in the binary or triple system, respectively. The results indicated that the silica gel modified by glutaraldehyde possesses excellent adsorption for Pb(II) in a binary and triple mixture. It is obvious that although the selectivity to Pb(II) deteriorated slightly in triple solutions (from 2.97 to 2.47 for Cu(II) and 2.43 to 2.29 for Cr(VI), respectively), the selectivity is still satisfying. It has been noticed that the adsorption selectivity of the silica gel-immobilized Schiff base is superior for Cu(II) than that for Cr(VI). We believed that the charges of heavy metals are responsible for this phenomenon. Schiff base binds more tightly with Cr(VI), while its affinity for Cu(II) deteriorates. We believed that the selectivity of the developed absorbent for Pb(II) may correlate with the formation of a multi-dentate coordination compound with the structure shown in Fig. S2. The developed adsorbent may find potential applications for selective removing Pb(II) from aqueous solutions.

3.4.3. Influences of pH

The pH value of a solution is one of the main factors controlling an adsorption process. Generally, the nitrogen atoms of Schiff base protonate and become positive at lower pH values, which may deteriorate the absorption performance. However, metal ions may precipitate at higher pH values. An optimal pH value should be selected for the quantitative adsorption to avoid decreasing the coordination capacity of the adsorbent. As illustrated in Fig. 6, the absorbance performance of SG-GA for Pb(II) did not change significantly with the variation of the pH value from 3.0 to 8.0. This indicates that pH value has little influence on the adsorption of Pb(II). The prepared inorganic-organic hybrid material is favorable and can be used for Pb(II) uptaking in environmental water with a wide pH range.

3.4.4. Adsorption kinetics

The adsorption kinetics of SG-GA for Pb(II) at an initial concentration of 100 mg L^{-1} were investigated, for a purpose of confirmation of the adsorbent equilibrium time. The Pb(II) adsorption properties for the adsorbent at different temperatures were also studied. The relationships between adsorption time and adsorption capacity at different temperatures are shown in Fig. 7. Temperature inputted a slight positive exertion on the adsorption capacities. About 98% of the equilibrium adsorption capacity was achieved during the first 2 h under the testing condition and the absorption process was completed in 8 h. In the fast adsorption stage, it was easy for Pb(II) to enter the accessible pore sites as well as to bind with the Schiff base ligands. Owing to the saturation of the peripheral active sites and the unfavorable of diffusion into the deeper pores for Pb(II), the absorption slows down at the following stage. The mechanism of adsorption and the main parameters related to the adsorption kinetics were analyzed according to the pseudo-first-order model

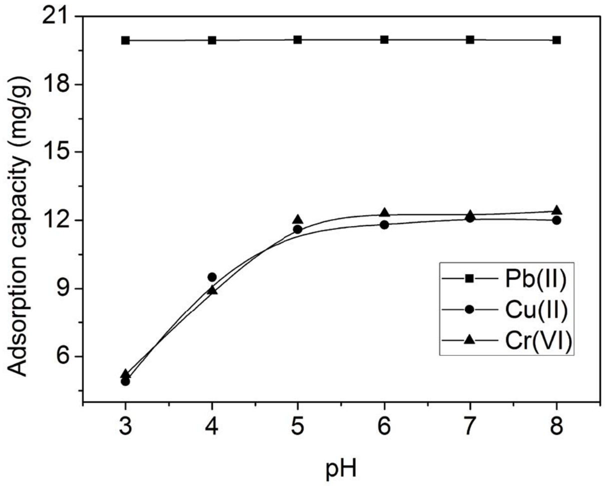

Fig. 6. Adsorption of Pb(II), Cu(II) and Cr(VI) by SiO_2-GA at different pH values.

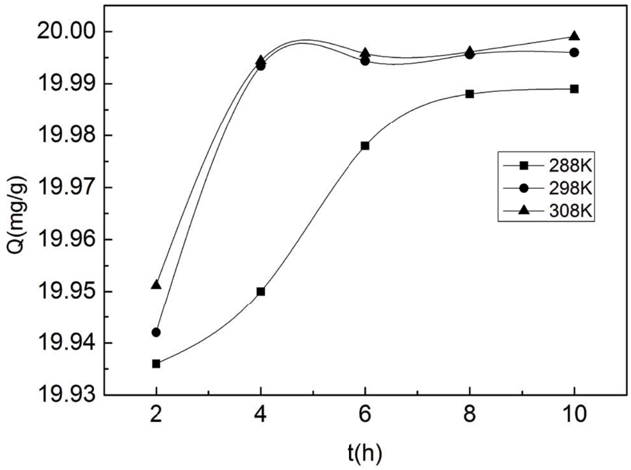

Fig. 7. Adsorption kinetics of SiO_2-GA for Pb(II) at different temperatures.

and pseudo-second-order model as described in Eqs. (2) and (3), respectively.

$$\ln\left(Q_e - Q_t\right) = \ln Q_e - k_1 t \tag{2}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \tag{3}$$

where Q_e is the amount of Pb(II) adsorbed at equilibrium per unit weight of the modified silica gel, mg g^{-1}. Q_t is the amount of Pb(II) adsorbed at a certain time, k_1 (h^{-1}) and k_2 (g mg^{-1} h^{-1}) are the rate constants of pseudo-first-order and pseudo-second-order adsorption. Pseudo-first-order kinetic and pseudo-second-order kinetic plots for the adsorption of Pb(II) onto chemically modified silica gel at different temperatures were presented in Fig. 8 and related parameters are listed in Table S1. The obtained coefficient values (R^2) of the pseudo-second-order equation were much better than those of the pseudo-first-order equation for the modified silica gel. It demonstrates that the pseudo-second-order model was more suitable to describe the adsorption kinetics of the adsorbent for Pb(II), suggesting that the adsorption processes follow the chemisorption mechanism.

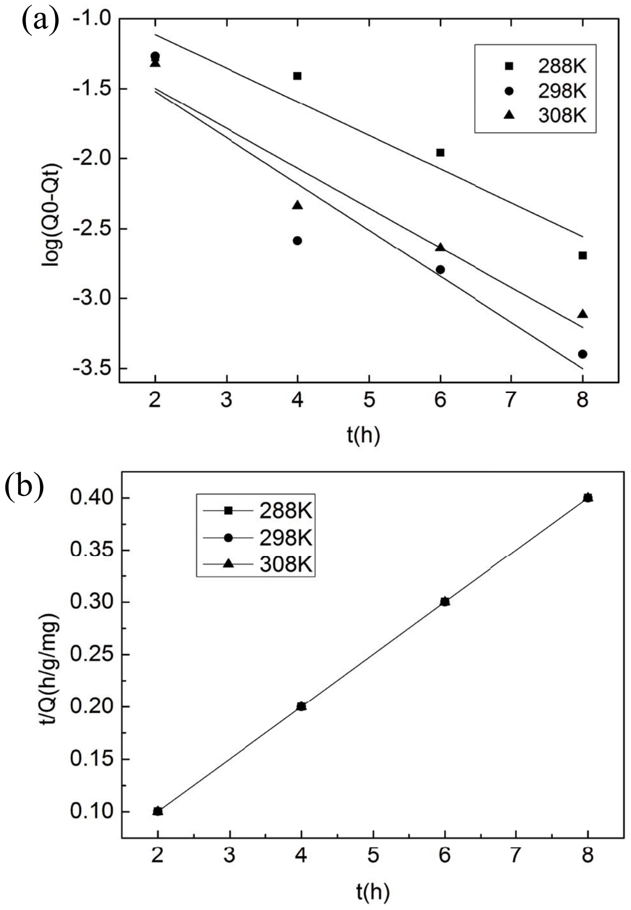

Fig. 8. Pseudo-first-order kinetic plot (a) and Pseudo-second-order kinetic plot (b) for the adsorption of Pb(II) at different temperatures.

3.4.4. Adsorption isotherms

The relationship between equilibrium concentration and equilibrium adsorption capacity was studied via isothermal experiments of the chemically modified silica gel in the same pH value solution at different temperatures. To evaluate the sorption characteristics of Pb(II) onto the adsorbent, experimental data were analyzed with the well-known adsorption isotherm models of the Langmuir equation and Freundlich equation. The Langmuir model used in homogeneous adsorption systems is represented as Eq. (4).

$$\frac{C_e}{q_e} = \frac{C_e}{q} + \frac{1}{qb} \tag{4}$$

where C_e is the equilibrium concentration of Pb(II), mg L^{-1}. q_e is the adsorption capacity, mg g^{-1}. q is the saturated adsorption capacity, mg g^{-1}. b is the constant of Langmuir model, L mg^{-1}. The Freundlich model that describes heterogeneous adsorption systems is expressed as Eq. (5).

$$\log q_e = \log k + \frac{\log C_e}{n} \tag{5}$$

where C_e is the equilibrium concentration of Pb(II), mg L^{-1}. q_e is the adsorption capacity, mg g^{-1}. n is Freundlich constant and k is the binding energy constant reflecting the affinity of the adsorbents to Pb(II), mg g^{-1}.

The linearization of the adsorption isotherms for Pb(II) according to the Langmuir and Freundlich model are shown in Fig. 9 and related parameters are listed in Table S2. The R^2 values in Table S2 reveal that the Freundlich isotherm fits the experimental results better than the Langmuir model, suggesting that adsorptions of Pb(II) onto SG-GA follow the mechanism of multilayer adsorption. This is reasonable considering that the Schiff base ligand grafted on the silica gel reacts with metal ions mainly via complexion. Moreover, it can be observed that the obtained maximum adsorption capacity (34.19–44.23 mg g^{-1} and 85.14–87.32 mg g^{-1} for Langmuir and Freundlich model, respectively) is larger than that from the kinetic experiments (Ca. 20 mg g^{-1}). Table 3 shows the comparison of the developed silica gel-immobilized Schiff base and other kinds of functional silica material in terms of adsorption capacity for Pb(II) from aqueous solution. Although the developed adsorbent showed lower adsorption capacities than KCC-1 and L-proline loaded silica gel (PLSG), they had a comparative or larger adsorption capacity with other functional groups decorated adsorbents such as SiO_2@SH and 2-furoyl loaded silica gel. All these results indicate that SG-GA is an interesting candidate for applications in selective adsorption of Pb(II) from wastewater.

3.4.5. Regeneration and reusability

Then the adsorption performance of the regenerated adsorbent for Pb(II), Cu(II) and Cr(VI) was investigated. Please see Fig. 10 for the results. The developed silica gel-immobilized Schiff base can be regenerated conveniently and

Table 3
Comparison of the maximum adsorption capacity with different types functional silica material reported in the literature for Pb(II) ion

Used material	Capacity (mg g^{-1})	Reference
Silica gel-immobilized Schiff base	20.00	This work
KCC-1(RHA)	26.95	[6]
KCC-1(C)	30.89	[6]
SG-HE-S-AO	ca. 4.0	[27]
SiO_2@SH	10.82	[29]
GH-T-P	16.78	[30]
Activated silica gel (ASG)	15.62	[31]
Thiophenecarbonyl loaded silica gel (TLSG)	17.85	[31]
2-furoyl loaded silica gel (FLSG)	19.60	[31]
L-proline loaded silica gel (PLSG)	22.22	[31]

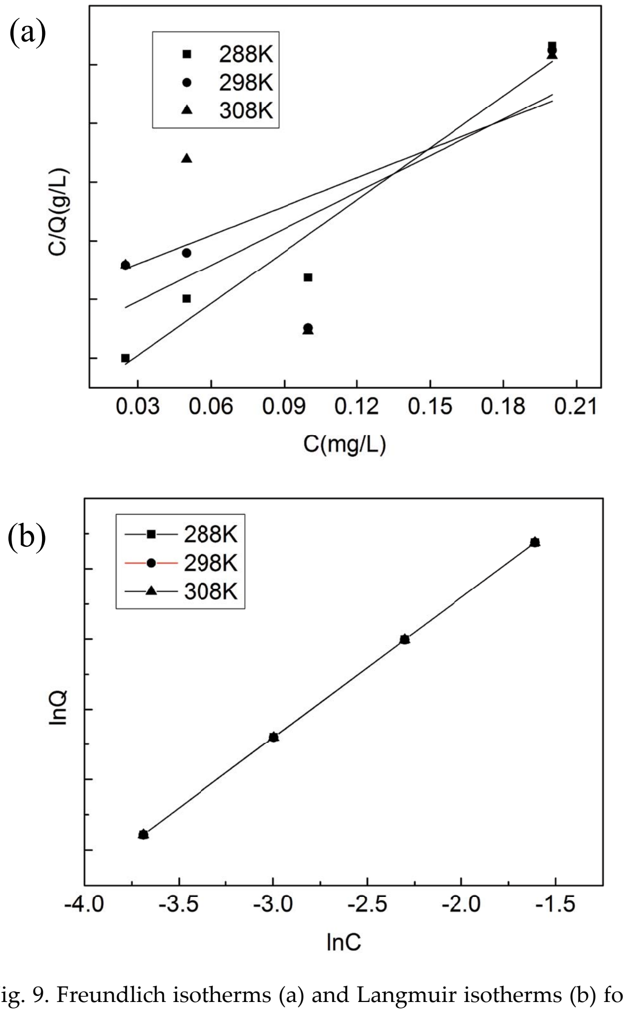

Fig. 9. Freundlich isotherms (a) and Langmuir isotherms (b) for the adsorption of Pb(II) obtained by a linear method.

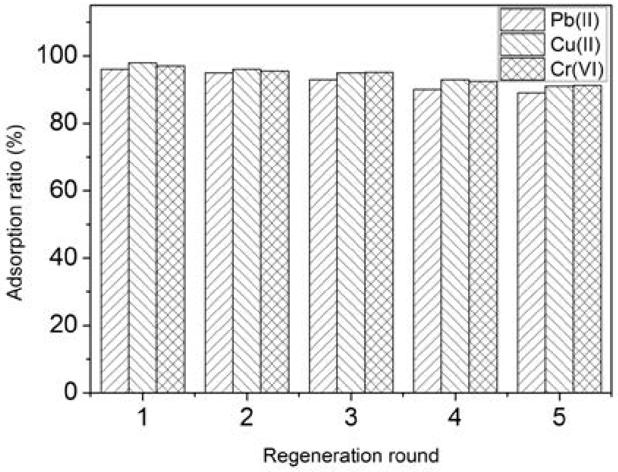

Fig. 10. Regeneration and reusability of the developed silica gel-immobilized Schiff base.

used as an efficient adsorbent for at least 5 rounds (89.0%, 91.0% and 91.2% adsorption capacities left for Pb(II), Cu(II) and Cr(VI), respectively). We also notice that Pb(II) saturated adsorbent was more difficult to regenerated, which correlated well with the selectivity results.

4. Conclusion

A new Schiff base functionalized silica gel SG-GA has been prepared and characterized. TG analysis indicated that the mass loss of the silica gel with glutaral was 30%, indicating its successful medication. Pore structure analysis showed that Schiff base functionalized silica gel possesses a stable pore structure, which is beneficial for absorption. SG-GA could selective adsorb Pb(II) metal ions from the aqueous solution at a wide pH range of 3–8 containing mixed metal ions of Cr(VI) and Cu(II), with a saturated adsorption quantity of 19.96 mg g^{-1} indicating that SG-GA is an interesting candidate for applications in selective adsorption of Pb(II) from wastewater. The prepared novel silica gel also possessed a good adsorption capability for Pb(II) in binary mixtures. The adsorption kinetics of Pb(II) followed the pseudo-second-order kinetic models and the adsorption isotherms fitted well by Langmuir models, these results implied that the absorption selectivity may be tuned by modifying the structural conformation for the sites of metal ion binding through complexion. This study provides an interesting material that could be used to effectively remove Pb(II) from water effluents containing mixed metal slats.

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Supplementary information

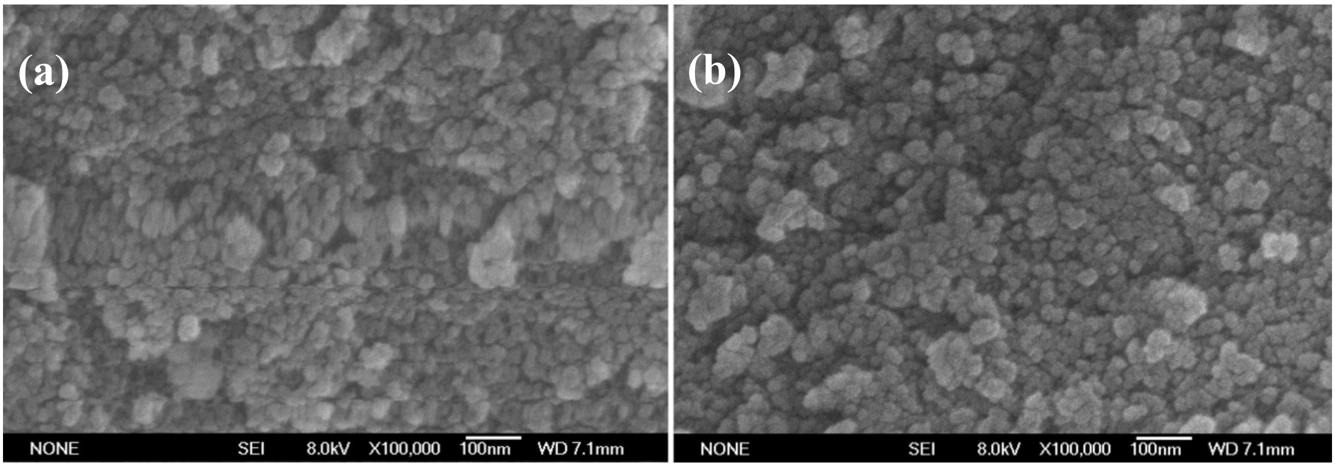

Fig. S1. SEM photograph of the adsorbent (a) before and (b) after adsorption.

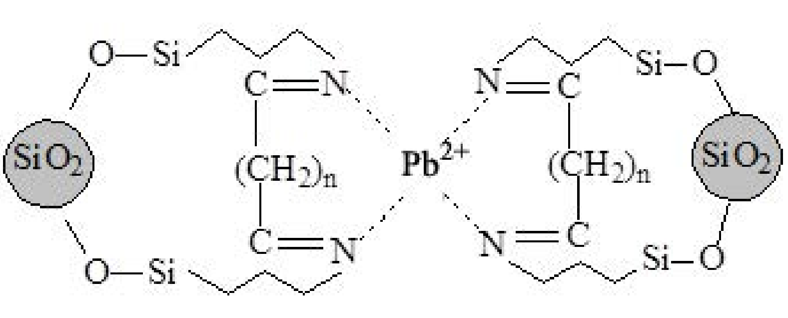

Fig. S2. Proposed mechanism of selective Pb(II) adsorption.

Table S1
Kinetic parameters for the adsorption of Pb^{2+} at different temperatures

Temperature (K)	Pseudo-first-order model			Pseudo second-order model		
	k_1 (h^{-1})	Q_e (mg g^{-1})	R_1^2	k_2 (h^{-1})	Q_e (mg g^{-1})	R_2^2
288	0.5536	19.989	0.925	8.3333	20	0.9999
298	0.7602	19.996	0.9008			
308	0.6552	19.999	0.9351			

Table S2
Isotherm parameters of Langmuir and Freundlich for the adsorption of Pb^{2+} obtained by using the linear method

Temperature(K)	Langmuir		Freundlich	
	q (mg g^{-1})	R_1^2	k (mg g^{-1})	R_2^2
288	34.1880	0.8129	85.1412	0.9999
298	39.3701	0.6116	86.1291	0.9999
308	44.2299	0.3753	87.3202	0.9999