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Chemical modification of silica gel with multidentate ligands for heavy metals removal

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ABSTRACT

Two kinds of silica-gel supported chelating adsorbents with different multidentate ligands were synthesized for heavy metals removal. The obtained adsorbents were named as SG-AD and SG-ASD. SG-AD was the silica-gel supported dithiocarbamate ligand adsorbent; SG-ASD was the silica gel-supported dithiocarbamate and Schiff's bases adsorbent. FT-IR analysis and thermogravimetry analysis were used to characterize the prepared adsorbents. Their adsorption properties of Pb(II), Hg(II), Cu(II), Zn(II), and Cd(II) were also investigated. The results showed that SG-AD and SG-ASD showed high performance toward Pb(II) and Hg(II) removal, especially toward Hg(II) removal. Adsorption kinetics suggested that the adsorption processes of Pb(II) and Hg(II) on SG-AD and SG-ASD were governed by film diffusion and followed a pseudo-second-order model. The Langmuir model and Scatchard model were applied to fit the experimental equilibrium data for SG-AD and SG-ASD. With increasing temperature, the adsorption capacities and affinity constants of SG-AD and SG-ASD for Pb(II) and Hg(II) were increased. SG-ASD which contained two kinds of multidentate ligands showed strong chelating affinity to Hg(II). Langmuir model and Scatchard model can be integrated in describing the processes of heavy metal adsorption.

Keywords: Chemical modification; Multidentate ligands; Silica gel; Adsorption; Heavy metals; Removal

1. Introduction

As a result of industrialization and urbanization, heavy metal pollution has become a serious problem [1]. Therefore, it is necessary to explore some new effective strategies for heavy metal removal from industrial effluents or water streams. Many treatment methods have been used for heavy metal removal, such as chemical precipitation, reverse osmosis, electrochemical reduction, ion exchange, and adsorption [2–4]. Among these methods, adsorption is generally preferred for the removal of heavy metal ions due to the high efficiency, remarkable simplicity, and low cost [5–9] and the adsorbents play the vital role in the efficient adsorption process [8]. Activated carbon, clay minerals, microbial biomasses, metal oxides, and polymeric materials are usually used as adsorbents for removal of heavy metal ions from aqueous solutions [6]. However, the inherent disadvantages of these

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materials are irreversible binding of the metal ions (e.g. biomasses), nonrenewable (e.g. biomasses), hard to be separated (e.g. biomasses), low selectivity for heavy metal ions (e.g. activated carbon and clay minerals), and relatively low loading capacities (clay minerals and biomasses) [10,11]. In order to remedy these limitations, some promising adsorbents are developed by functionalizing the inorganic supports with organic groups [12]. These adsorbents have relatively high loading capacities and selectivity for targeted metal ions, which can be increased by the proper selection of chelating ligands [10–12].

Silica gel is the most common inorganic solid adsorbent and widely applied in chromatography [13], solid phase extraction [14], pesticides removal [15], and metal ion preconcentration [16] due to its excellent thermal and mechanical stability, unique large surface area, and well-modified surface properties [17–19]. Recently, great attention has been paid to the chemical modification of the surface of silica gel with certain functional groups, as it can obviously improve the physical and chemical properties of silica gel [17–19]. The groups on the surfaces of the silica gel have important effects on the effectiveness, capacity, selectivity, and reusability of the adsorbents. Amine groups have been found to be one of the most efficient functional groups for heavy metal removal [19,20]. In many earlier literatures, various types of polyamines were anchored to silica gel to remove and separate heavy metals from different systems [21,22]. Nevertheless, those chelating adsorbents possessing polyamines as a sole functional group still suffered from disadvantages, including the low selectivity and binding affinity toward divalent metals [23]. Therefore, those polyamines-functionalized adsorbents are usually as starting materials to prepare further chelating adsorbents, which showed higher selectivity and stronger binding affinity toward targeted heavy metal ions. Multidentate ligands are expected to have better complexing abilities to heavy metal ions in comparison with other polymer ligands because they can form stable metal complexes with heavy metal ions [23]. The dithiocarbamates [5], iminodiacetate [7], phospho methyl [24], and acrylate methyl [25] derivatives of polyamines are the most common multidentate ligands. Among them, dithiocarbamates derivatives which can be formed by the reaction with carbon disulfide and amine show good performance in heavy metal adsorption [26]. Therefore, the silica gel-supported adsorbent containing dithiocarbamates derivatives of polyamines was prepared. On the other hand, the salicylaldehyde can easily react with primary amine to form a typical multidentate ligand-Schiff's base [20]. To further enhance selectivity and binding affinity of chelating adsorbent to heavy metal ions, a novel adsorbent containing two kinds of multidentate ligands was synthesized via the primary and secondary amines of amine-functionalized silica gel, respectively.

In order to synthesize adsorbents owning high selectivity and binding affinity to heavy metal ions, two adsorbents containing one and two kinds of multidentate ligands were synthesized by reaction of amine-functionalized silica gel with carbon disulfide and salicyaldehyde. FT-IR analysis and thermogravimetry analysis were used to characterize the prepared adsorbents. Their adsorption capabilities for Cu(II), Zn(II), Pb(II), Cd(II), and Zn(II) were also determined.

2. Experimental

2.1. Materials and methods

Silica gel (SG) was purchased from the Jiyida Chemical Factory, Qingdao, Shandong, China, with particle size in the range 100–200 mesh. The silica gel was activated as reported previously [20]. 3-Chloropropyltrimethoxysilane (CPTS), diethylenetriamine (DETA), carbon disulfide (CS_2), and salicyaldehyde were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Copper, Zinc, $Pb(NO_3)_2$, $HgCl_2$, and $Cd(NO_3)_2$ used to prepare metal ion stock solutions were purchased from Shanghai Chemical Factory of China. All solvents were of analytical reagent grade. Stock solutions of heavy metal ions ($1.00\ g\ L^{-1}$) were prepared as follows: Metals and metal salts were dissolving in 20 mL $0.5\ mol\ L^{-1}$ of HNO_3, respectively, then diluted to 1 L.

Infrared spectra were determined by Nicolet 6700 Fourier transform infrared spectrophotometer (Thermo Scientific Co., USA), using KBr pellet in the 4,000–400 cm^{-1} region with a resolution of 4 cm^{-1}, by accumulating 16 scans. The mass loss determinations were performed on a Germany Netzsch sta409pc Luxx, using 10–20 mg of the sample under nitrogen at a heating rate of 10 $K\ min^{-1}$. The particle numbers per gram of adsorbents were determined by the hemocytometer-microscope counting method. Synthetic materials were placed in the high-speed stirring water, sampled and placed under a microscope to observe during the stirring process, and then the numbers of particles per gram adsorbent were calculated.

2.2. Synthesis of amine-functionalized silica gel and amine-salicyaldehyde-functionalized silica gel

Amine-functionalized silica gel (SG-A) was synthesized as reported previously [20]. Twenty gram of silica gel reacted with 20 mL of CPTS in toluene, refluxed for 24 h in dry nitrogen, and then the solid (SG-Cl) was filtered, washed several times, and dried under vacuum at 50℃ over 48 h as reported previously [20]. Then, SG-Cl (10.0 g) was reacted with DETA (50.0 mL) for 16 h and the product was filtered, washed, and dried [20].

Amine-salicyaldehyde-functionalized silica gel (SG-AS) was synthesized as reported previously [27]. 5.0 mL salicyaldehyde was dissolved in 50 mL ethanol, then 10.0 g of SG-A was added to the solution. The mixture was refluxed for 2 h at 60℃, left to cool, filtered, washed with toluene and ethanol, and dried under vacuum at 80℃ for 5 h.

2.3. Synthesis of dithiocarbamate-functionalized SG-A and SG-AS

Dithiocarbamate-functionalized SG-A and SG-AS, named for SG-AD and SG-ASD, were synthesized following the procedures previously reported to incorporate the dithiocarbamate to other supports [25,26,28]: Under a nitrogen atmosphere, a mixture of 10.0 g of SG-A or SG-AS and 150 mL of CS_2 was added to a 500-mL flask with 100 mL of toluene as solvent. The mixture was stirred at 25℃ for 2 h. The product was then filtered off, rinsed with toluene, and dried in an oven at 100℃ for 2 h.

The ideal synthetic scheme is illustrated in Fig. 1.

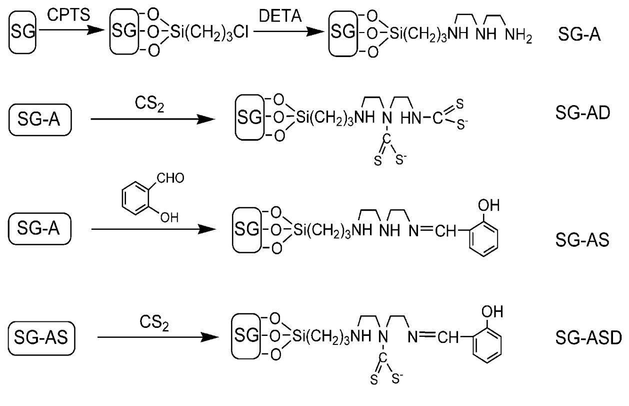

Fig. 1. The ideal synthetic routes of chelating adsorbents.

2.4. Adsorption experiments

The static adsorption experiment was employed to determine the adsorption capability of the two adsorbents. The experiments were carried out by shaking 50.0 mg of adsorbent with 50.0 mL of working solution with a certain metal ion concentration. The pH of the heavy metal solutions was adjusted to 4.5. The samples were shaken for a predetermined time period at a certain temperature and the solid was separated by centrifugation. Initial and equilibrium metal ion concentrations in the aqueous solutions were determined using flame atomic absorption spectrometer (AAS) for Pb, Cu, Zn, Hg, and Cd. The amount of metal ions adsorbed by adsorbents was calculated according to the following Equation: $Q = V(C_0 - C_t) W$, where Q is the amount of metal ions adsorbed onto the unit amount of the adsorbents (mg g^{-1}), C_0 and C_t are the initial and the equilibrium concentrations of the metal ions in aqueous phase (mg L^{-1}), and W is the dry weight of the adsorbent (g).

3. Results and discussion

3.1. Adsorption properties

The aim of grafting functional groups onto the surface of silica gel was to prepare the modified silica gel with most excellent coordination properties. Adsorption capacities for metal ions were essential parameters for evaluating the ability of modified silica gel to bind and extract different metal ions from aqueous solutions [20]. The adsorption experiments for all metal ions (pH 4.5) were studied at 298 K. In order to avoid the decrease of the coordination capacity of the adsorbent at low pH and formation of precipitate of the metal ions at high pH, the pH 4.5 of metal ion solutions were selected for quantitative adsorption. Twenty-four hours of contact time was selected in this study to ensure that the metal ions can be completely adsorbed.

Fig. 2 shows the adsorption capacities of SG, SG-A, SG-AD, SG-AS, and SG-ASD for Pb(II), Hg(II), Cu(II),

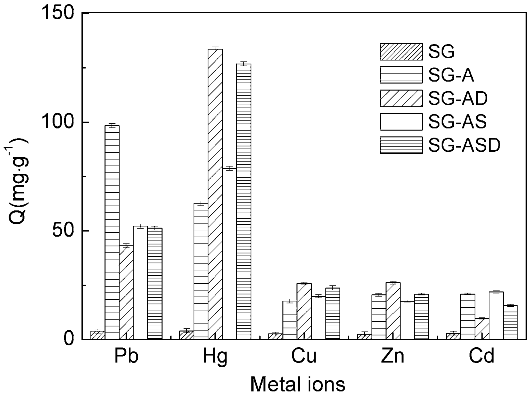

Fig. 2. Adsorption capacities of synthetic adsorbents for Pb (II), Hg(II), Cu(II), Zn(II), and Cd(II) at 298 K (adsorption conditions: initial concentration, 200 mg g^{-1}, pH 4.5, contact time: 24 h).

Zn(II), and Cd(II). Obviously, all adsorbents except the free silica gel (SG) had good adsorption capabilities for Hg(II) and Pb(II), especially for Hg(II). From Fig. 2, it can be seen that as follows: (1) When the SG-A was modified with salicylaldehyde, its adsorption capacities for Hg(II), Cu(II), and Cd(II) increased, while the adsorption capacities for Pb(II) and Zn(II) decreased, implying that the salicylaldehyde group showed a stronger chelating ability for Hg(II) but a weaker chelating ability for Pb(II). (2) When the SG-A or SG-AS was modified with dithiocarbamate, its adsorption capacities for Hg(II), Cu(II), and Zn(II) increased, among which the adsorption capacities for Hg(II) increased significantly, implying that the dithiocarbamate group showed a stronger chelating ability for Hg(II), Cu(II), and Zn(II), especially for Hg(II). Finally, we obtained two adsorbents (SG-AD and SG-ASD), which had higher adsorption capacities for Pb(II) and Hg(II), especially for Hg(II). Therefore, SG-AD and SG-ASD were selected as absorbents to further characterize through FT-IR and thermogravimetry analysis. Their adsorption kinetics and isothermal adsorption to Pb(II) and Hg(II) were also studied.

3.2. *Characterizations of SG-AD and SG-ASD*

3.2.1. *The particle numbers of SG-AD and SG-ASD*

The particle numbers of SG-AD and SG-ASD absorbents were 4.450 ± 0.313 and 3.709 ± 0.372 ($\times 10^{11}$ g^{-1}), respectively. The mole numbers of particles contained in each gram of SG-AD and SG-ASD were 7.392 and 6.161 ($\times 10^{-13}$ mol g^{-1}), respectively, calculated according to the Avogadro constant (6.02×10^{23} mol^{-1}).

3.2.2. *FT-IR characterization*

The presence of the organic functional groups on the surface of silica gel was confirmed by the infrared spectra, as shown in Fig. 3. Those samples had the bands around 1,100, 801, and 472 cm^{-1}, which were attributed to the typical asymmetric stretching, symmetric stretching, and bending vibrations of Si–O-Si of the silica network, respectively [29]. The strong peak around 3,422 cm^{-1} was found, which is due to the O–H stretching vibration of the adsorbed water [19]. The spectrum of SG-A displayed that two new bands appeared at 2,933 and 2,851 cm^{-1}, which corresponded to the typical asymmetric and symmetric stretching vibration of $–CH_2–$, due to the presence of the carbon chain of 3-chloropropyltrimethoxysilane and polyamines attached to the silica gel [9]. Moreover, new band appeared at 1,391 cm^{-1} was assigned to the bending vibration of N–H transferred to lower frequencies due to the stretching vibration of remaining Si–O of the silica gel, which strongly absorbed at 1,633 cm^{-1} [24]. Compared with the spectrum of SG-A, the spectrum of SG-AD showed the vibration of N–C=S at 1,460 cm^{-1} and the unobvious stretching vibration of C=S at 1,232 cm^{-1} covered by the strong peak of asymmetric stretching of Si–O–Si around 1,100 cm^{-1}, suggesting the successful modification of SG-A with dithiocarbamate [5,30]. The peaks of 1,500 and 757 cm^{-1} in SG-AS should confirm the presence of aromatic rings of salicylic [31]. After SG-AS was modified with dithiocarbamate, the spectrum of SG-ASD showed the vibration of N–C=S at 1,460 cm^{-1}, suggesting the successful modification of SG-AS with dithiocarbamate. The peak of 1,500 cm^{-1} in the spectrum of SG-ASD is unobvious, which may be due to the angular vibration of water molecules which strongly absorbed at 1,630 cm^{-1}.

3.2.3. *Thermal analysis*

The thermal stabilities of silica gel and its derivatives have been determined by thermogravimetric analysis in the range of 25–800℃, and the results were shown in Fig. 4. Four adsorbents had two obvious weight loss processes at a range of 25–800℃. The first loss of mass between room temperature and 200℃ was due to physically adsorbed water. An increase in temperature caused the decomposition of organic functional groups on the surface of silica gel, which gave a second mass loss step. The dehydration losses of physisorbed water were 4.2, 3.66, 2.06, and 3.19% for SG-A, SG-AD, SG-AS, and SG-ASD, respectively. This fact indicated that those four kinds of adsorbents should be applied under temperature of 200℃. The second losses in this temperature range of 200–800℃ were 10.2, 11.94, 15.45, and 12.71% for SG-A, SG-AD, SG-AS, and SG-ASD, respectively, due to the breakage of the organic chain anchored on the silica gel surface. All these thermogravimetric results showed a direct relationship between the loss of mass and the amount of the organic molecules anchored on the silica gel surfaces. It should be noted that the order of relative organic functional groups' molecular weight onto the silica gel was SG-AS > SG-ASD > SG-AD > SG-A.

3.3. *Adsorption kinetics*

The adsorption kinetics processes for Pb(II) and Hg(II) on SG-AD and SG-ASD were presented in Fig. 5. At the beginning, the adsorption rate of Pb(II) and Hg(II) adsorption was very fast, then slowed, and

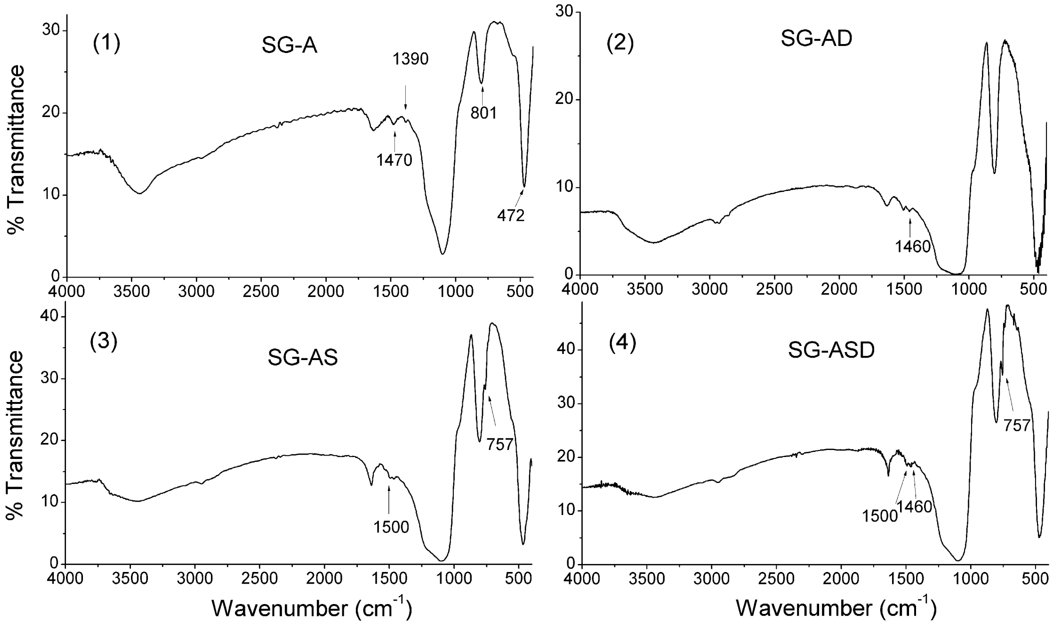

Fig. 3. FT-IR spectra of (1): SG-A; (2): SG-AD; (3): SG-AS and (4): SG-ASD.

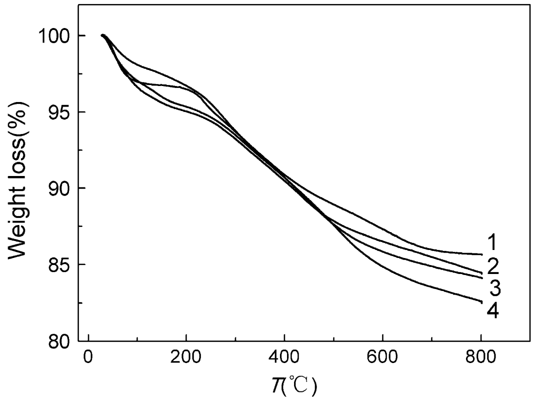

Fig. 4. Thermogravimetric curves of (1): SG-A; (2): SG-AD; (3): SG-ASD; and (4): SG-AS.

finally reached the adsorption equilibrium. In general, the adsorption procedure of adsorbents for metal ions is considered to take place through two mechanisms of film diffusion and particle diffusion [32]. Usually, the Boyd et al. [33] and Reichenberg [34] models are used to analyze the experimental data for distinguishing film diffusion from particle diffusion controlled adsorption. In order to interpret the kinetic characteristics of metal adsorption processes, determine the adsorption equilibrium time and adsorption rates, pseudo-first-order [35] and pseudo-second-order [36] models were also used to evaluate experimental data.

The equations and parameters of Boyd models were given in Table 1. As can be seen from Table 1, the Boyd model provided good correlation coefficients R^2 for Pb(II) and Hg(II) on the two adsorbents, suggesting the Boyd model was suitable to describe the adsorption kinetics of the two adsorbents for Pb(II) and Hg(II) and the adsorption procedures of adsorbents for Pb(II) and Hg(II) were considered to take place through film diffusion. The results of testing the pseudo-second-order models were shown in Fig. 5. The fitting results were given in Table 1. As can be seen from Table 1, the pseudo-second-order model provided good correlation coefficients ($R^2 > 0.995$), suggesting the pseudo-second-order model was suitable to describe the adsorption kinetics of SG-AD and SG-ASD for Pb(II) and Hg(II). At the same time, the fact of equilibrium adsorption capacities calculated Q_c (mg g^{-1}) depending on the pseudo-second-order model was closer to the experimental data Q_e (mg g^{-1}) also proved the suitability of pseudo-second-order model. The adsorption rate (*k*) for Pb(II) was higher than for Hg(II) on both SG-AD and SG-ASD. Compared with SG-AD, SG-ASD which contained Schiff's base showed a higher adsorption rate (*k*) for Pb(II) and Hg(II).

3.4. Adsorption isotherms

The effect of initial concentrations of metal ions on adsorption capacities of SG-AD and SG-ASD was investigated by varying the initial concentrations of metal ions at optimum pH value and 24 h of equilibration time. The results were presented in Fig. 6. At low

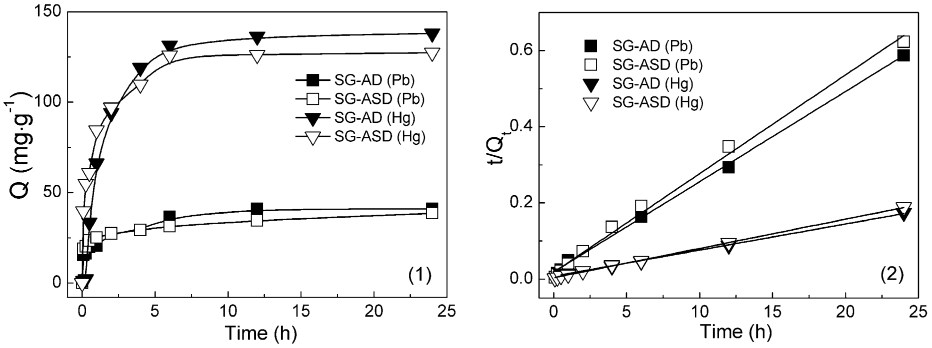

Fig. 5. (1): Adsorption kinetic curves and (2): pseudo-second-order kinetic curves for Pb(II) and Hg(II) on SG-AD and SG-ASD (adsorption conditions: Pb(II) concentration: 100 mg L^{-1}, Hg(II) concentration: 200 mg L^{-1}, pH 4.5, 298 K).

Table 1
Boyd and pseudo-second-order kinetics parameters for the adsorption of Pb(II) and Hg(II) on SG-AD and SG-ASD at 298 K

		Boyd model			Pseudo-second-order model			
Metal ions	Adsorbent	Equation	k (h^{-1})	R^2 value	k (g (mg h) $^{-1}$)	Q_e (mg g^{-1})	Q_c (mg g^{-1})	r^2 value
Pb(II)	SG-AD	$-\ln(1-Q_t/Q_e) = 0.271t + 0.454$	0.271	0.9452	30.0	40.94	42.19	0.9961
	SG-ASD	$-\ln(1-Q_t/Q_e) = 0.283t + 0.709$	0.283	0.9113	37.9	38.53	38.61	0.9949
Hg(II)	SG-AD	$-\ln(1-Q_t/Q_e) = 0.380t + 0.210$	0.380	0.9622	7.6	138.0	144.9	0.9993
	SG-ASD	$-\ln(1-Q_t/Q_e) = 0.389t + 0.638$	0.389	0.8709	16.9	127.4	129.9	0.9994

metal concentration, the adsorption capacities of SG-AD and SG-ASD increased rapidly with the concentration Pb(II) and Hg(II) increasing; when the concentrations of Pb(II) and Hg(II) continued to increased, a saturation constant value was reached, respectively. At low concentration (<100 mg L^{-1} for Pb(II) and <200 mg L^{-1} for Hg(II)), the adsorption amounts of Pb(II) and Hg(II) on SG-ASD had no significant difference with the adsorption amounts on SG-AD. At high concentration (>100 mg L^{-1} Pb(II) and >200 mg L^{-1} Hg(II)), SG-ASD which contained two kinds of multidentate ligands showed a higher adsorption amount of

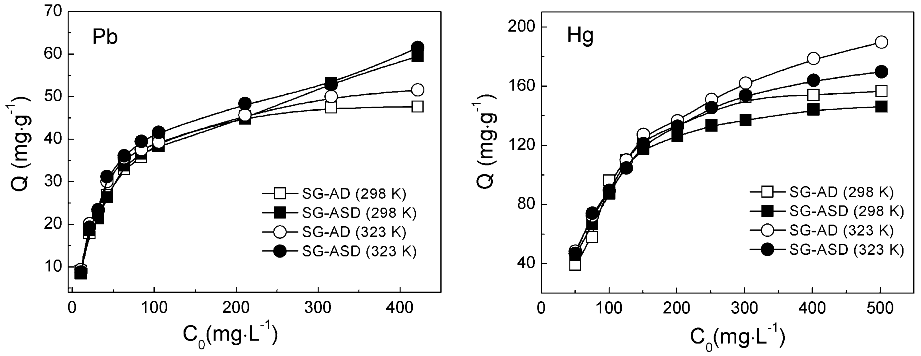

Fig. 6. Effects of initial concentrations of metal ions on adsorption capacities of SG-AD and SG-ASD to Pb(II) and Hg(II) (adsorption conditions: Pb(II) concentration: 50–400 mg L^{-1}, Hg(II) concentration: 50–500 mg L^{-1}, pH 4.5, contact time: 24 h).

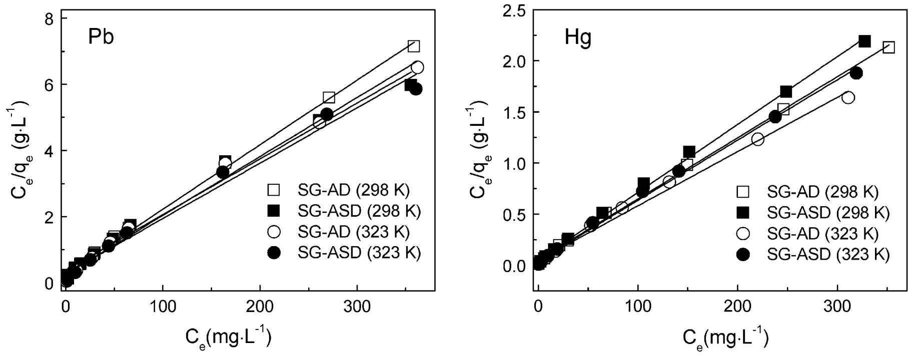

Fig. 7. Langmuir curves of the adsorption for Pb(II) and Hg(II) on SG-AD and SG-ASD.

Table 2
Langmuir isotherm parameters for the adsorption of Pb(II) and Hg(II) on SG-AD and SG-ASD

	Parameters	K_L (L mg^{-1})		$Q_{m(c)}$ (mg g^{-1})		$Q_{m(e)}$ (mg g^{-1})		R^2 (value)	
Adsorbent	T (K)	298	323	298	323	298	323	298	323
SG-AD	Pb(II)	0.055	0.070	52.08	56.18	47.61	51.58	0.9989	0.9915
	Hg(II)	0.206	0.210	158.7	188.7	156.6	189.8	0.9999	0.9986
SG-ASD	Pb(II)	0.045	0.061	59.17	59.88	59.49	61.52	0.9955	0.9961
	Hg(II)	0.239	0.244	147.1	169.5	145.9	169.7	0.9998	0.9994

Pb(II) but a lower adsorption amount for Hg(II), compared with SG-AD.

In order to well understand the adsorption behaviors, herein we employed Langmuir and Freundlich equations to fit the experimental data [32]. The results of testing the Langmuir models were shown in Fig. 7. The fitting equation, Langmuir constants, and correlation coefficients (R^2) were listed in Table 2. As can be seen from Table 2, the Langmuir model provided good correlation coefficients ($R^2 > 0.991$), suggesting the Langmuir model was suitable to describe the adsorption process of SG-AD and SG-ASD for Pb(II) and Hg(II). At the same time, the fact of equilibrium adsorption capacities calculated Q_c (mg g^{-1}) depending on the Langmuir model much closer to the experimental data Q_e (mg g^{-1}) also proved the suitability of Langmuir model. The above fact showed that the adsorption processes of Pb(II) and Hg(II) on the two adsorbents were attributed to homogeneous monolayer adsorption [19]. Compared with SG-AD, SG-ASD which contained two kinds of multidentate ligands showed a higher adsorption capacity (Q_m) for Pb(II) and higher equilibrium constant for Hg(II). With increasing temperature, the adsorption equilibrium constants and adsorption capacity of two adsorbents for Pb(II) and Hg(II) increased.

3.5. Determination of affinity constants and binding sites

Saturated adsorption capacities for metal ions were essential parameters to evaluate the adsorption ability of adsorbent, while the binding affinity of adsorbent for targeted metal ions is another vital parameter to evaluate the adsorbent's ability to bind and extract different metal ions from aqueous solutions. The strong and specific affinity of target heavy metal ions to the binding sites of adsorbents can be expressed by affinity constants (K_A). The binding of heavy metal ions (M) to binding sites of adsorbents (S) can be expressed as [37]:

$$M + S \rightleftharpoons MS \tag{1}$$

In the state of reaction equilibrium, the K_A can be formulated as:

$$K_A = \frac{[M \cdot S]}{[M]_f \cdot [S]_f} \tag{2}$$

where $[S]_f$ is the concentration of free binding sites of adsorbents, $[M]_f$ is the equilibrium concentration of heavy metal ions, and $[M \cdot S]$ is the concentration of the heavy metal ions and adsorbents complex. Given

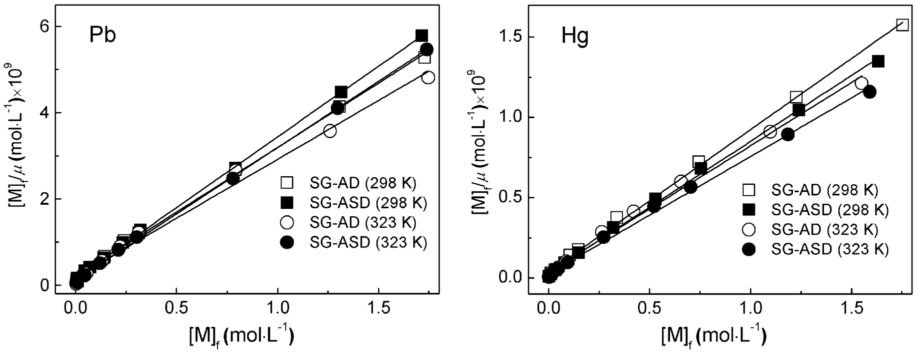

Fig. 8. Scatchard curves of the adsorption for Pb(II) and Hg(II) on SG-AD and SG-ASD.

Table 3
The affinity constants (K_A) and binding sites (n) of SG-AD and SG-ASD to Pb(II) and Hg(II)

	Parameters	$K_A \times 10^4$ (L mol^{-1})		n ($\times 10^8$) (mol^{-1})		R^2 (value)	
Adsorbent	T (K)	298	323	298	323	298	323
SG-AD	Pb(II)	1.134	1.454	3.709	3.996	0.9989	0.9915
	Hg(II)	4.151	4.217	11.63	13.91	0.9999	0.9986
SG-ASD	Pb(II)	0.934	1.277	4.223	4.258	0.9955	0.9961
	Hg(II)	4.795	4.881	10.84	12.50	0.9998	0.9994

that every single binding site of adsorbents is independent from each other and has the same ability to bind heavy metal ions, we can get that $[M]_b = [M \cdot S]$ and $[S]_f = n[S] - [M]_b$, where $[M]_b$ is the concentration of bound metal ion; $[S]$ and n are the concentration of adsorbent and the binding sites per adsorbent particle.

Eq. (2) can be rearranged to give:

$$[M]_f/\mu = 1/(K_A \cdot n) + [M]_f/n \qquad (3)$$

where μ represents $[M]_b/n \cdot [S]$. Eq. (3) is the derivative of the Scatchard model [38]. According to Eq. (3), the K_A and n can be determined from the plots of $[M]_f/\mu$ vs. $[M]_f$, as shown in Fig. 8 and Table 3. As can be seen from Table 3, the Scatchard model provided good correlation coefficients ($R^2 > 0.99$), suggesting the Scatchard model was suitable to describe the adsorption processes of SG-AD and SG-ASD for Pb(II) and Hg(II). With temperature increasing, affinity constants (K_A) and adsorption sites (n) for Hg(II) and Pb (II) increased. Both SG-AD and SG-ASD showed much higher affinity constants and more binding sites for Hg(II) than for Pb(II). SG-ASD which contains the Schiff base and dithiocarbamate showed higher affinity constant for Hg(II) than SG-AD. Therefore, SG-ASD which contains two multidentate ligands, dithiocarbamate and Schiff base, showed a strong affinity to Hg(II). But the Hg(II) adsorbed to the two adsorbents could not be well eluted even with acid or EDTA. We have to say that we do not exactly have a good solution to regenerate and reuse the two adsorbents due to low efficient eluents in this study.

4. Discussion

In order to determine affinity constants and binding sites of SG-AD and SG-ASD to Pb(II) and Hg(II), we employed the Scatchard model to analyze the adsorption processes and compared with the results obtained from Langmuir model. The adsorption result obtained from Scatchard model was consistent with the adsorption result obtained from Langmuir model. Both were that SG-AD and SG-ASD showed much higher affinity constants/equilibrium constants and more binding sites/adsorption capacity for Hg(II) than for Pb(II). SG-ASD showed higher affinity constants/equilibrium constants, but fewer binding sites/adsorption capacity for Hg(II) than SG-AD. Furthermore, the relationship between Q_m and n is $Q_m = (n \cdot N/N_A) \cdot G$ and the relationship between K_L and K_A is $K_L = K_A/G$, where N is the mole numbers per gram adsorbent, N_A is the Avogadro's constant, and G is the relative atomic mass of metal ions. Therefore, Langmuir model and Scatchard model can be integrated. Langmuir model is widely used to determine the saturated adsorption capacity of adsorbent, while Scatchard is focused on determination of affinity constant of adsorbent to heavy metal ions as well as binding sites per adsorbent particle.

The adsorption capacity of chelating adsorbent for heavy metal ions depend on the amounts, types, cross-linking degrees, and structures of functional groups. According to the principle of hard and soft acids and bases (HSAB), nitrogen-containing groups are namely hard bases and therefore, it is easy to combine hard and junction acids like Pb(II), while sulfur-containing groups are namely soft bases and therefore, it is much more efficient to chelate soft acids like Hg(II), Cu(II), and Cd(II). In this article, both SG-AD and SG-ASD showed a much higher adsorption capacity to Hg(II) but a lower adsorption capacity to Pb(II). All of these indicated that dithiocarbamate as a sulfur-containing group showed a stronger chelating ability to Hg(II) but a weaker chelating ability to Pb(II) compared with amines, which was in accordance with HSAB.

There are many silica gel-supported Schiff's bases adsorbents which showed high binding affinity to Cu(II) or Fe(III) due to that the Schiff's bases can form highly stable complexes with heavy metal ions [27,28]. The dithiocarbamate as sulfur-containing functional group is much more efficient to chelate soft acids like Hg(II). Therefore, the SG-ASD which contains both Schiff's base and dithiocarbamate not only showed relatively high adsorption capacity but also strong binding affinity Hg(II). Moreover, the adsorption capacity of SG-ASD to Hg(II) (169.7 mg g^{-1}) is higher than that of the silica-supported dithiocarbamate adsorbent (80.23 mg g^{-1}) synthesized by anchoring the chelating agent of macromolecular dithiocarbamate to the chloro-functionalized silica matrix [5]. SG-A can be modified with dithiocarbamate through primary and secondary amines, while SG-AD can only be modified through secondary amines due to that its primary amines were occupied by salicyaldehyde. Thus, the amount of dithiocarbamate on SG-ASD was less than SG-AD and SG-ASD showed relatively lower adsorption capacity to Hg(II) than SG-AD, consequently.

Therefore, SG-ASD which contains two multidentate, ligands-dithiocarbamate and Schiff base, not only showed relatively high adsorption quality to Hg(II) but also showed high affinity to Hg(II), which will be plays a vital role in heavy metal ion preconcentration, removal, and recovery.

5. Conclusion

The following conclusions can be deduced from the above results: FT-IR confirmed the two kinds of efficient modification of amine-functionalized silica gel with multidentate ligands. Thermogravimetric analysis revealed that the two synthetic adsorbents had high stability and can be applied in the case of no more than 473 K. An adsorption kinetics study indicated that pseudo-second-order model provided an excellent fitting of the two synthetic adsorbents to Pb(II) and Hg(II). The isotherm adsorption data of Pb(II) and Hg(II) on the two synthetic adsorbents were well fitted by the Langmuir and Scatchard isotherm model. Langmuir model and Scatchard model can be integrated in describing the adsorption processes of adsorbents to heavy metal ions. The maximum adsorption capacity for Hg(II) was observed on SG-AD and the strongest chelating affinity to Hg(II) was observed on SG-ASD.

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