

Preparation of Iminodiacetic Acid-Type Composite Chelating Material IDAA-PGMA/SiO₂ and Preliminary Studies on Adsorption Behavior of Heavy Metal Ions and Rare Earth Ions

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ABSTRACT: A kind of iminodiacetic acid (IDAA)-type composite chelating materials was prepared by first graft polymerization and subsequent polymer reaction. Monomer glycidyl methacrylate (GMA) was grafted on micron-sized silica gel particles in the manner of "graft through" in a solution polymerization system, resulting in the grafted particles poly(glycidyl methacrylate) (PGMA)/silicon dioxide (SiO₂). Subsequently, the ring-opening reaction of the epoxy groups of the grafted PGMA was carried out with IDAA as reaction reagent, resulting in the bonding of IDAA groups onto PGMA/SiO₂ and obtaining the composite chelating material IDAA-PGMA/SiO₂ particles. The effects of the main factors on the graft polymerization of GMA and the bonding reaction of IDAA were examined emphatically, and the adsorption behavior of IDAA-PGMA/SiO₂ particles toward several kinds of heavy metal ions and rare earth ions was preliminarily explored. The experiments results show that: (a) to obtain the grafted particles PGMA/SiO₂ with high grafting degree, in the graft polymerization step, the reaction temperature and

the used amount of initiator should be controlled. The suitable temperature is 70°C and the appropriate used amount of initiator is 1.4 % of the monomer mass. Under the optimal conditions, the grafted degree of PGMA can reach 17.50 g/100 g. (b) It is feasible to introducing of IDAA groups onto PGMA/SiO₂ particles via ring-opening reaction of epoxy groups of the grafted PGMA under alkaline conditions, and the bonding rate of IDAA group can get up to 70% based on epoxy groups of the grafted PGMA. (c) The composite chelating material IDAA-PGMA/SiO₂ possesses very strong chelating adsorption ability for heavy metal ions, and especially toward Pb²⁺ ion, the adsorption capacity can reach 24 g/100 g. (d) The adsorption ability of IDAA-PGMA/SiO₂ for rare earth ions is weaker than that for heavy metal ions. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2529–2538, 2012

Key words: iminodiacetic acid; glycidyl methacrylate; graft polymerization; chelating adsorption; heavy metal ion

INTRODUCTION

Environmental contamination with heavy metal ions is a serious problem owing to their tendency to accumulate in living organisms and toxicities in relatively low concentration. There is a continuous need for new separation techniques, by which metal ions can be selectively extracted and removed from dilute waste waters and industrial process streams. Many separation methods such as precipitation, chemical reduction, ion exchange, membrane separation, adsorption, and biological treatment have been used to remove heavy metal ions from wastewater. Among these methods, adsorption is an effective and simple method, but the solid adsorbent can be reused. Nowadays, among various solid adsorbent, chelating resins are increasingly used in the removal of heavy metal ions from aqueous medium due

to their high adsorption capacity and excellent selectivity.^{1–5}

There are many types of chelating resins with different chelation groups, such as iminoacetate, Schiff base, aminophosphonate, 8-hydroxyquinoline, amidoxime, and so on. Among to various chelating resins, iminodiacetate group-containing chelating resins universally have strong chelating adsorption ability for various heavy metal ions and rare earth ions because of the chelation suitability of iminodiacetic acid (IDAA) group for diverse metal ions.^{6–8} They are widely used in the removal of toxic and harmful heavy metal ions from water and industrial effluent^{9–12} as well as in the concentration and extraction of rare earth ions.^{13,14}

Except chelating resins, recently, novel composite chelating materials, which consist of chelating polymer and inorganic particle matrix, have attracted much attention in the applications of removing heavy metals from different industrial waste waters. Such new composite materials combine well the strong chelating property of the chelating polymer, which comes from high density of chelating ligand,

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with the many excellent properties of inorganic particles. For preparing such composite chelating materials, two methods can be adopted. One is coating or impregnating the inorganic particles with chelating polymer solutions,^{15–17} and this is a conventional and simple method, but the chelating polymers are easy to be leached out; another method is to try to chemically bond the chelating polymer onto the surfaces of the inorganic particles (chemically anchoring or grafting).^{18–20} This method is more effective due to the binding stability of chelating polymers on inorganic particles. However, a few studies in this respect are reported, and it is probably owing to the preparation difficulty.

This work is aimed at preparing an IDAA-type chelating material, and it is expected that the prepared chelating material as a solid sorbent can be used in the high effective removal of heavy metal ions from aqueous medium and in the concentration and extraction of rare earth ions. This IDAA-type chelating material is a polymeric/inorganic composite material, and it consists of the grafted poly(glycidyl methacrylate) (PGMA) bearing IDAA groups and silica gel (SiO₂) matrix. Monomer glycidyl methacrylate (GMA) was first graft-polymerized on the surfaces of micro-sized silica gel particles, and then IDAA groups were introduced onto the side chains of the grafted PGMA via ring-opening of epoxy groups of the grafted PGMA, resulting in the IDAA-type composite chelating material, IDAA-PGMA/SiO₂. In this work, the preparing process of IDAA-PGMA/SiO₂ was investigated in detail, and at the same time, its chelating adsorption property for heavy metal ions and rare earth ions was examined preliminarily. The composite chelating material IDAA-PGMA/SiO₂ not only possesses strong chelation adsorption ability toward heavy metal ions because of bearing IDAA group with high density, but also it combines the excellent physicochemical properties of silica gel particles such as fine mechanical property, thermal and chemical stability, as well as low cost. IDAA-PGMA/SiO₂ is one of the promising and potential materials in the environmental protection field and in the extraction area of rare earth ions, so the route to prepare such composite chelating material is significant and valuable.

EXPERIMENTAL

Material and equipment

Silica (120–160 mesh, about 125 μm in diameter; Ocean Chemical Limited Company, Qingdao City, China) was of agent grade. γ -Methacryloylpropyl trimethoxysilane (MPS; Nanking Chuangshi Chemical Aux Ltd., Province Jiangsu, China) was of analytical grade. GMA (Suzhou Nanhong Chemical Ltd., Prov-

ince Jiangsu, China) was of analytical grade and was purified by vacuum distillation before use. Azobisisobutyronitrile (ABIN, Guanfu Fine Chemical Institute, Tianjin, China) was of analytical grade and was purified by recrystallization from ethanol. IDAA (Nanton Yongsheng Chemical Ltd., Province Jiangsu, China) was of analytical grade. The other chemicals used were all of commercial analytical grade, and were purchased from Chinese companies.

The instruments used in this study were as follows: Perkin-Elmer1700 infrared spectrometer (Perkin-Elmer Company, USA); LEO-438VP scanning electronic microscope (SEM, LEO Company, UK); PHS-3C pH meter (Shanghai Precision Scientific Apparatus, Shanghai, China); STA449 thermogravimetry analyzer (Netzsch Company, German); THZ-92C constant temperature shaker equipped with gas bath (Shanghai Boxun Medical Treatment Equipment Factory, Shanghai, China).

Preparation and characterization of grafted particles PGMA/SiO₂

According to the procedures described in Ref. 21, silica gel particles were surface-modified with the coupling agent MPS, and the polymerizable double bonds were introduced on the surfaces of silica gel particles, resulting in modified silica gel particles MPS-SiO₂. The double bond content was determined with a KBr-KBrO₃ method, and the modified particles used in this investigation had a double bond content of 1.04 mmol g⁻¹. The graft-polymerization of GMA was performed in a solution polymerization system. 1.5 g of the modified particles MPS-SiO₂ was added into a four-necked flask equipped with a mechanical agitator, a reflux condenser, a thermometer and a N₂ inlet, followed by adding 100 mL of *N,N*-dimethylformamide as solvent and 5 mL the monomer GMA. N₂ was bubbled for 30 min to exclude air and then the content was heated to 70°C. Initiator ABIN, which was 1.4 wt % of monomer mass, was added, and the graft-polymerization was carried out under N₂ atmosphere at the constant temperature of 70°C with stirring. After finishing the polymerization, the resultant particles were extracted with acetone in a Soxhlet extractor for 24 h to remove the polymer attached physically to the particles, and dried under vacuum, obtaining the grafted particles PGMA/SiO₂. The infrared (IR) spectrum of PGMA/SiO₂ particles was determined with KBr pellet method and their morphology was examined with SEM. The grafting degree (GD, g/100 g) of PGMA/SiO₂ particles was determined with hydrochloric acid-acetone method.²² The GD was also determined by thermalogravimetric analysis, and the determination result was coincident with that of the above chemical analysis. The reaction time,

reaction temperature, and the used amount of initiator were varied in series, respectively, to examine their effects on the graft polymerization of GMA.

Preparation and characterization of functional composite particles IDAA-PGMA/SiO₂

Grafted particles PGMA/SiO₂ (2 g) were placed into a four-necked flask of 100 mL, followed by adding 60 mL of a mixed solvent of distilled water (50 mL) and dimethylsulfoxide (DMSO, 10 mL). The grafted particles were allowed to be swelled for 12 h. Subsequently, 5 g of IDAA was added and the pH value of this solution was adjusted to 12 with diluted sodium hydroxide solution, and the ring-opening reaction between the epoxy groups of the grafted PGMA with IDAA as reagent was conducted at 70°C with stirring for 24 h. When the reaction finished, the product particles were collected via filtering, and fully washed with distilled water. After drying under vacuum, the functional composite particles IDAA-PGMA/SiO₂ were obtained.

The IR spectrum of particles IDAA-PGMA/SiO₂ was determined with the KBr pellet method to characterize their chemical structure. The extent (mol %) of the ring-opening reaction of the epoxy groups of the grafted PGMA, namely, the bonding rate (BR; mol %) of IDAA, was measured by weighing method and calculated according to eq. (1)

$$BR = \frac{(m_2 - m_1)/M'}{m_1 \times GD/(M \times 100)} \times 100 \quad (1)$$

where m_1 (g) was the mass of the grafted particles PGMA/SiO₂; m_2 (g) was the mass of the functional particles IDAA-PGMA/SiO₂; M' (177.07) was the molar mass difference between the GMA unit that had undergone the ring-opening reaction and on which IDAA had been bound and the original GMA unit; GD (g/100g) was the PGMA grafting degree of the grafted particles PGMA/SiO₂; M (142.15) was the molar mass of the original GMA unit.

Preliminary estimation of the chelating adsorption property of IDAA-PGMA/SiO₂ particles

The aqueous solutions of Pb(NO₃)₂, Cd(NO₃)₂, and Ni(NO₃)₂ with different concentrations were prepared, respectively, in a range of 1.0 to 20 × 10⁻³ mol · L⁻¹. Pb(NO₃)₂ solutions (20 mL) with different concentrations were placed in several conical flasks, respectively. The functional particles IDAA-PGMA/SiO₂ (0.1 g) accurately weighed were added to these solutions, respectively. These mixtures were shaken in a constant temperature shaker for 3 h. After standing statically, 10 mL of the supernatants were withdrawn and the concentrations of Pb²⁺ ion in these supernatants were determined with ETDA

complexometric titration (using xylenolorange as indicator), respectively, and the equilibrium adsorption amount Q_e (g/100 g) of IDAA-PGMA/SiO₂ particles for Pb²⁺ ion was calculated according to eq. (2) and the adsorption isotherm was figured.

$$Q_e = \frac{V(C_0 - C_e) \times 207}{m \times 10} \quad (2)$$

where C_0 (mol · L⁻¹) was the concentration of Pb²⁺ ion of the initial Pb(NO₃)₂ solution; C_e (mol · L⁻¹) was the concentration of Pb²⁺ ion of the supernatant; V (mL) was the volume of the solution of Pb(NO₃)₂; m (g) was the weight of the adsorbent IDAA-PGMA/SiO₂ particles; the molar mass of Pb atom is 207 g · mol⁻¹.

The adsorption abilities of IDAA-PGMA/SiO₂ particles toward Cd²⁺ and Ni²⁺ ions were also tested with the same method. The concentrations of Cd²⁺ and Ni²⁺ ions in these supernatants were also determined with ETDA complexometric titration, but the used indicators were different from Pb²⁺ determination. For Cd²⁺ ion determination, the used indicator was eriochrome black T, and for Ni²⁺ ion determination, murexide was used as indicator. The adsorption isotherms of IDAA-PGMA/SiO₂ toward Cd²⁺ and Ni²⁺ ions were also plotted.

Similarly, the adsorption abilities of IDAA-PGMA/SiO₂ toward rare earth ions, Nd³⁺, and Sm³⁺ were also tested and the adsorption isotherms of IDAA-PGMA/SiO₂ toward the two rare earth ions were also determined.

RESULTS AND DISCUSSIONS

Reaction process to prepare functional composite particles IDAA-PGMA/SiO₂

Silica gel particles were surface-modified with coupling reagent MPS so as to introduce polymerizable double bonds onto the surfaces of silica gel particles, resulting in modified particles MPS-SiO₂. Then, the graft polymerization of GMA was allowed to be conducted on the surfaces of MPS-SiO₂ particles by initiating of ABIN in the manner of "grafting through" (in the strict sense of the word, grafting techniques include three methods, "grafting to", "grafting through" and "grafting from" methods, and in the "grafting through" method, polymerizable groups are introduced on the surface of the particle^{23,24}), forming grafted particles PGMA/SiO₂. Finally, via the ring-opening reaction of epoxy groups of the grafted PGMA, IDAA molecules were bound on the side chains of PGMA, resulting in the functional composite particles IDAA-PGMA/SiO₂. The entire chemical process to prepare the composite particles IDAA-PGMA/SiO₂ is expressed schematically in Scheme 1.

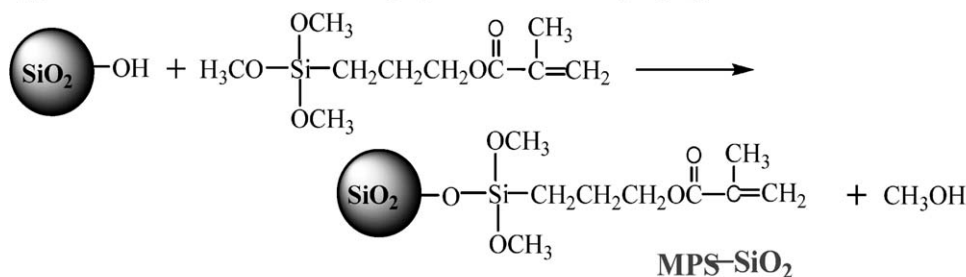
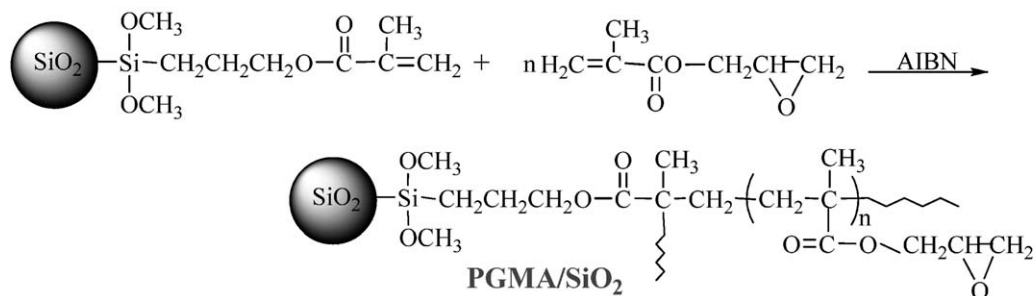
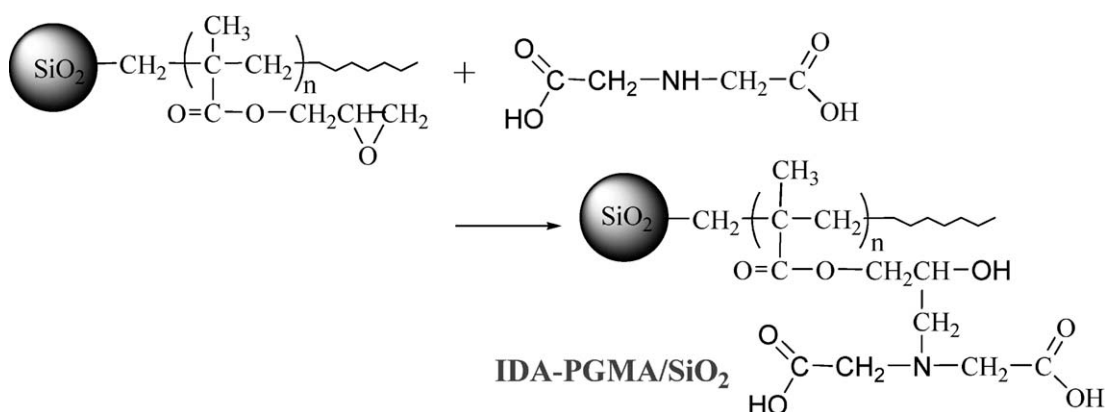
(1) Surface modification of silica gel particles with coupling agent MPS**(2) Graft-polymerization of GMA on silica gel particle****(3) Ring-opening reaction between epoxy group of grafted PGMA and iminodiacetic acid**Scheme 1 Reaction process for preparing composite chelating particle IDAA-PGMA/SiO₂.**Characterization of PGMA/SiO₂ and IDAA-PGMA/SiO₂****Infrared spectra**

Figure 1 presents the infrared spectra of four kinds of particles, silica gel particles SiO₂, modified particles MPS-SiO₂, grafted particles PGMA/SiO₂, and functional particles IDAA-PGMA/SiO₂. In comparison to the spectrum of SiO₂, in the spectrum of MPS-SiO₂, the wide band at 3440 cm⁻¹ that is associated with the silanol groups as well as the adsorbed water has been weakened, and the stretching vibration absorption band of the carbonyl group C=O of ester group appears at 1711 cm⁻¹, showing that the coupling agent MPS has bound onto the surfaces of silica gel particles via the reaction between MPS and

silanol groups, and the modified particles MPS-SiO₂ have formed. In the spectrum of PGMA/SiO₂, the stretching vibration absorption band of the carbonyl group C=O of ester groups has shifted to 1732 cm⁻¹, and it is aroused by the structure difference between the ester groups in the grafted polymer PGMA and that in MPS. More important, the characteristic vibration absorption of epoxy groups appears at 905 cm⁻¹, implying the realization of the graft-polymerization of GMA on the surfaces of SiO₂ particles and the formation of the grafted particles PGMA/SiO₂. In the spectrum of IDAA-PGMA/SiO₂, the absorption of epoxy groups at 905 cm⁻¹ has disappeared, and the absorption of hydroxyl groups at 3440 cm⁻¹ has been strengthened. At the same time,

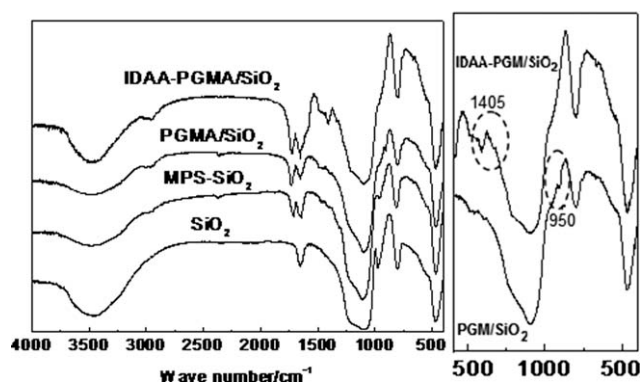


Figure 1 Infrared spectra of four kinds of particles.

the vibration absorption of C—N bond of tertiary amine groups has been produced at 1405 cm⁻¹. All the above changes of spectrum data sufficiently indicate that IDAA has been bound onto particles PGMA/SiO₂ through the ring-opening reaction of the epoxy groups of the grafted macromolecules

PGMA and the functional particles IDAA-PGMA/SiO₂ have been formed. It needs to be pointed out that all of the above various absorption bands of PGMA/SiO₂ and IDAA-PGMA/SiO₂ look very weak because of the affect of the strong absorption background of SiO₂.

SEM image

Figure 2(a,b) present the SEM images of raw silica gel particles and the grafted particles PGMA/SiO₂. It can be found that before the grafting of PGMA, the surfaces of raw silica gel particles are rough and scraggy. After the grafting of PGMA, the surfaces of the grafted particles PGMA/SiO₂ become smoother, and this is caused by the coating and filling up action of the grafted PGMA macromolecules.

Effects of main factors on graft-polymerization of GMA

Effect of time

Figure 3 displays the variation of the GD of PGMA on the grafted particles PGMA/SiO₂ with graft-polymerization time. At the start, the GD of PGMA increases with the reaction time, and up to about 20 h (having a GD of about 16%), the GD nearly no longer changes with time. This reflects a general rule of graft polymerization on solid surface. The reason for this is that a kinetic barrier is produced on the surfaces of the grafted particles during the graft-polymerization.²⁵ As the graft-polymerization is carried out to a certain extent, an entwining and overlapping polymer layer will be formed on the surfaces of silica gel particles, and it produces a kinetic hindrance to blocks monomers diffused to the active sites on the surfaces of the particles and to inhibit

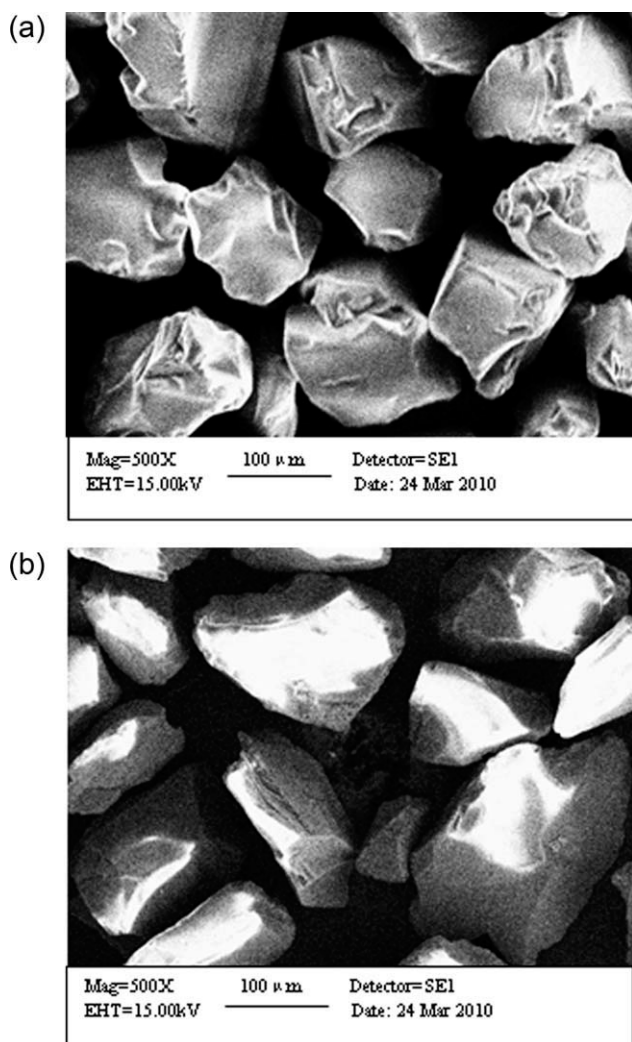


Figure 2 SEM image of two kinds of particles. a: Image of silica gel particles. b: Image of PGMA/SiO₂ particles.

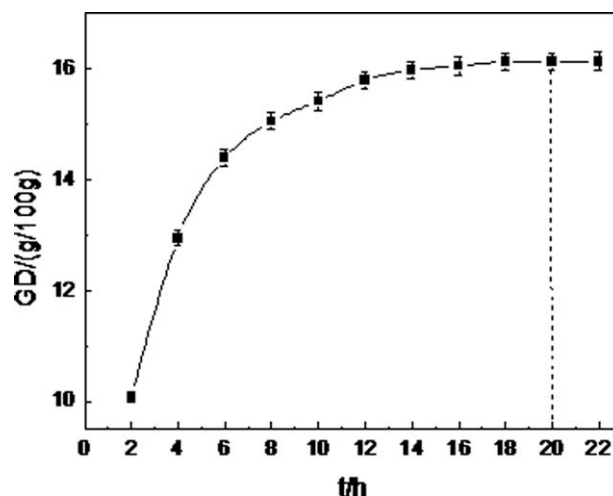


Figure 3 GD of PGMA as a function of graft polymerization time. Temperature: 70°C; Used amount of initiator: 0.9 wt %; GMA concentration: 5%.

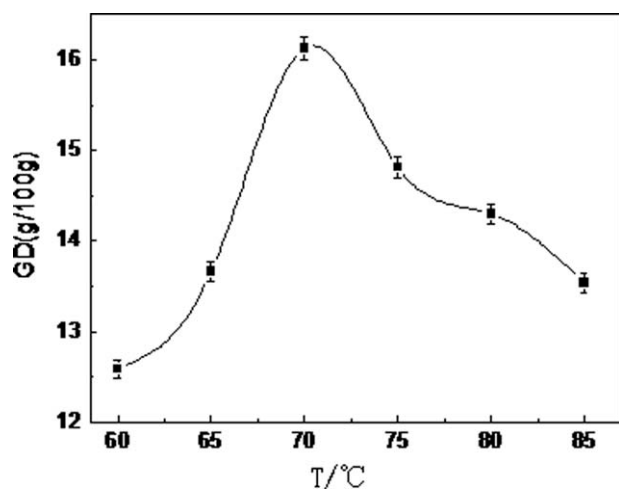


Figure 4 Effect of temperature on PGMA GD. Reaction time: 20 h; Used amount of initiator: 0.9 wt %; GMA concentration: 5%.

the graft-polymerization, leading to no further changing of the GD after a certain period of time. It is obvious that for this system, an effective graft-polymerization time is 20 h.

Effect of temperature

For the grafted particles PGMA/SiO₂, the GD of PGMA in 20 h as a function of graft-polymerization temperature is given in Figure 4. It can be found that the PGMA GD first increases and then declines with raising the temperature, and the GD has a maximum value (16.13 g/100 g) at 70°C. At a lower temperature, the decomposition rate of the initiator is low, it is enhanced with the raising of the temperature, and graft polymerization is accelerated, resulting in the increase of the GD of PGMA with the raising of the temperature. However, if the temperature is too high, the graft-polymerization is carried out too rapidly, so that in a very short period of time, a dense overlapping and enwinding polymer layer will form on the surfaces of silica gel particles to block the grafting polymerization. In addition, the higher the temperature, the lower the molecular weight of the polymer. The produced grafted polymer with low molecular weight is more likely to form denser overlapping polymer layer.²⁵ The denser "kinetic wall" formed prematurely will block the grafting polymerization reaction badly, resulting in the declining of the GD of PGMA in the fixed period of time (20 h) with the raising of the temperature as the temperature is over 70°C. Obviously, for this graft polymerization system, to obtain the grafted particles PGMA/SiO₂ with a high GD, the suitable temperature should be controlled at 70°C.

Effect of used amount of initiator

Figure 5 displays the variation curve of the GD of PGMA in 20 h with the used amount of initiator

(designated as the percentage of monomer mass). It can be seen in Figure 5 that the variation of the GD of PGMA with the used amount of initiator also exhibits a trend similar to that with temperature, namely, the GD first increases and then declines with increasing the used amount of initiator and a maximum value (17.50 g/100 g) appears as the initiator amount is 1.4 wt %. As the used amount of initiator is small, the concentration of the primary free radical is very low, and the graft polymerization rate is very slow. Along with the increase of the used amount of initiator, the number of active free radicals in the system increases rapidly, and the graft polymerization is accelerated greatly, resulting in the enhancement of the graft degree of PGMA in the fixed period of time, 20 h. However, as the amount of initiator is excessive, the grafting reaction carries out too rapidly, so that in a very short period of time, a dense overlapping and enwinding polymer layer will form on the surfaces of silica gel particles to block the graft polymerization. Furthermore, the greater the used amount of the initiator, the lower the molecular weight of the polymer, and the produced grafted polymers with low molecular weight will easily form a denser overlapping polymer layer. The denser "kinetic wall" formed prematurely will hinder the grafting polymerization, resulting in the declining of the GD of PGMA in 20 h with increasing the amount of initiator as the initiator is in excess of 1.4 wt %.

Effects of main factors on bonding reaction of IDAA on PGMA/SiO₂ particles

Effect of time

Figure 6 shows the variation of the BR of IDAA on IDAA-PGMA/SiO₂ particles with the reaction time.

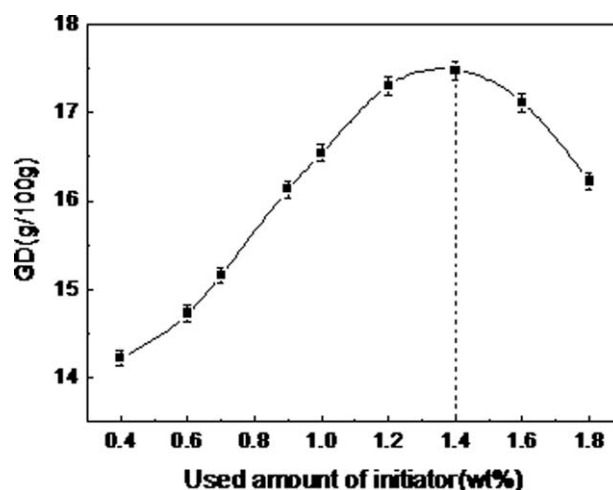


Figure 5 Effect of initiator amount on PGMA GD. Reaction time: 20 h; Temperature: 70°C; GMA concentration: 5%.

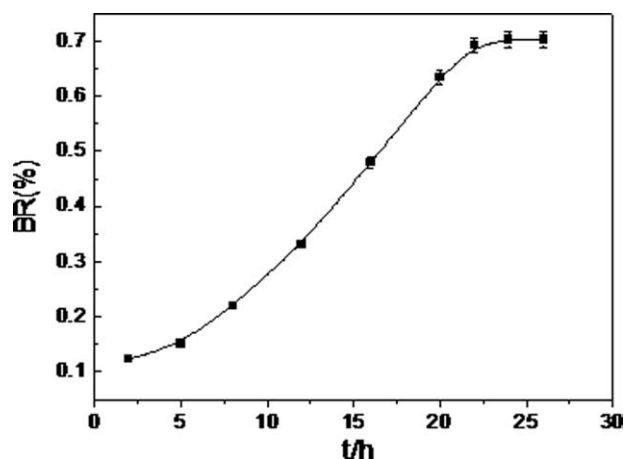


Figure 6 BR of IDAA as a function of reaction time. Temperature: 70°C; pH value: 12.5.

At the beginning, the BR of IDAA increased slowly because the swelling property of the grafted PGMA in aqueous medium (a mixed solvent of water and DMSO in a volume ratio of 5:1) is poorer, and the diffusion of IDAA molecule (actually, in this system it is the sodium salt of IDAA, i.e., IDAA disodium salt) from the solution into inner PGMA macromolecules is difficult, leading to the slow reaction. However, as soon as the BR of IDAA reaches a certain extent (8%), the rate of the ring-opening reaction of the epoxy groups of the grafted PGMA is obviously accelerated and the BR of IDAA increases rapidly because the hydrophilicity of IDAA disodium salt that has been bound onto the side chains gives the grafted polymer better swelling property. As the reaction is carried out to about 24 h, the BR of IDAA reaches a plateau (~70%) and barely changes. The above facts indicate: (1) the bonding of IDAA on the grafted PGMA via the ring-opening reaction of epoxy groups is feasible, and a higher conversion (~70%) can be obtained; (2) the ring-opening reaction of the epoxy groups of the grafted PGMA by IDAA cannot be carried out to a completed extent. This is probably caused by a greater steric hindrance of IDAA groups. At the last stage of the reaction, the bound IDAA groups with greater size will have a strong impact on the reaction between the residual epoxy groups and free IDAA molecules, leading to the stopping of the reaction. It is obvious that for this reaction system, the maximum reaction extent of the epoxy groups of the grafted PGMA, namely the BR of IDAA, can only reach 70% and the effective reaction time is 24 h.

Effect of medium pH

It was found that the bonding reaction of IDAA on the grafted PGMA nearly did not occur in acetic or neutral solution. Therefore, the bonding reaction of IDAA was carried out under the alkaline condition.

The pH value of the aqueous medium was adjusted gradually in a range of 10–12.5 to optimize the pH condition. Figure 7 gives the BR of IDAA in 24 h as a function of pH value.

It can be seen that the bonding reaction of IDAA in 24 h increases with medium pH. As pH = 12.5, the bonding reaction of IDAA reaches about 70%. There are two reasons for the above fact: (1) the ring-opening reaction between the epoxy groups of the grafted PGMA and IDAA is a nucleophilic substitution reaction, the existence of alkali has a great catalysis action, and so the bonding reaction rate of IDAA increases with medium pH; (2) under alkaline condition with higher pH value, the bound IDAA exists as disodium salt, its hydrophilicity makes the grafted macromolecules to have better swelling property, and it is beneficial to the ring-opening reaction of the epoxy groups of the grafted PGMA. However, the pH value of the medium can not be adjusted to be over 12.5 because of the sensibility of silica gel to alkali. It was found in the experiment that as the pH value of the medium was over 12.5, the caking phenomenon of the silica gel particles in the system would occur. Therefore, to prepare the functional composite particles IDAA-PGMA/SiO₂ with high bonding amount of IDAA and fine performance, the pH value should be adjusted to 12.5.

Preliminary researching on chelating adsorption property of IDAA-PGMA/SiO₂ particles

Chelating adsorption character of IDAA-PGMA/SiO₂ particles for metal ions

The adsorption isotherms of IDAA-PGMA/SiO₂ and PGMA/SiO₂ for two metal ions, Pb²⁺ ion (heavy metal ion) and Nd³⁺ ion (rare earth ion), are shown in Figure 8. It can be clearly seen that the grafted

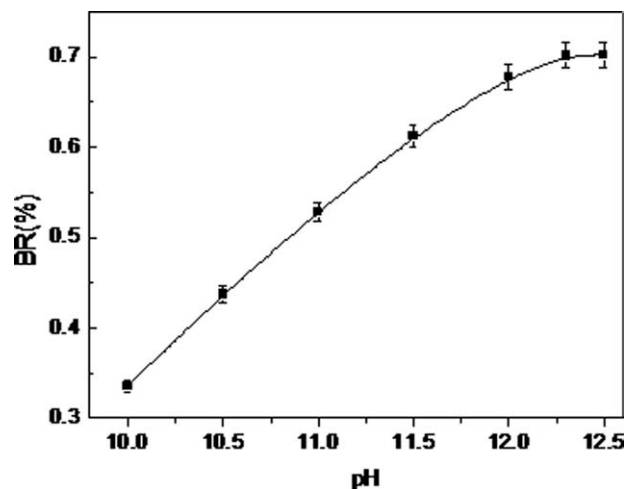


Figure 7 BR of IDAA as a function of medium pH. Reaction time: 24 h; Temperature: 70°C.

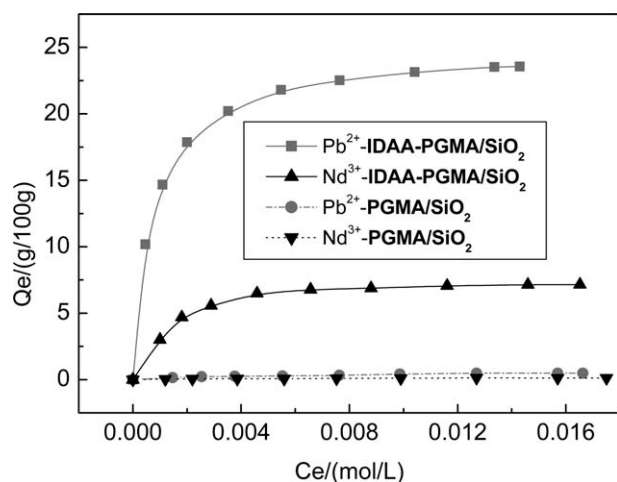
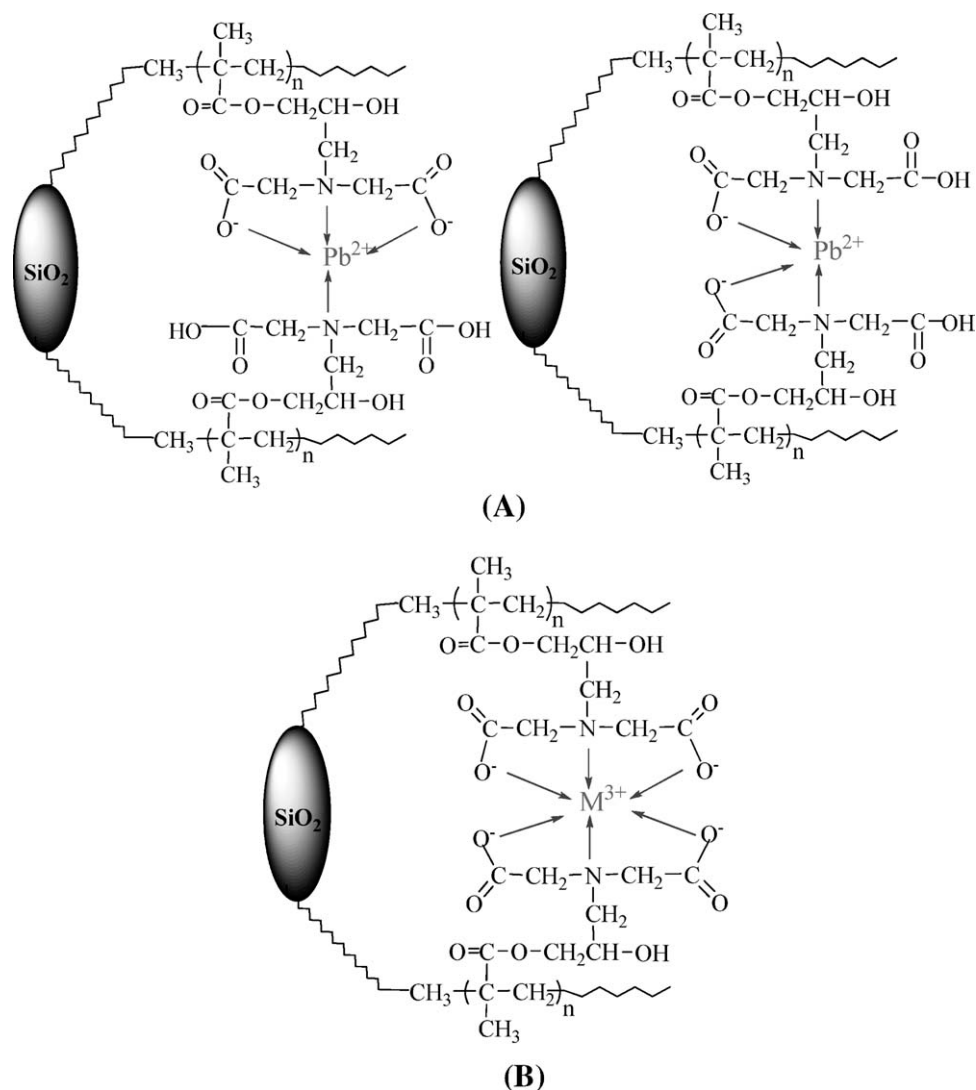


Figure 8 Adsorption isotherms of IDAA-PGMA/SiO₂ and PGMA/SiO₂ particles for Pb²⁺ and Nd³⁺ ions. Temperature: 30°C; pH = 5.

particles PGMA/SiO₂ have very little adsorption ability for Pb²⁺ and Nd³⁺ ions, or rather the grafted particles PGMA/SiO₂ nearly have no adsorption ability for Pb²⁺ and Nd³⁺ ions, whereas the functional particles IDAA-PGMA/SiO₂ possess strong adsorption ability for Pb²⁺ and Nd³⁺ ions, displaying the chelating adsorption function of IDAA-PGMA/SiO₂ particles. Especially for Pb²⁺ ion, the maximum adsorption capacity reaches 24 g/100 g unexpectedly. On one hand, the powerful adsorption action of IDAA-PGMA/SiO₂ for Pb²⁺ ion originated from the strong chelating action of IDAA group toward metal ion, and on the other hand, it comes from the high density of IDAA group on IDAA-PGMA/SiO₂ particles. IDAA group is a tridentate ligand, and several stable five-membered chelating ring can form as one metal ion is chelated by IDAA groups of IDAA-PGMA/SiO₂. There are various possible combining modes of the IDAA groups of



Scheme 2 Possible model of chelating adsorption of IDAA-PGMA/SiO₂ for two metal ions. A: Toward Pb²⁺ ion. B: Toward Nd³⁺ ion.

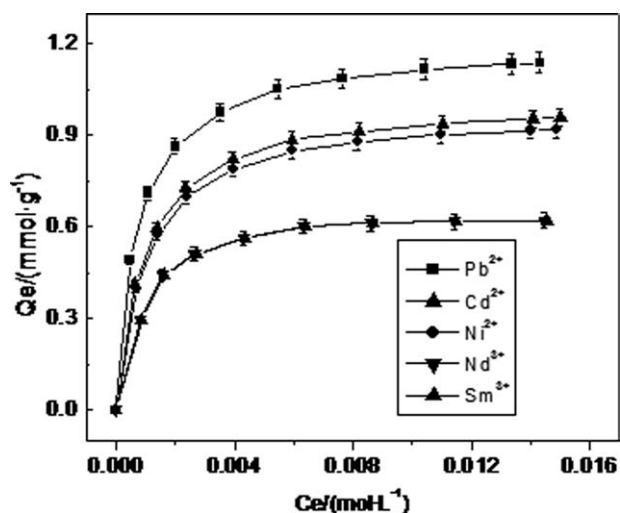


Figure 9 Adsorption isotherm of IDAA-PGMA/SiO₂ for different metal ions. Temperature: 30°C; pH = 5.

IDAA-PGMA/SiO₂ with one Pb²⁺ ion, and two modes are presented in Scheme 2(a), showing the possible co-chelating effect of the adjacent IDAA groups on IDAA-PGMA/SiO₂ particles for Pb²⁺ ion. The possible combining mode of the IDAA groups of IDAA-PGMA/SiO₂ with one Nd³⁺ ion is also given in Scheme 2(b), similarly indicating the possible co-chelating effect of the adjacent IDAA groups on IDAA-PGMA/SiO₂ particles for Nd³⁺ ion.

Chelating adsorption abilities of IDAA-PGMA/SiO₂ particles for different metal ions

The isothermal adsorption experiments of IDAA-PGMA/SiO₂ particles toward three kinds of heavy metal ions, Pb²⁺, Cd²⁺ and Ni²⁺ ions, and two kinds of rare earth ions, Nd³⁺ and Sm³⁺ ions, were conducted at the same temperature and at identical pH, respectively, and Figure 9 gives the corresponding adsorption isotherms. It needs to be pointed out that to substantively display the chelating adsorption abilities of IDAA-PGMA/SiO₂ particles toward various metal ions, for the adsorption isotherms in Figure 9, the equilibrium adsorption amount is expressed as mmol · g⁻¹.

It is displayed in Figure 9 that the adsorption capacities of the three kinds of heavy metal ions on IDAA-PGMA/SiO₂ particles are in the order: Pb²⁺ >> Cd²⁺ > Ni²⁺. It is obvious that IDAA-PGMA/SiO₂ particles exhibit the strongest chelating adsorption affinity for Pb²⁺ ions among the three heavy metal ions, and the saturated adsorption amounts get up to 1.14 mmol g⁻¹. The different adsorption abilities of the identical chelating adsorbent toward various heavy metal ions are dependent on the property and the structures of the valence electron orbit of these heavy metal ions probably. The elec-

tronegativity order of Pb and Cd is Pb(1.6) > Cd(1.5),^{26,27} and the adsorption capacity order of Pb²⁺ >> Cd²⁺ is completely consistent with this electronegativity order. It shows that the high adsorption capacity of Pb²⁺ ion on IDAA-PGMA/SiO₂ particles is led to by the strong electrostatic interaction between Pb²⁺ ion and IDAA ligands on IDAA-PGMA/SiO₂.^{26,27}

It is also can be found from Figure 9 that the adsorption capacity of two rare earth ions, Nd³⁺ and Sm³⁺ ions, is much lower than that of the heavy metal ions. The structures of the valence electron orbit of lanthanide series ions are 4fⁿ5s²5p⁶, and 4f electrons are sheltered from outer shell electrons. It makes the interaction between 4f electrons and the ligands to be weaker, and the coordinate bond is electrostatic interaction-dominated and is weaker. Therefore, rare earth ions exhibit poor absorption capacity on IDAA-PGMA/SiO₂ particles. Besides, rare earth ions have greater coordination number (generally it is six), and it meanings that greater ligands are needed for chelating one rare earth ion. This is another reason that leads a lower adsorption capacity of rare earth ions on IDAA-PGMA/SiO₂ particles. Figure 9 also shows that the adsorption capacities of Nd³⁺ and Sm³⁺ ions are nearly identical, and this is led to by very similar physicochemical property of lanthanide series ions.

CONCLUSIONS

By using a two-step chemical process, graft-polymerization and polymer reaction (ring-opening reaction of epoxy groups), composite chelating material IDAA-PGMA/SiO₂ on which IDAA groups were chemical attached were successfully prepared. This composite chelating material not only possesses strong chelation adsorption ability toward heavy metal ions because of bearing IDAA group with high density, but also it combines the excellent physicochemical properties of silica gel particles. It is one of the promising materials in the environmental protection field and in the extraction of important metal ions from water medium. In the step of the graft polymerization of GMA, only the reaction temperature and the used amount of initiator are controlled to be suitable, the grafted particles PGMA/SiO₂ with a high GD can be obtained. The optimum temperature for the graft polymerization is 70°C and the initiator addition of about 1.4% of the monomer mass is adequate. Under these conditions, the grafted particles PGMA/SiO₂ with a PGMA GD of 17.50 g/100 g can be prepared. In the ring-opening reaction of epoxy groups, namely, the bonding reaction of IDAA, to make the BR of IDAA to reach a higher extent, the medium pH should be adjusted to the alkaline pH values. In 24 h, the BR of IDAA group

can get up to 70% based on epoxy groups of the grafted PGMA. The preliminary adsorption experiments show that the composite chelating material IDAA-PGMA/SiO₂ has very strong chelating adsorption ability for heavy metal ions, and especially toward Pb²⁺ ion, the adsorption capacity can reach 24 g/100 g.

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