



Comparison of synthesis of chelating resin silica-gel-supported diethylenetriamine and its removal properties for transition metal ions

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ABSTRACT

Four kinds of silica-gel (SG)-supported diethylenetriamine (DETA) chelating resins SG-DETA-1, SG-DETA-2, SG-DETA-3, and SG-DETA-4 were prepared by functionalization of silica-gel via so-called "heterogeneous-direct-amination" (hetero-DA), "homogeneous-direct-amination" (homo-DA), "heterogeneous end-group protection" (hetero-EGP), and "homogeneous end-group protection" (homo-EGP) routes, respectively. These functionalized reactions on silica-gel were confirmed through elemental analysis, infrared spectroscopy, X-ray diffractometry, porous analysis, and thermogravimetry. Element analysis revealed that the direct-amination routes and homogeneous condition were more beneficial than the corresponding end-group protection routes and heterogeneous condition to the syntheses of chelating resins with high N content. Several metal ions, such as Ag^+ , Cu^{2+} , Ni^{2+} , Hg^{2+} , Zn^{2+} and Pb^{2+} , were chosen as representatives to investigate the relationship between adsorption capacities and N content of ligands onto the surface of silica-gel. The experiments results showed that all resins, SG-DETA-1, SG-DETA-2, SG-DETA-3 and SG-DETA-4, had a better adsorption for Hg^{2+} and Cu^{2+} than others. One conclusion should be drawn from the above compared experiments, that is, higher N content of silica-gel resins does not ensure a higher utilization ratio of N.

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1. Introduction

Recently, mechanically stable synthetic or natural inorganic solid matrices have been utilized in many applications, such as extraction of cations from aqueous and non-aqueous solvents [1], ion-exchange reactions [2], chemically bonded phase in chromatography [3], or catalytic reactions [4]. One of the important properties explored is the adsorption of trace elements onto solid surface. Taking preconcentration or separation into account, a single element or a series of similar elements can be separated and quantitatively determined from a complex mixture [5].

This class of inorganic support replaces organic polymers from the point of view of insolubility in organic solvents and accessibility of reactive centers, practicality with respect to structural stability, swelling behavior, thermal properties, and aging. Among a large number of inorganic supports, silica-gel (SG) clearly fulfills a significant role due to its ability to anchor organic chains designed to embrace desired chelating ligands [6–9].

It is difficult for chelating ligands to bond to silica-gel because of the relative inertness of the original surface of silica-gel. However,

bonding of chelating ligands to silica-gel surface can be achieved after surface activation/modification. On the surface of active silica-gel, the structure terminates in a large number of silanol groups ($\equiv\text{Si}-\text{OH}$). The most common method of silica-gel surface modification involves the reaction of surface hydroxyl group with silane coupling reagents which act as precursors for further immobilization of organic ligands [10–15].

Generally, the reaction of silane coupling reagents with surface silanol groups leads to the existence of desirable terminal functional groups on the surface of silica-gel, where special chelating properties can be finally obtained. This is mainly related to the structure of the organic ligands, nature of the functional groups present and the incorporated (O, S, N and P) donor atoms. Consequently, a large number of silica-gel-supported organic molecules have been synthesized, examples of these silica-gel resins are those modified with nitrogen-containing chelating groups [16,17], oxygen-containing derivatives [18,19], and sulfur-containing complexing reagents [20].

Among the chelating ligands, linear polyamine in the forms of $\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH})_{n-1}\text{H}$, i.e. ethylenediamine (EDA, $n=2$), diethylenetriamine (DETA, $n=3$), triethylenetetramine (TETA, $n=4$), etc., can form stable metal complexes with a variety of metal ions. And the immobilization of this kind of polyamine onto the surface of silica-gel has been studied [21]. In addition, these polyamines are

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convenient starting materials for preparing further multidentate ligands. For example, Soliman et al. have reported diethylenetriamine mono-naphthaldehyde and mono-salicylaldehyde Schiff bases chemically bonded on the surface of silica-gel [22].

However, intra- and inter-strand bridging reaction in the preparation of polyamine functionalized silica-gel are inevitable due to *N*-alkylation at different primary amino and imino groups in the ligands. These bridging reactions should reduce the number of immobilized ligands. Moreover, complicated cross-linkings among the ligands should bring about steric restrictions on formation of metal chelate. Suzuki had successfully immobilized diethylenetriamine ligands on chloromethylated polystyrene beads via an end-group protection method [23].

In the present paper, diethylenetriamine as a simple chelating ligand was loaded on the surface of silica-gel by four different kinds of routes, heterogeneous-direct-amination (hetero-DA), homogeneous-direct-amination (homo-DA), heterogeneous end-group protection (hetero-EGP) and homogeneous end-group protection (homo-EGP) routes. The structures and properties of all grafted products were characterized by FTIR, XRD, TG, and porous structural analysis, and the amount of diethylenetriamine loaded on the silica-gel was determined by elemental analysis. The similarities and differences of four resins in structure and property were discussed in detail. The adsorption capacity and the utilization ratio of N of all resulting resins, SG-DETA-1, SG-DETA-2, SG-DETA-3 and SG-DETA-4, for Ag⁺, Cu²⁺, Ni²⁺, Hg²⁺, Zn²⁺ and Pb²⁺ were investigated. The objective of the present investigation is expected to find out the relationship between the structures and adsorption properties of resins prepared by different routes, which may be able to provide novel ideas to design and prepare metal ions adsorbents.

2. Experimental

2.1. Materials and methods

The silica-gel used was of chromatographic grade (60–100 mesh size), obtained from Tenghai Chemical Institute, Qingdao, Shandong, China. It was activated with nitric acid (HNO₃:H₂O = 1:1) at refluxing temperature for 3 h, hydrochloric acid (HCl:H₂O = 1:1) at room temperature for 6 h, then filtered off, washed thoroughly with doubly distilled water till acid-free and finally calcined in muffle at 160 °C for 10 h.

γ-Chloropropyltrimethoxysilane (CPTS) (Wanda Chemicals Factory, Qufu, China) was used without further purification. Salicylaldehyde and DETA which were offered by Shanghai Chemical Factory of China were both chemically pure and used as-received. Organic solvent toluene was redistilled just before use. The other reagents were analytical grade and used as received without any further purification.

C, N analysis of SG-DETA products were subjected to elemental analysis by the Elementar VarioEL III instrument, Elementar Co., Germany. Infrared spectra were obtained on a Fourier transform-infrared spectrophotometer using KBr pellets in the 4000–400 cm⁻¹ region with a resolution of 4 cm⁻¹, by accumulating 32 scans. The wide-angle X-ray diffraction (WAXD) was determined on a rotating target X-ray diffractometer, D/max-2500VPC, Rigaku Corporation, Japan. Porous structure parameters were characterized using an automatic physisorption analyzer ASAP 2020 by BET and BJH methods through N₂ adsorption at 77 K. Thermogravimetric curves recorded on a Netzsch TG 209 thermal analyzer, using 3.0–10.0 mg of the sample under nitrogen at a heating rate of 10–30 K/min. Atomic absorption analysis of the various metal ions was performed with a flame atomic absorption spectrophotometer (Model 932B, made in Australia). The operating condition is presented in Table 1.

Table 1

Operating parameters used for recording AAS for different metal ions

Metal ion	Lamp current (mA)	Slit width (nm)	Wavelength (nm)	Sensitivity (μg/ml)
Ag ⁺	4.0	0.5	338.1	0.06
Cu ²⁺	3.0	0.5	327.4	0.05
Ni ²⁺	4.0	0.2	232.0	0.04
Hg ²⁺	3.0	0.5	253.7	1.6
Zn ²⁺	5.0	0.5	307.6	66
Pb ²⁺	5.0	0.5	283.3	0.16

The flame type of AAS used in this paper was air–acetylene (oxidizing).

2.2. Preparation of chloro-modified silica-gel (SG-Cl)

The introduction of chlorine-containing groups onto the surface of silica-gel was achieved by the treatment of surface silanol groups with CPTS. A typical procedure was similar to the method described in Ref. [24]. A sample of 50.0 g of activated silica-gel was suspended in 200 ml of dry toluene and 50.0 ml of CPTS was added to this suspension. The mixture was mechanically stirred under reflux of the solvent in a nitrogen atmosphere for 12 h. The suspension was filtered and the solid was transferred to a Soxhlet extraction apparatus for reflux-extraction in toluene and ethanol for 12 h, respectively. The product was dried under vacuum at 50 °C over 48 h, to give the modified silica-gel, named SG-Cl. The Cl content (determined by energy dispersive X-ray analysis system, ORAN EVER-2) was 5.4 mmol/g.

2.3. Preparation of SG-DETA-1 by hetero-DA route

Diethylenetriamine was directly introduced onto the surface of SG-Cl by hetero-DA route. A mixture of SG-Cl (10.0 g) and DETA (462 mmol) in ethanol (100 ml) was refluxed for 12 h with continuous stirring under a nitrogen atmosphere. The solid product was then filtered off and transferred to the Soxhlet extraction apparatus for reflux-extraction in ethanol for 24 h. After extraction, the product was dried under vacuum at 50 °C over 48 h and resin SG-DETA-1 was obtained.

2.4. Preparation of SG-DETA-2 by homo-DA route

The first stage in the preparation of functionalized silica-gel resin via homogeneous route was the synthesis of the new silane coupling reagent by reaction of CPTS with DETA. Ten milliliter (54.2 mmol) of CPTS was mixed with 100 ml of ethanol, and then DETA was added in a 1:8 stoichiometry (CPTS:DETA). The mixture was refluxed for 48 h with magnetic stirring under a nitrogen atmosphere. After cooling, the solvent was evaporated and the product (CPTS-DETA) was obtained. Then the product (CPTS-DETA) was reacted with 10.0 g of activated silica-gel in 100 ml of dry toluene with magnetic stirring for 12 h under reflux conditions being protected by nitrogen. The resulting modified silica-gel (SG-DETA-2) was filtered off and extracted with toluene, ethanol for 12 h, respectively. Finally, the product was dried for 48 h at 50 °C under vacuum.

2.5. Preparation of bis[2-(salicylideneamino ethyl)]amine (DETA-bis-S)

This ligand was prepared by the method described in the literature [25]. The Schiff base DETA-bis-S was produced immediately on mixing DETA with salicylaldehyde in ethanol in 1:2 molar ratios. The reaction mixture in ethanol was refluxed for 2 h to ensure the completion of the reaction.

2.6. Preparation of SG-DETA-3 by hetero-EGP route

Ten grams of silica-gel were added to 10.0 g (31.3 mmol) of DETA-bis-S in 100 ml ethanol and refluxed for 12 h with continuous stirring under nitrogen atmosphere. The solid materials were filtered off and then extracted with ethanol for 24 h. After extraction, the product SG-DETA-S-1 was collected and dried at 50 °C under vacuum. Then the resulting product SG-DETA-3 was obtained by the method described in Ref. [23]. A suspension of 6.1 g SG-DETA-S-1 and 100 ml of 6 mol/l HCl aqueous solution were stirred for 24 h at 60 °C. Salicylaldehyde was liberated as yellow oil during the hydrolysis. Yellow product (SG-DETA-3) which was the hydrochloride form was filtered off, washed with ethanol and dried under vacuum. The resulting resin in the free amine form was obtained by treatment with 2 mol/l sodium hydroxide followed with water until the washings were neutral.

2.7. Preparation of SG-DETA-4 by homo-EGP route

Ten milliliter (54.2 mmol) of CPTS was reacted with 35 g (109.6 mmol) of the DETS-bis-S in 100 ml of ethanol. The mixture was refluxed under dry nitrogen atmosphere for 12 h and the solvent was evaporated subsequently. This condensed solution was added to a suspension of 9.9 g of silica-gel in 100 ml dry toluene. After refluxing for 12 h under a dry nitrogen atmosphere, the solid was filtered, washed with toluene and ethanol and dried under vacuum to give the product named SG-DETA-S-2. The salicylaldehyde was liberated during hydrolysis as previously described and the resulting product (SG-DETA-4) was obtained.

2.8. The adsorption properties for metal ions of SG-DETA-1, SG-DETA-2, SG-DETA-3, SG-DETA-4

Static adsorption experiment was employed to determine the adsorption capabilities of SG-DETA-1, SG-DETA-2, SG-DETA-3 and SG-DETA-4 for different kinds of metal ions. The 0.1 M stock solutions of Cu²⁺, Ni²⁺, Zn²⁺ and Pb²⁺ were prepared in distilled water and the those (0.1 M) of Ag⁺ and Hg²⁺ were prepared in 2% HNO₃. Buffer solution of acetic acid/acetate (pH 5.0) was used for the experiments.

Static adsorption experiments were carried out by shaking 0.05 g of resins with 20 ml of metal ion solution, where the concentration of the metal ion was (5×10^{-3} M) at pH 5.0. The mixture was equilibrated for 24 h on a thermostat-cum-shaking assembly at 25 °C. Then a certain volume of the solutions was separated from the adsorbent and the residual concentration of metal ions was detected by means of atomic absorption spectrometry (AAS). The adsorption amounts were calculated according to the following Eq. (1) and the utilization ratio of N was calculated from Eq. (2)

$$Q = \frac{(C_0 - C)V}{W} \quad (1)$$

$$\frac{Q}{N} = \frac{Q_0}{N\%} \quad (2)$$

where Q is the adsorption amount (mmol/g), C_0 and C , the initial and the final concentrations of metal ions in solution, respectively (mmol/ml), V the volume (ml), W the weight of SG-DETA-1, SG-DETA-2, SG-DETA-3, SG-DETA-4 (g), Q/N the utilization ratio of N, Q_0 the saturation adsorption (mmol/g), and $N\%$ is the content of N functional group (mmol/g).

The adsorption kinetics on the uptake of Hg²⁺ by resins was studied by placing 0.05 g of resins with 20 ml of metal ion solution in a flask, where the concentration of the metal ion was (5×10^{-3} M) and pH 5.0. One milliliter of the solution was taken at different

time intervals, where the residual concentration of metal ion was determined via AAS.

3. Results and discussion

3.1. Preparation

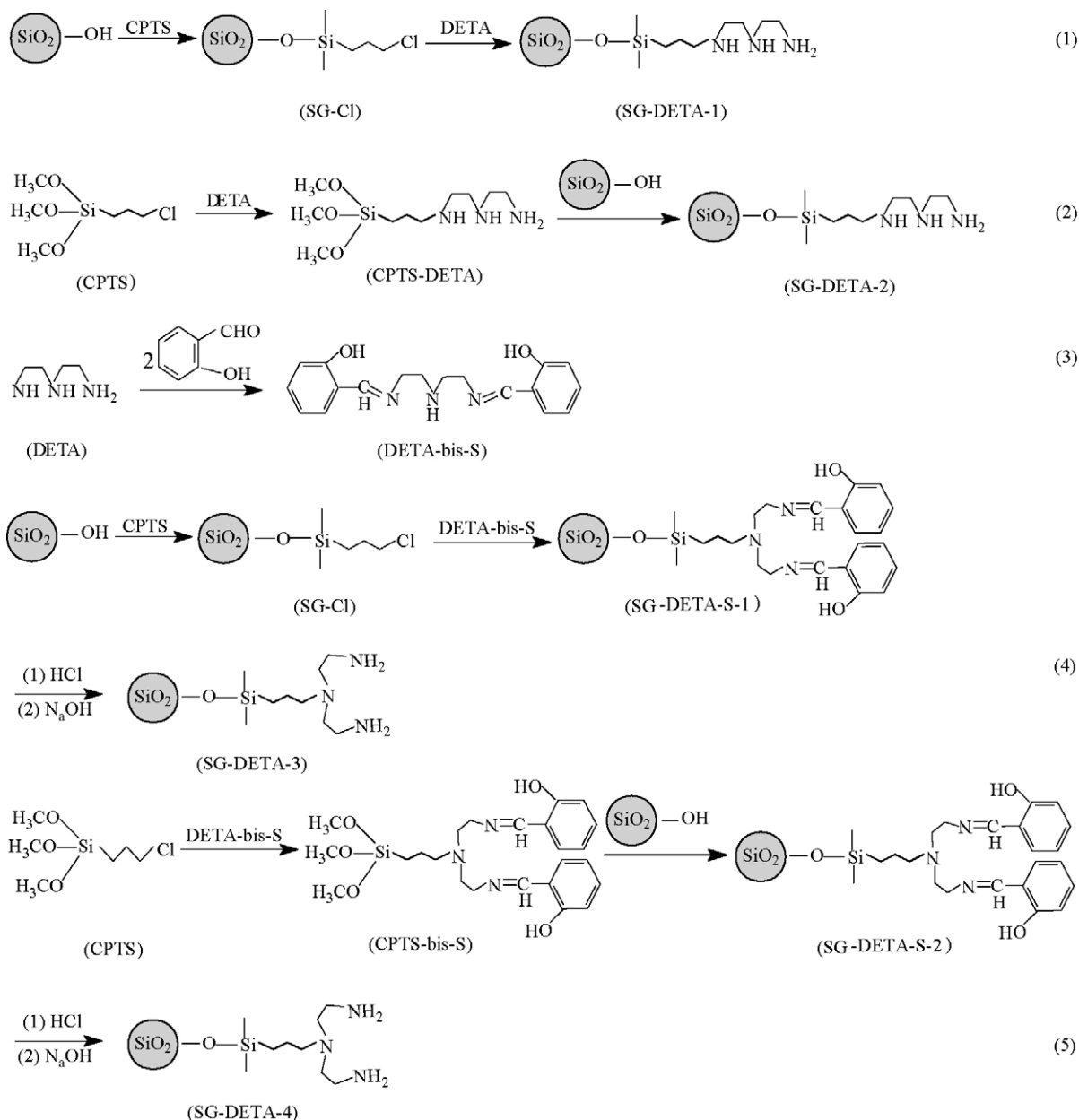
In order to investigate the effects of the variation of preparation methods on the structures of chelating resins and the relationship between properties and their structures, four kinds of synthetic routes were designed to prepare chelating resin silica-gel-supported DETA. The ideal synthetic scheme is illustrated in Scheme 1.

The immobilization could be achieved in two distinct ways, that is, heterogeneous route and homogeneous route [26,27]. For the reaction of DETA with chlorinated activated silica-gel (i.e. SG-Cl) through hetero-DA route, cross-linking reactions are inevitable because the *N*-alkylation reaction can occur at primary amino and secondary amino groups in DETA [21]. These cross-linking reactions should decrease the amount of immobilized ligand (DETA). Moreover, complicated cross-linkings should bring about steric restrictions on the formation of metal chelate. In order to minimize the formation of cross-linkings, a homo-DA route was designed. That is, the reaction of CPTS with DETA was carried out in the presence of excessive DETA.

As is well known, diethylenetriamine readily forms 1:2 Schiff base with salicylaldehyde [25], and the original amine can be regenerated by acid hydrolysis. Thus we intended to protect the primary amino groups of the DETA by Schiff base formation prior to immobilization. Scheme 1 showed the synthetic scheme for the preparation of silica-gel-supported DETA in which the Schiff base DETA-bis-S was introduced onto the surface of silica-gel. The resulting yellow resins SG-DETA-S were presumed to have a structure as depicted in Scheme 1(3) in which DETA was linked to silica-gel uniquely through the secondary amino nitrogen.

In the heterogeneous route, the silane coupling reagent CPTS was first grafted onto silica-gel and then reacted with DETA or DETA-bis-S to give a final product SG-DETA-1 or an intermediate product SG-DETA-S-1. Subsequently, the salicylaldehyde in SG-DETA-S-1 was removed by acid hydrolysis to give the final product SG-DETA-3. The homogenous route was based on the immobilization of the new coupling reagent CPTS-DETA (or CPTS-bis-S), prepared by the reaction of CPTS with DETA (or DETA-bis-S), onto silica-gel surface to form resulting resins SG-DETA-2 (or the intermediate product SG-DETA-S-2). And then salicylaldehyde in SG-DETA-S-2 was also removed by acid hydrolysis to give the final product SG-DETA-4.

The loading results of the elemental analysis of functionalized silica-gel are summarized in Table 2. Generally, the degree of cross-linking of polyamine on the surface of silica-gel can be expressed by the molar ratio of C/N. Yoshitake and his coworkers [21] have reported that when an amine molecule such as NH₂(CH₂CH₂NH)_{*n*-1}H (for DETA *n* = 3) was attached with *m* chloropropyl chains (*m* = 1, 2, 3, ..., <3*n*), the respective C/N becomes (3*m* - 2)*n*⁻¹ + 2. The comparison in Table 2 clearly revealed that the C/N of SG-DETA-1 were *m* = 1.52, indicating one DETA molecule reacted with more than one but less than two chloropropyl chains on the surface of silica-gel. This indicated that about 34% of DETA on the surface of silica-gel were in the bridged form as illustrated in Scheme 2(a and b). In contrast, the C/N of SG-DETA-2 were *m* = 1.28, meaning that about 21.8% of DETA on the surface of silica-gel were in the bridged form and about 77.2% of DETA were in the linear forms as illustrated in Scheme 2(c and d). The above fact demonstrated the homo-DA was a more effective route than hetero-DA to minimize cross-linking reaction. It should be noted that the C/N of



Scheme 1. The ideal synthetic schemes of chelating resins silica-gel-supported diethylenetriamine.

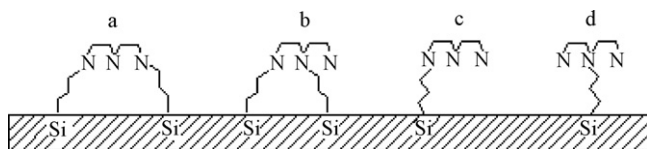
SG-DETA-3 was surprisingly high. There were two possible explanations for this as follows: (1) in the preparation of SG-DETA-S-1, the compound DETA-bis-S was being too large to bind with the site of every chloropropyl chain (see Scheme 3A), the residual chloropropyl chains with high content of carbon led to the increase of C/N of SG-DETA-3; (2) the hydrolysis of SG-DETA-S-1 was incomplete.

However, the hydrolysis condition adopted in this study should be considered as the suitable condition according to the reference [23]. In addition, there were no previous peaks representing benzene ring appeared in the FTIR spectrum of the final product. Accordingly, the former reason, that is, the steric hindrance of chloropropyl chain should be the major factor leading to the high C/N. For SG-DETA-4,

Table 2
Results of elemental analysis of (SG-DETA-1; SG-DETA-2; SG-DETA-S-1; SG-DETA-S-2; SG-DETA-3; SG-DETA-4)

Samples	Nitrogen (wt%)	Nitrogen (mmol/g)	Carbon (wt%)	C/N ^a	L ₀ (mmol/g)	m
SG-DETA-1	2.424	1.731	5.932	2.85	0.577	1.52
SG-DETA-2	3.969	2.835	8.891	2.61	0.945	1.28
SG-DETA-S-1	0.155	0.111	6.385	47.89	0.037	
SG-DETA-S-2	2.030	1.450	13.51	7.76	0.483	
SG-DETA-3	0.075	0.054	2.406	37.10	0.0181	35.77
SG-DETA-4	1.282	0.916	8.939	8.12	0.305	6.78

^a Molar ratio.



Scheme 2. Possible models of the surface structure of SG-DETA.

the value of C/N was higher than SG-DETA-1 and SG-DETA-2, but lower than SG-DETA-3. One factor should be confirmed that the incomplete hydrolysis was not the major reason as SG-DETA-3. A reaction of chloropropyl chain with the hydroxyl group of DETA-bis-S was assumed. This reaction might generate an ether bond (Ph–O–R) which was not easy to be broken by acid (Scheme 3B). This deduction will be confirmed in the further study.

Furthermore, it is possible to calculate the amount of attached ligands onto the surface of silica-gel (L_0) from the percentage of nitrogen in the functionalized silica-gel, calculated by elemental analysis, using the following expression:

$$L_0 = \frac{\%N \times 10}{14n}$$

where %N is the weight percentage of nitrogen in product and n is the number of nitrogen in the ligand (here $n=3$). In addition, as can be observed from Table 2, the quantity of anchored ligands was always superior via the homogeneous functionalization routes. For example, the amount of amine using the homo-DA route, SG-DETA-2, gave a value of 0.945 mmol/g and the resin obtained through the hetero-DA route, SG-DETA-1, gave 0.577 mmol/g. In the homo-EGP route, the amount of amine of the resin SG-DETA-4 (0.305 mmol/g), was much bigger than SG-DETA-3 (0.0181 mmol/g) obtained by hetero-EGP route. The presence of three alkoxy groups in the silane coupling reagent (CPTS) meant that they could react with the hydroxyl groups on the surface of silica-gel via one, two or all alkoxy groups. The steric hindrance induced by pendant chloropropyl chains covalently bond to the silica-gel surface may explain the low degree functionalized by heterogeneous routes. Comparing the amount of attached ligands on the surface of silica-gel, it can be concluded that the degree of functionalization obtained by end-group protection routes was lower than that obtained by direct routes. The degree of functionalization of the silica-gel, SG-DETA-3 and SG-DETA-4, was low because of the steric hindrance of Schiff base. Just due to end-group protection, almost all the amine molecules existed in the forms of bicultural form (Scheme 2d) on the

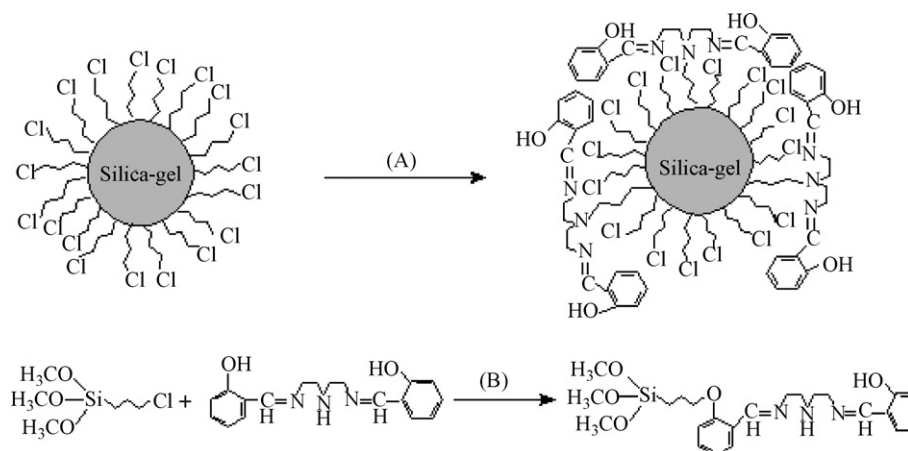
surface of the resins. Moreover, the chance of forming the cross-linking structure between amine groups and silica-gel matrix in the reaction course was small and the ligands could be dispersed uniformly on the surface of silica-gel.

3.2. X-ray diffraction analysis

The X-ray diffraction patterns for all products of silica-gel were obtained by rotating target X-ray diffractometer. All the strong diffraction peak of the original and chemically modified silica-gel appeared at about 22° , which was the amorphous diffraction of SiO_2 . This result indicated that the topological structure of silica-gel did not change obviously after grafting reactions, and silica-gel was stable enough to experience the functionalized reactions. Moreover, no novel diffraction peak appeared after reactions, which indicated that the grafting moieties did not form novel crystal structure on the silica-gel surface. However, the relative intensity decreased at 22° for SG-Cl and increased for SG-DETA-1, SG-DETA-2, SG-DETA-S-3 and SG-DETA-S-4. The weak interaction between silanol and chlorine probably explained the decrease of relative intensity for SG-Cl. Meanwhile, N atom might be involved in a strong interaction $\text{Si}-\text{O}-\text{H} \cdots \text{N}-$, which increased the relative intensity for SG-DETA-1, SG-DETA-2, SG-DETA-S-3 and SG-DETA-S-4. The relative intensity of SG-DETA-3 (or SG-DETA-4) was higher than its counterpart SG-DETA-S-1 (or SG-DETA-S-2). That was because the primary amino was exposed again after acid hydrolysis and the probability of forming hydrogen bond increased.

3.3. FTIR spectroscopy analysis

Infrared spectroscopy was employed in order to identify the immobilization onto the surface of silica-gel (FTIR spectra omitted). A large broad band between 3200 and 3400 cm^{-1} of the silica-gel spectra attributed to the presence of the O–H stretching frequency of silanol groups and also to the remaining adsorbed water. The broad and intense band at 1100 cm^{-1} was assigned to the siloxane vibration (Si–O–Si). And Si–O bond stretching was detected at 962 cm^{-1} . Other bands at 801 and 472 cm^{-1} was due to Si–O–Si stretching and Si–O–Si bending, respectively. In the spectrum of SG-Cl, a new band appeared at 2961 cm^{-1} corresponded to the (C–H) stretching frequency, due to the presence of the carbon chain of CPTS attached to the silica-gel. New band appeared at 697 cm^{-1} was assigned to the C–Cl rocking vibration of Si– CH_2Cl , whose intensity was observed to disappear or decline after the reaction with the diethylenetriamine. The relative



Scheme 3. The illustration of the possible structure of SG-DETA-S-1 and CPTS-bis-S.

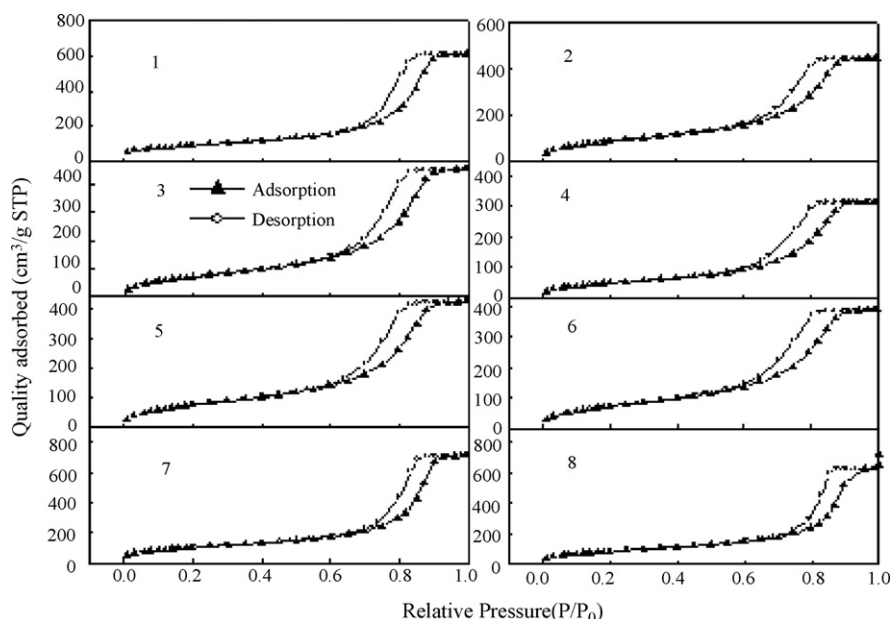


Fig. 1. Nitrogen adsorption–desorption isotherms of the products (1: silica-gel; 2: SG-Cl; 3: SG-DETA-1; 4: SG-DETA-2; 5: SG-DETA-S-1; 6: SG-DETA-S-2; 7: SG-DETA-3; 8: SG-DETA-4).

intensity of the band at 962 cm^{-1} for the silanol groups (Si–OH) reduced considerably as expected in such immobilization processes [28].

The binding of the Schiff base complexation agents to silica-gel surface was confirmed by IR spectral analysis of the SG-DETA-S-1 and SG-DETA-S-2, where new bands 1458 cm^{-1} presented because of incorporation of aromatic rings of salicylic. The band of interest are observed at 1397 cm^{-1} , which can be assigned to the bending vibration (N–H) transferred to lower frequencies, and the band of C=N was not obvious. Both of them could be explained by the stretching vibration of remaining Si–O of the silica-gel which strongly absorbed at 1630 cm^{-1} [29]. Moreover, stretching vibration (O–H) of aromatic hydroxyl groups and stretching vibration (N–H) of aliphatic diethylenetriamine located were overlapped in the range of $3840\text{--}2975\text{ cm}^{-1}$. And in the hydrolysates, SG-DETA-3 and SG-DETA-4, the relative intensity of two bands at 1458 and 1397 cm^{-1} decreased or disappeared.

3.4. Pore structure analysis

Fig. 1 showed the nitrogen adsorption–desorption isotherms for silica-gel and its derivatives. Silica-gel, SG-Cl, SG-DETA-1, SG-DETA-2, SG-DETA-S-1, SG-DETA-S-2, SG-DETA-3 and SG-DETA-4 were type IV according to the acknowledged BDDT classification and each had a hysteresis loop that was representative of mesoporous. The volume adsorbed for all isotherms sharply increased at a relative pressure (P/P_0) of approximately 0.7, representing capillary condensation of nitrogen within the uniform mesoporous structure. The inflection position shifted slightly toward lower relative pressures, and the quantity of nitrogen adsorbed decreased with functionalization except for SG-DETA-3 and SG-DETA-4. This special phenomenon was probably because sodium hydroxide, which was utilized to remove hydrochloric acid to make amine free (see Section 2.6), partially destroyed the framework of silica-gel and made its pore diameter increase.

Fig. 2 showed the BJH desorption pore size distributions of silica-gel, SG-Cl, SG-DETA-1, SG-DETA-2, SG-DETA-S-1, SG-DETA-S-2, SG-DETA-3 and SG-DETA-4. As illustrated in Fig. 2, the pores between 5 and 12 nm were dominant for all products. With the

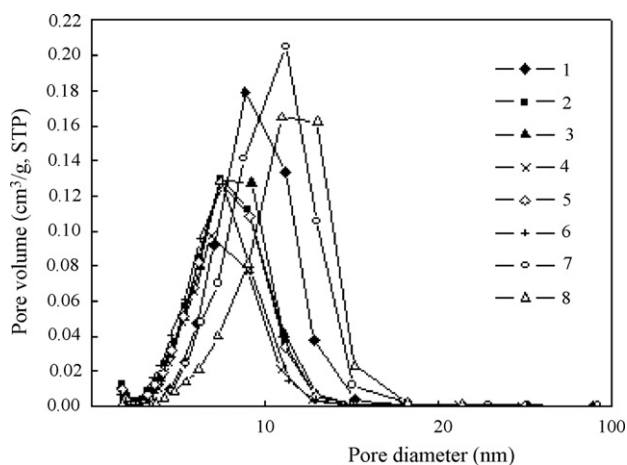


Fig. 2. BJH desorption pore size distributions of the products (1: silica-gel; 2: SG-Cl; 3: SG-DETA-1; 4: SG-DETA-2; 5: SG-DETA-S-1; 6: SG-DETA-S-2; 7: SG-DETA-3; 8: SG-DETA-4).

proceeding of the reaction, the pore size became small gradually, except curves 7 and 8. The porous structure parameters of the products from the basis of the nitrogen adsorption data are summarized in Table 3. A BET surface area of $331.32\text{ m}^2/\text{g}$ and a BJH desorption

Table 3

Parameters of porous structure of the products (silica-gel; SG-Cl; SG-DETA-1; SG-DETA-2; SG-DETA-S-1; SG-DETA-S-2; SG-DETA-3; SG-DETA-4)

Resins	BET surface area (m^2/g)	BJH desorption cumulative volume of pores (cm^3/g) ^a	BJH desorption average pore diameter (nm)
Silica-gel	331.32	0.95	8.92
SG-Cl	322.14	0.69	7.34
SG-DETA-1	273.88	0.71	7.69
SG-DETA-2	186.15	0.49	7.25
SG-DETA-S-1	295.36	0.67	7.38
SG-DETA-S-2	275.94	0.61	7.05
SG-DETA-3	379.06	1.12	9.87
SG-DETA-4	321.86	0.97	10.06

^a The total volume of pores between 1.7 and 300 nm diameter.

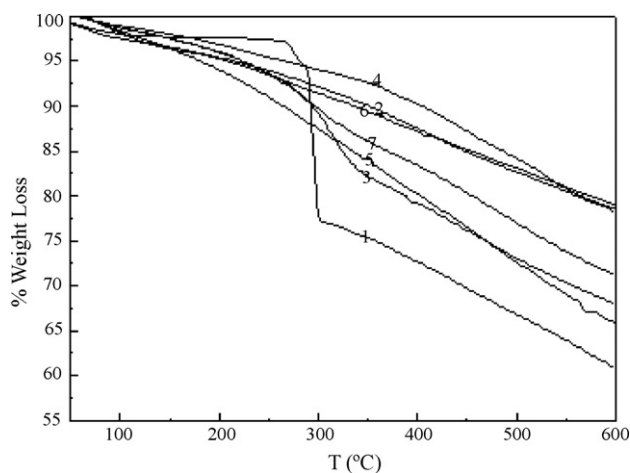


Fig. 3. Thermogravimetric curves of 1: SG-Cl; 2: SG-DETA-1; 3: SG-DETA-2; 4: SG-DETA-S-1; 5: SG-DETA-S-2; 6: SG-DETA-3; 7: SG-DETA-4.

volume of $0.95 \text{ cm}^3/\text{g}$ were obtained for silica-gel, which decreased to $322.14 \text{ m}^2/\text{g}$ and $0.69 \text{ cm}^3/\text{g}$, respectively, after grafting chloropropylsilane. In addition, the pore size decreased from 8.92 to 7.34 nm. Further decreases in the BET surface area, pore diameter and pore volume were clearly found with DETA-attached silica-gel. The slight decrease of the pore size could be attributed to the formation of an organic layer in the pores, which blocked the adsorption of nitrogen molecules. Due to the hydrolysis by sodium hydroxide as explained in the part of nitrogen adsorption–desorption isotherms, the pore diameter of hydrolysates, SG-DETA-3 and SG-DETA-4, was larger than all above (Table 3). It also should be noted that in SG-DETA-2 prepared by the homo-DA route, the BET surface area, BJH desorption cumulative volume and BJH average pore diameter of pores were lower than SG-DETA-1 prepared by the hetero-DA route. These results confirmed the higher degree of functionalization obtained with the homogeneous route. The similar regularity for SG-DETA-3 and SG-DETA-4 was presented.

3.5. Thermogravimetry analysis

The thermogravimetric curves reflect the thermal stability of these new materials. The thermal stabilities of chelating resins prepared and their intermediates were detected at the range of $0\text{--}600^\circ\text{C}$. As can be seen in Fig. 3, the curve of SG-Cl presented a first mass loss of 2.1% from 33 to 110°C , which was attributed to condensation of the remaining silanol groups, yielding siloxane groups (Si–O–Si). The physically adsorbed water also contributed to the above mass loss. A pronounced increase in mass loss was observed for the second step from 290°C , which was related to the decomposition of the immobilized silane coupling agent and also related to the condensation of the remaining silanol groups. The decomposition process was responsible for the increase of siloxane bonds as the temperature increases. The resulting products SG-DETA-1, SG-DETA-2, SG-DETA-3 and SG-DETA-4 also presented two distinct stages of mass loss. Following the preceding interpretation, the first mass loss was assigned to adsorbed water, and the other mass loss from 170°C which was attributed to the organic ligands immobilized on the surface. And for all functionalized silica-gel, the expected small degree of silanol condensation was hidden by the loss of organic groups in the second step of decomposition. The thermal stability indicated that these resins satisfied the demand for leaching metal ions because the lowest decomposition temperature of organic group was at 170°C .

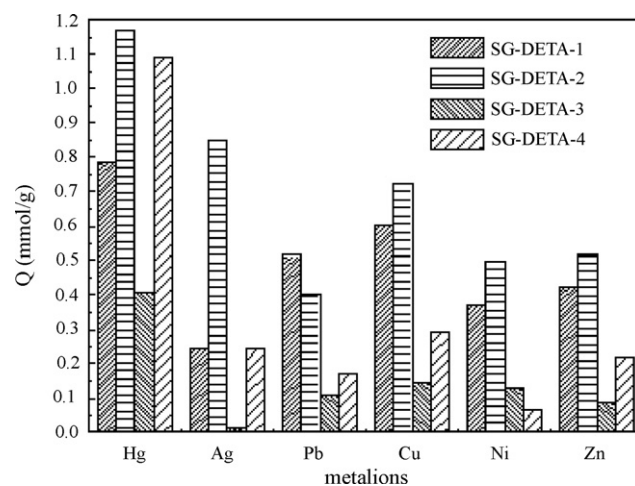


Fig. 4. The saturation adsorption capacities of SG-DETA-1, SG-DETA-2, SG-DETA-3 and SG-DETA-4 for metal ions at pH 5.0. Initial solution (20 ml): $5 \times 10^{-3} \text{ M}$. Temperature: 25°C .

3.6. Adsorption properties

The aim of grafting functional groups onto the surface of silica-gel is to prepare the modified silica-gel with most excellent coordination properties. Saturated 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. The saturated adsorption experiments for all metal ions at pH 5.0 were studied at 25°C . In order to avoid the decrease of coordination capacity of adsorbent due to the protonation of N atom at lower pH and formation of precipitate of the metal ions at high pH [30,31], the pH 5.0 was selected for quantitative sorption Ag^+ , Cu^{2+} , Ni^{2+} , Hg^{2+} , Zn^{2+} and Pb^{2+} . Twenty-four hour of contact time was selected in this study to ensure the metal ions can be completely adsorbed although the equilibrium adsorption time of functionalized silica-gel for metal ion was reported to be 4 h in reference [11]. The kinetic experiment also proved the equilibrium adsorption times of the four above-mentioned resins for Hg^{2+} were about 6–8 h (see Fig. 5).

Fig. 4 showed the saturation adsorption capacities of SG-DETA-1, SG-DETA-2, SG-DETA-3 and SG-DETA-4 for Ag^+ , Cu^{2+} , Ni^{2+} , Hg^{2+} , Zn^{2+} and Pb^{2+} . Obviously, all resins had good adsorption capability for Hg^{2+} , Ag^+ and Cu^{2+} , especially for Hg^{2+} and Cu^{2+} . So in the following part, the adsorption of all the resins for Hg^{2+} and Cu^{2+} were explained particularly. No matter what metal ions was used, the resins, SG-DETA-1 and SG-DETA-2 prepared by the direct-amination routes, revealed much higher adsorption capacities than the corresponding resins, SG-DETA-3 and SG-DETA-4 prepared by the end-group protection routes. That was because the amount of ligands anchored by the direct-amination routes was higher than that by the end-group protection routes. Meanwhile, the resins, SG-DETA-2 and SG-DETA-4, which obtained by homogeneous route had good adsorption capability. As mentioned before, both resins had a higher amount of ligands anchored on the surface of silica-gel.

However, it can be seen that higher N content of silica-gel resins do not ensure a higher utilization ratio of N. As illustrated in Fig. 4, the resins, SG-DETA-1 and SG-DETA-2, had relatively the high adsorption capacity for metal ions, whereas they did not have the higher utilization ratio of N versus SG-DETA-3 and SG-DETA-4 (Table 4). Specifically, the utilization ratio of N was out of proportion to the adsorption capacity. In the case of resins SG-DETA-1 and SG-DETA-2, much steric hindrance by complicated cross-linkings between primary amino and secondary amino groups gave rise to

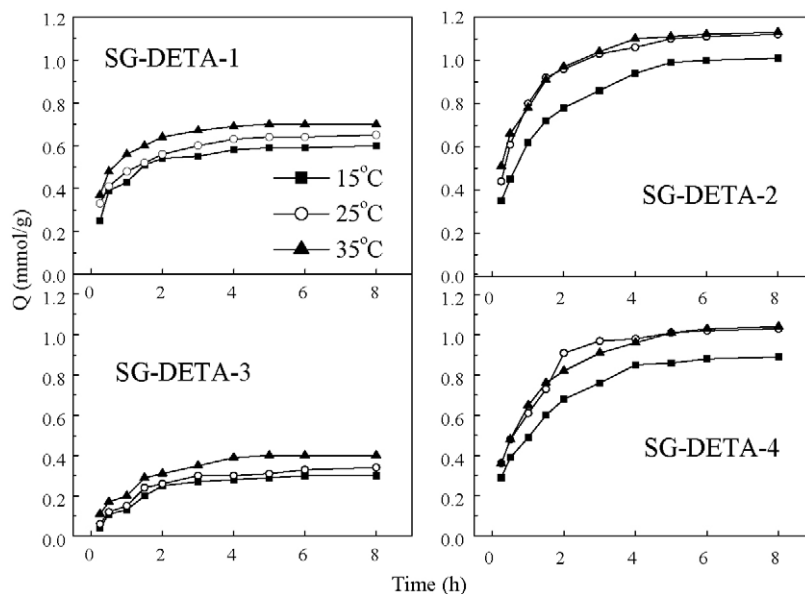
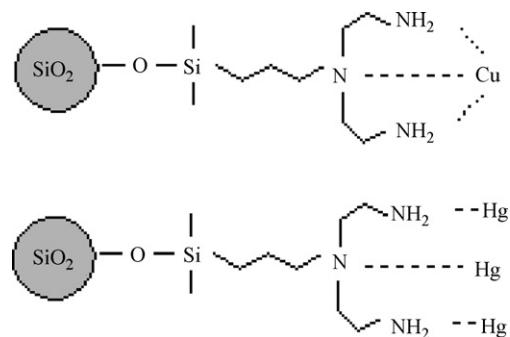


Fig. 5. Effect of contact time on the adsorption of Hg^{2+} by SG-DETA-1, SG-DETA-2, SG-DETA-3 and SG-DETA-4 at different temperature and pH 5.0. Initial solution (20 ml): 5×10^{-3} M.

a decrease in the ligands capacity, whereas the resins SG-DETA-3 and SG-DETA-4 contained dispersing ligand units gave rise to a good coordination. Interestingly, the resin SG-DETA-3 was of the lowest N content but the highest utilization ratio of N. This experimental fact can be interpreted that: (1) no cross-linking among ligand units and the uniform distribution of ligand units on the surface of silica-gel was beneficial to the efficient utilization of N atoms; (2) the ampleness of the surface pores and high surface area of resins SG-DETA-3 was propitious to the metal ion accessing to coordinate with N atom in ligands. For the same reason, the adsorption capacity of resin SG-DETA-4 for above metal ions was lower than resins SG-DETA-1 and SG-DETA-2, but the utilization ratio of N was much the same, SG-DETA-4's was even higher. The result indicated that the amount of immobilized functional groups was not the only factor affecting the metal adsorption, but the surface pore structure might also affect the metal binding. Moreover, the adsorption capacity of resin SG-DETA-4 for Cu^{2+} was 0.29 mmol/g, which was close to the ligands content (0.305 mmol/g). Thus, most of the functional groups of resin SG-DETA-4 seemed to form 1:1 complex with Cu^{2+} . On the other hand, the adsorption capacity for Hg^{2+} (1.09 mmol/g) was almost three times as that for Cu^{2+} . According to the above fact, we proposed the structures of the chelates as illustrated in Scheme 4. So the utilization ratio of N of resin SG-DETA-4 for Hg^{2+} was higher than Cu^{2+} and the better selective adsorption was expected.

In order to further confirm the equilibrium time of adsorption, the adsorption kinetics of Hg^{2+} on the four different resins at initial Hg^{2+} concentration of 5×10^{-3} M and pH 5.0 was investigated. The results are shown in Fig. 5. From Fig. 5, it was obvious that about 90% of the equilibrium adsorption capacity could be achieved after 4 h and the adsorption equilibrium was completely achieved after



Scheme 4. Proposed models of chelates between ligand of resin SG-DETA-4 and Cu^{2+} and Hg^{2+} .

6–8 h. In initial fast adsorption step, Hg^{2+} might enter easily the accessible pore sites and bind with the ligands, while in the slow adsorption step; some Hg^{2+} might be hampered to diffuse into the deeper pores. Fig. 5 also showed that the effect of temperature on the adsorption of Hg^{2+} by the four kinds of resins. From the experiment result, it was demonstrated that temperature has only a slight positive effect on the adsorption capacities.

From the results of adsorption, it can be concluded that valuable adsorbents should possess some features as follows: firstly, high surface area, abundant surface pores, uniform distribution of functional groups to ensure the furthest utilization of donor atoms; secondly, numerous surface functional groups with no cross-linkings to ensure high adsorption capacity.

4. Conclusion

Modification of silica-gel had been successfully carried out via hetero-DA route, homo-DA route, hetero-EGP route and homo-EGP route. Preparation, characterization and adsorption properties of four kinds of resins had been compared in detail. Both the X-ray diffraction and pore structure analysis indicated that the silica-gel matrix was so stable that the porous structure still remained. The thermogravimetry analysis showed that the resulting resins satisfied for adsorption experiments because the organic func-

Table 4

The utilization ratio of N of SG-DETA-1, SG-DETA-2, SG-DETA-3 and SG-DETA-4 for metal ions

Resins	Hg^{2+}	Ag^+	Pb^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}
SG-DETA-1	0.46	0.10	0.30	0.35	0.21	0.25
SG-DETA-2	0.41	0.30	0.14	0.26	0.18	0.15
SG-DETA-3	7.52	0.28	1.98	2.63	2.35	1.56
SG-DETA-4	1.19	0.27	0.18	0.32	0.07	0.24

tional groups were not decomposed less than 170 °C. The results of all characterization showed that homo-DA route and homo-EGP route were easier procedures to produce immobilization than corresponding heterogeneous routes. The results showed that temperature had a slight positive effect on adsorption capacity and equilibrium adsorption time of four kinds of resins for Hg²⁺ was 6–8 h. Hetero-DA route and homo-DA route provided larger amount of N content than corresponding end-group protection routes. The resins obtained by direct-amination route had good adsorption capability to adsorb metal ions from aqueous solution, especially for Hg²⁺ and Cu²⁺. But the end-group protection routes especially hetero-EGP route could bring out the high utilization ratio of N due to the uniform dispersions of ligands on the surface of resins. So an interesting conclusion presented that higher N content did not ensure the high utilization ratio of N. Based on specific requirement, an appropriate route can be chosen, that is, the homo-DA route for high adsorption capacity and the hetero-EGP route for high utilization ratio of nitrogen. Having the advantage of low cost and easy steps, the homo-DA route and hetero-EGP route could be considered as better approaches to prepare adsorbents for metal ions especially for toxic Hg²⁺ and Cu²⁺.

Acknowledgments

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