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Studies on Preparation of Composite Chelating Material Poly(amidoxime)/SiO$_2$ with Grafting-Type

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Micron-sized silica gel particles were first surface-modified with a coupling agent, γ-methacryloylpropyl trimethoxysilane (MPS), so polymerizable double bonds were introduced onto the surfaces of silica gel particles. Then, acrylonitrile (AN) was graft polymerized on the surfaces of the modified particles in the manner of "grafting from", resulting in the grafted particles PAN/SiO$_2$. In succession, the grafted PAN was transformed into the grafted poly (amidoxime) (PAO) via aminoximation transformation reaction with hydroxylamine hydrochloride as a reaction reagent, and the composite chelating particles PAO/SiO$_2$ with graft-type were obtained. In this work, the effects of main factors on the graft polymerization of AN and on the aminoximation transformation reaction were investigated in depth. At the same time, the chelating adsorption property of PAO/SiO$_2$ particles for heavy metal ions and rare ions was preliminarily examined. The experiments results show that: (a) In graft polymerization, the reaction temperature and the used amount of initiator should be controlled to obtain the grafted particles with high grafting degree; (b) It is feasible to transform the grafted particles PAN/SiO$_2$ into the functional particles PAO/SiO$_2$ via aminoximation reaction, and the nitrile groups conversion can get up to 78%; (c) In aminoximation transformation reaction, the reaction temperature and the pH value of the medium should be selected as 70°C and pH=6-7, respectively. The experiment results also indicate that PAO/SiO$_2$ particles possess a very strong chelating adsorption ability for heavy metal ions, Pb^{2+}and Cu^{2+}, and rare earth ions, Eu^{3+} and Sm^{3+}, by right of the strong chelating action of amidoxime groups.

Keywords: Amidoxime, polyacrylonitrile, composite material, graft polymerization, chelating adsorption

1 Introduction

Heavy metal pollution has become more serious with the rapid increase in global industrial activities. Heavy metal pollution has accumulating characteristics in nature and cannot be biodegraded, and this environmental issue is seriously threatening the health of human beings. There is a continuous need for new separation techniques, by which metal ions can be selectively extracted 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 reused. Nowadays, among various solid adsorbent, chelating resins are increasingly used in the removal of metal ions due to their high adsorption capacity and selectivity (1–5). Except chelating resins, recently, composite chelating materials, which consist of the chelating agent and inorganic particle matrix, such as silica gel, attapulgite, smectite and bentonite hydroxyapatite (6–9), have been developed to a great extent. Among such materials, type of novel composite chelating materials, which consist of chelating polymer and inorganic particle matrix, has 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 appears from high density of chelating ligand, 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 (10–12), and this is a conventional and simple method; another method is to try to chemically bond the chelating polymer onto the surfaces of the inorganic particles (chemically anchoring or grafting) (13, 14). This method is more effective due to the combined stability of chelating polymers and inorganic particles, but a few studies in this respect are reported, and it is probably owing to the preparation difficulty.

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There are many types of chelation groups, such as iminoacetate, Schiff base, aminophosphonate, 8-hydroxyquinoline and amidoxime. Among these chelation groups, amidoxime group has very strong chelation action towards many rare earth and heavy metal ions, so the chelating materials carrying amidoxime groups attract much attention in the enrichment, recovery and removal of rare earth and heavy metal ions (15–18). In particular, in uranium recovery from seawater, the amidoxime-type chelating materials play a unique role (19–22). Most amidoxime-type chelating adsorption materials are derived from the chemical transform of polyacrylonitrile (23–25). The objective of this study is to prepare a composite chelating material carrying grafted poly(amidoxime) macromolecules. polyacrylonitrile is first grafted on the surfaces of silica gel particles, and then the grafted polyacrylonitrile is converted into the grafted poly(amidoxime), PAO, resulting in the composite chelating material PAO/SiO_2. The preparation process is mainly studied, and the chelating adsorption property of PAO/SiO_2 for some heavy metal ions and rare earth ions is preliminarily investigated. The investigation result indicates that the composite material PAO/SiO_2 has powerful adsorption ability for heavy metal ions and rare earth ions by right of strong chelating action of amidoxime groups with high density. Recently, Anirudhan et al. prepared a new polyacrylonitrile/organobentonite composite with amidoxime functionality using an *in situ* intercalation polymerization technique for the removal of toxic heavy metals such as Cu(II), Cd(II), and Zn(II) from aqueous solutions (26). Although, some adsorbents with admidoxime functional groups were developed, to our knowledge, it has not been reported that the polymeric/inorganic composite material containing PAO is prepared via graft-polymerization of AN and subsequent chemical transformation (only radiation graft polymerizations of AN on some polymeric materials for preparing the functional material containing PAO were reported (27, 28)). The composite material PAO/SiO_2 combines the strong chelation adsorption ability of PAO for heavy metal ions and rare earth ions with the excellent physicochemical properties of silica gel particles such as fine mechanical property, thermal and chemical stability, as well as low cost. This route to prepare the composite chelating material PAO/SiO_2 with high performance is significant in environmental protection, as well as in energy sources science field.

2 Experimental

2.1 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. Acrylonitrile (AN, Fuchen Chemical Reagent Plant, Tianjin, China) was of analytical grade, and was purified by vacuum distillation before use. Hydroxylamine hydrochloride (HAHC, Chengyuan Trade Ltd., Tianjin, China) was of analytical grade. Azobisisobutyronitrile (ABIN, Guanfu Fine Chemical Institute, Tianjin, China) was of analytical grade, and was purified by recrystallization from ethanol. 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 Inc., Shanghai, China); STA449 thermogravimetric analyzer (TGA, Netzsch Company, Germany); THZ-92C constant temperature shaker equipped with gas bath (Shanghai Boxun Medical Treatment Equipment Factory, Shanghai, China).

2.2 Preparation and Characterization of Grafted Particles PAN/SiO_2

According to the procedures described in Ref. (29), 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-SiO_2. The double bond content was determined with a KBr-$KBrO_3$ method, and the modified particles used in this investigation had a double bond content of 2.11 mmol/g.

1.23 g of the modified particles MPS-SiO_2 was added into a four-necked flask equipped with a mechanical agitator, a reflux condenser, a thermometer and a N_2 inlet, followed by adding 100 mL of *N*, *N*-dimethylformamide (DMF) solution in which 11.79 mL of monomer AN was dissolved. The content was stirred and the modified particles MPS-SiO_2 were made to be dispersed fully. $N_2$was bubbled for 30 min to exclude air. The content was heated to 75°C, and 0.143 g of initiator ABIN was added. The graft polymerization was performed under N_2 atmosphere at 75°C for 5 h. The resultant particles were extracted with acetone in a Soxhlet for 24 h to remove the polymer attached physically to the particles, dried under vacuum, and finally, the grafted particles PAN/SiO_2 were obtained. The IR spectrum of PAN/SiO_2 particles was determined with KBr pellet method and their morphology was examined with SEM. The grafting degree (GD, g/100g) of PAN/SiO_2 particles was determined with the TGA method: air atmosphere and a raising temperature rate of 10°C/min.

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

2.3 Preparation and Characterization of Functional Composite Particles PAO/SiO_2

2.3.1. *Amidoximation Transformation of Grafted Particles PAN/SiO_2*

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

2.3.2. *Characterization of Composite Particles PAO/SiO_2*

The IR spectrum of particles PAO/SiO_2 was determined with the KBr pellet method to characterize their chemical structure. The weighing method was used to measure the amount of the AN unit of PAN that has converted into a amidoxime unit for the grafted PAN, and according to Equation (1), the conversion (Conv.) of nitrile group (mol%) was calculated.

$$Conv. = \frac{(m_2 - m_1)/M'}{m_1 \times GD/M \times 100} \times 100\% \qquad (1)$$

where $m_1(g)$was the mass of the grafted particles PAN/SiO_2; $m_2(g)$was the mass of the particles after amidoximation conversion, namely the mass of the composite particles PAO/SiO_2; M' (30.03) was the molar mass difference between amidoxime unit and acrylonitrile unit; $GD(g/100g)$was the grafting degree of the grafted particles PAN/SiO_2; M(53.06) was the molar mass of acrylonitrile unit.

2.3.3. *Examining Effects of Main Factors on Amidoximation Transformation Reaction*

By reaction conditions, reaction time, temperature and pH value of the medium were changed in series, respectively, to examine the effects of main factors on amidoximation transformation reaction of PAN and to determine the optimal reaction conditions.

2.4 Preliminary Estimation of the Adsorption Property of Composite Particles PAO/SiO_2

The aqueous solutions of $Pb(NO_3)_2$ and $Cu(NO_3)_2$ with different concentrations at pH=4 were prepared, respectively, in a range of 2.5–35 × 10^{-3} mol/L. 25 mL of Pb $(NO_3)_2$ solutions with different concentrations and were placed in several conical flasks, respectively. The functional particles PAO/SiO_2 (0.1 g) accurately weighed were added to these solutions, respectively. These mixtures were shaken in a constant temperature shaker for 3.5 h. After standing statically, 10 mL of the supernatants were withdrawn, and the concentrations of Pb^{2+} ion in these supernatants were determined with ETDA complexometric titration (using eriochrome black T as indicator), respectively, and the equilibrium adsorption amount Qe(g/100g) of PAO/SiO_2 particles for Pb^{2+} ion was calculated according to Equation (2) and the adsorption isotherm was determined.

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

where C_0(mol/L) was the concentration of Pb^{2+} ion of the initial Pb $(NO_3)_2$ solution; C_e(mol/L) was the concentration of Pb^{2+} ion of the supernatant; V(ml)was the volume of the solution of Pb $(NO_3)_2$; m(g)was the weight of the adsorbent PAO/SiO_2 particles; the molar mass of Pb atom is 207 g/mol.

The adsorption ability of PAO/SiO_2 towards Cu^{2+} ion was also tested with the same method, and the adsorption isotherm of PAO/SiO_2 towards Cu^{2+} ion was also determined.

Similarly, the adsorption abilities of PAO/SiO_2 towards rare earth ions, Eu^{3+} and Sm^{3+}, were also tested, and the adsorption isotherms of PAO/SiO_2 towards the two rare earth ions were also ascertained.

3 Results and Discussions

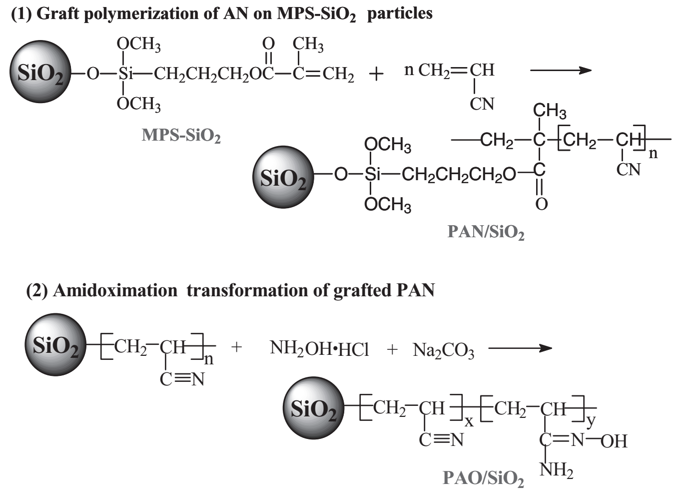
3.1 Reaction Process to Prepare Functional Composite Particles PAO/SiO_2

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

3.2 Characterization of PAN/$SiO_2$and PAO/SiO_2

3.2.1. *Infrared Spectra*

Figure 1 presents the infrared spectra of three kinds of particles, silica gel particles SiO_2, grafted particles PAN/SiO_2 and functional particles PAO/SiO_2. In comparison to the spectrum of SiO_2, in the spectrum of PAN/SiO_2,



Sch. 1. Schematic illustration of process to prepare composite particles PAO/SiO_2.

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

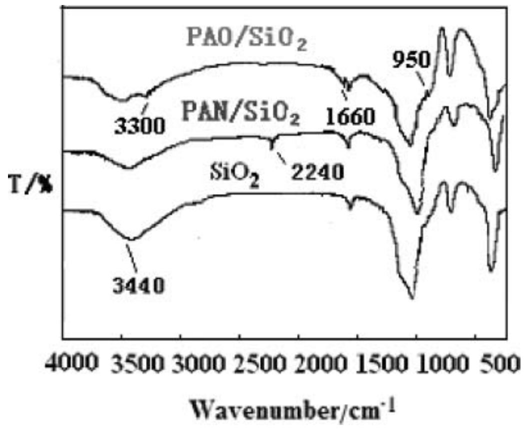


Fig. 1. Infrared spectrum of three kinds of particles.

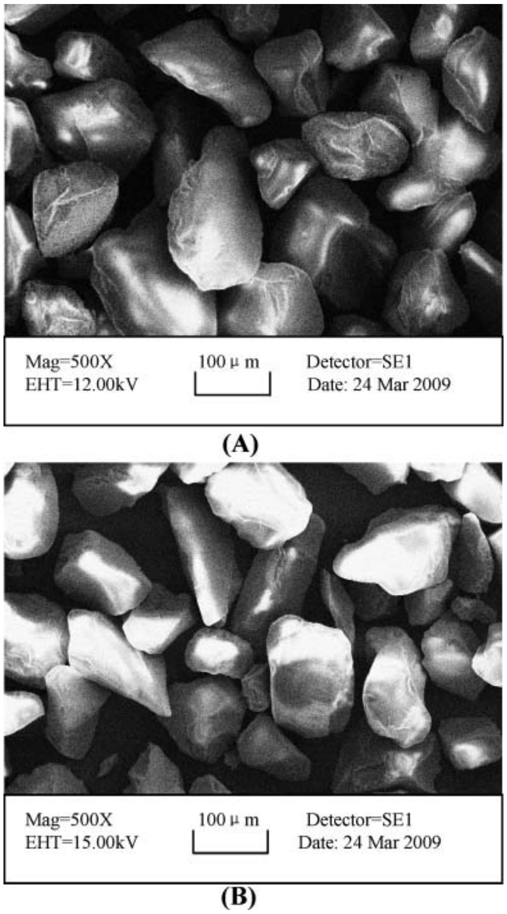


Fig. 2. SEM image of two kinds of particles: (A) Image of silica gel particles, (B) Image of PAN/SiO_2 particles.

3.2.2. *SEM Image*

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

3.2.3. *Thermogravimetric Analysis (TGA) Curve of PAN/SiO_2*

Figure 3 shows the TGA curve of PAN/SiO_2. The curve indicates that the measured sample of the grafted particles PAN/SiO_2 exhibits obvious heat decomposition at 326°C, and the heat decomposition finishes basically at 600°C. The weightlessness ratio is 13.71%, implying that the measured sample of the grafted particles PAN/SiO_2 has a PAN grafting degree of 13.71 g/100 g.

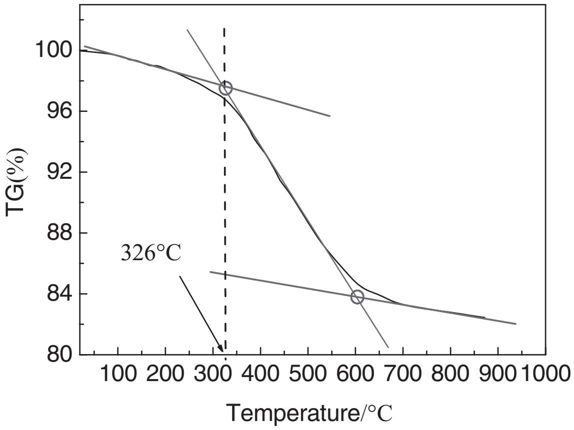


Fig. 3. TGA curve of PAN/SiO$_2$.

3.3 Effects of Main Factors on Graft-Polymerization of AN

3.3.1. *Effect of Time*

Figure 4 displays the variationg of the grafting degree of PAN on the grafted particles PAN/SiO$_2$ with graft-polymerization time. At the start, the grafting degree of PAN increases with the reaction time, and up to about 5 h (having a grafting degree of about 14%), the grafting degree 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 (30). As the graft-polymerization is carried out to a certain extent, an enwinding and overlapping polymer layer will be formed on the surfaces of silica gel particles, and it produces a kinetic hindrance to blocks monomers to diffuse to the active sites on the surfaces of the particles and to inhibit the graft-polymerization, leading to no further changing of the grafting degree after a certain period of time. It is obvious that for this system, an effective graft-polymerization time is 5 h.

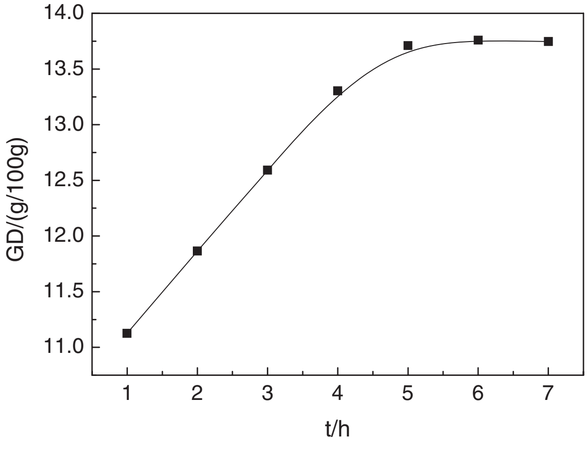


Fig. 4. Grafting degree of PAN as a function of graft polymerization time. Initiator: 1.5 wt%; Temperature: 75°C; AN concentration: 9 wt%.

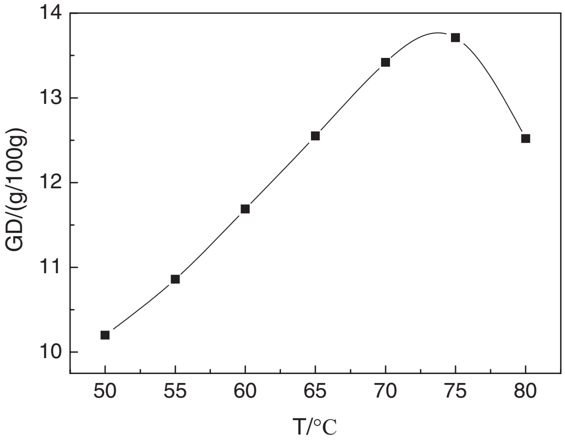


Fig. 5. Effect of temperature on PAN grafting degree. Time: 5 h; Initiator: 1.5 wt%; AN concentration: 9 wt%.

3.3.2. *Effect of Temperature*

For the grafted particles, PAN/SiO$_2$, the grafting degree of PAN in 5 h as a function of graft- polymerization temperature is given in Figure 5. It can be found that the PAN grafting degree first increases and then declines with raising the temperature, and the grafting degree has a maximum value (13.71 g/100g) at 75°C. At a lower temperature, the decomposition rate of the initiator is low, it is enhanced with the raising of the temperature, and the graft polymerization is accelerated, resulting in the increase of the grafting degree of PAN 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, and the produced grafted polymer with low molecular weight is more likely to form denser overlapping polymer layer (30). The denser "kinetic wall" formed prematurely will block the grafting polymerization reaction badly, resulting in the declining of the grafting degree of PAN in the fixed period of time (5 h) with the raising of the temperature as the temperature is over 75°C.Obviously, for this graft polymerization system, to obtain the grafted particles PAN/SiO$_2$ with a high grafting degree, the suitable temperature should be controlled at 75°C.

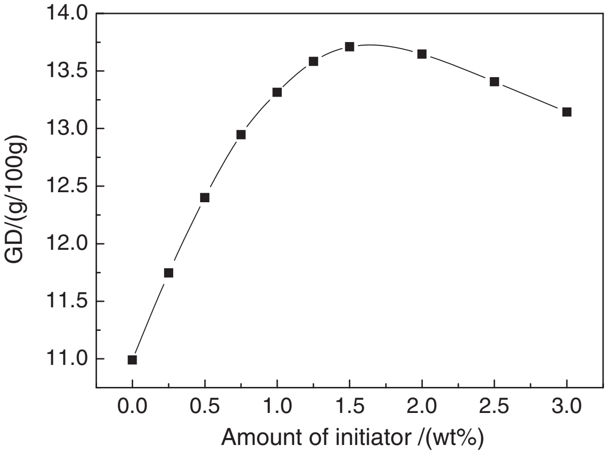


Fig. 6. Effect of initiator amount on PAN grafting degree. Time: 5 h; Temperature: 75°C; AN concentration: 9 wt%.

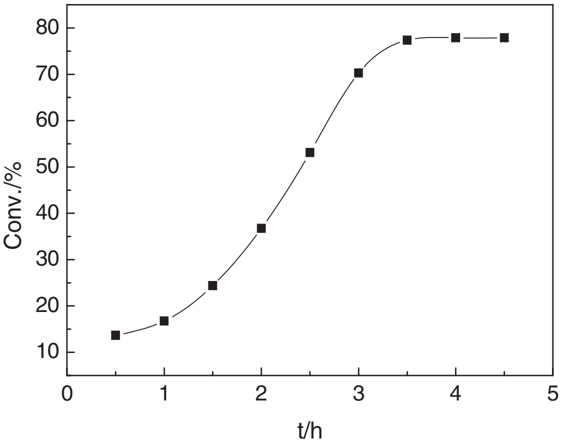


Fig. 7. Nitrile group conversion as a function of reaction time. Temperature: 70°C; pH value: 6.5; HAHC concentration: 1.0 mol/L.

3.3.3. *Effect of Amount of Used Initiator*

Figure 6 displays the variation curve of the grafting degree of PAN in 5 h with the used amount of initiator (designated as the percentage of monomer mass). It can be seen in Figure 6 that the variation of the grafting degree of PAN with the used amount of initiator also exhibits a trend similar to that with temperature, namely, the grafting degree first increases and then declines with increasing the used amount of initiator and a maximum value appears as the initiator amount is 1.5 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 PAN in the fixed period of time, 5 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 grafting degree of PAN in 5 h with increasing the amount of initiator as the initiator is in excess of 1.5%.

3.4 Effects of Main Factors on Amidoximation Transform of Grafted PAN

3.4.1. *Effect of Time*

Figure 7 shows the variation of the nitrile group conversion of the grafted PAN with the reaction time. At the beginning, the conversion of the nitrile increased slowly because the swelling property of the grafted PAN in aqueous medium is very poor, and the molecular diffusion of hydroxylamine molecules from the solution into inner PAN macromolecules is difficult, leading to the slow reaction. However, as soon as the nitrile group conversion of the grafted PAN reaches a certain extent (20%), the rate of the amidoximation reaction is obviously accelerated and the conversion of the nitrile group increases rapidly because of the hydrophilicity of amidoxime group and better swelling property of the grafted polymer. As the reaction is carried out to about 3.5 h, the conversion of the nitrile group slows, and after 4 h, the conversion (about 78%)barely changes. The above facts indicate: (1) the amidoximation transformation reaction of the grafted PAN is feasible, and a higher conversion (about 78%) can be obtained; (2) the transformation reaction of the nitrile groups cannot be carried out to a completed extent. This seems to be a common rule for the amidoximation transform reaction of PAN (31). This is probably caused by a greater steric hindrance of aminoxme groups (31). At the last stage of the reaction, the transformed aminoxme groups with greater size will have a strong impact on the reaction between the residual nitrile groups and hydroxylamine, leading to the stopping of the reaction. It is obvious that for this reaction system, the maximum conversion of the nitrile groups of the grafted PAN can only reach 78%, and the effective reaction time is 4 h.

3.4.2. *Effect of Medium pH*

By fixing other reaction conditions and varying the added amount of Na_2CO_3 so as to change the pH values of the medium in series, the amidoximation transformation reactions were performed, and Figure 8 presents the conversion of the nirile groups of the grafted PAN in 4 h as a function of pH value. It can be found that the conversion of the nirile

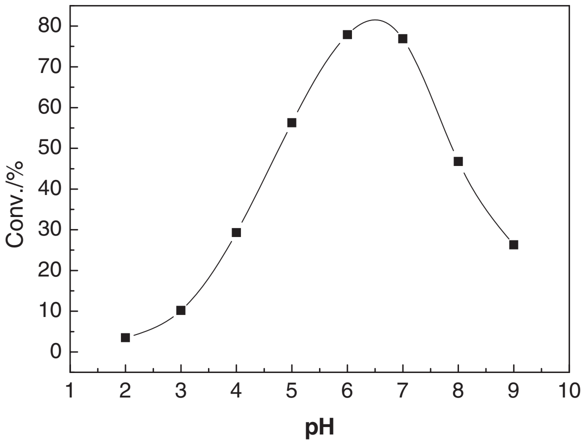


Fig. 8. Nitrile group conversion as a function of medium pH. Time: 4 h; Temperature: 70°C; HAHC concentration: 1.0 mol/L.

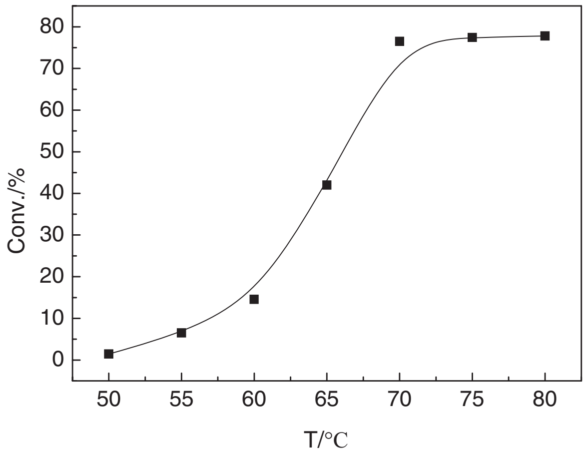


Fig. 9. Nitrile group conversion as a function of reaction temperature. Time: 4 h; pH=6.5; HAHC concentration: 1.0 mol/L.

groups exhibits a trend of first increasing and then declining with increasing pH value of the medium. At the pH range of 6-7, a maximum conversion, 78%, appears. In the amidoximation transformation reaction, the reaction reagent hydroxylamine is unstable, so the industrial product of hydroxylamine exists only as solid hydroxylamine hydrochloride (HAHC). In the reaction solution containing hydroxylamine hydrochloride (pH=3), Na_2CO_3 was added, and free hydroxylamine molecules were released via the neutralization action. With increasing pH value, the amount of the released hydroxylamine increases, and the amidoximation transformation reaction is accelerated greatly, leading to the enhancement of the nitrile group conversion. However, as pH is over 7, partial hydroxylamine will be decomposed because a large quantity of hydroxylamine will be released. It is more important that here the system is alkaline, a part of the nitrile groups will be transformed into a amido group (32), and besides, the structure of silica gel will probably be destroyed under basic conditions. As a result of the cooperative action of the several factors, the decrease of the nitrile group conversion is resulted in as pH>7. By this token, for this investigated system, the pH range of 6-7 is appropriate, and the functional composite particles PAO/SiO_2 with a nirile group conversion of 78% can be obtained.

3.4.3. *Effect of Temperature*

By fixing other conditions and varying the reaction temperatures, the aminoximation transformation reactions were conducted, and Figure 9 displays the nitrile group conversion in 4 h as a function of temperature. Figure 9 shows that at a lower temperature (<50°C), the rate of the aminoximation reaction is very slow and the nitrile group conversion in 4 h is very low (only about 1.4% at 50°C in 4 h). As the temperature is over 60°C, the reaction rate is enhanced rapidly and the nitrile group conversion in 4 h is remarkably increased. However, after 70°C, the reaction seems to stop and the nitrile group conversion no longer changes. At the same time, it was found in the experiments that a coking phenomenon of the particles in the reactor occurred. The above fact is probably related to the physical state of the grafted PAN. The glass-transition temperature of PAN is about 80°C (33). As the temperature is over 70°C and approaches the glass-transition temperature of PAN, it is possible that the change of the aggregation form of PAN macromolecules affected the reaction. This shows that for this system, the temperature of the aminoximation transformation reaction of the grafted PAN should be controlled at 70°C.

3.5 Preliminary Researching on Chelating Adsorption Property of PAO Particles

The adsorption isotherms of PAO/SiO_2 and PAN/SiO_2 particles for two heavy ions, Pb^{2+} and Cu^{2+} ions, are shown in Figure10. It is can be clearly seen that the grafted particles PAN/SiO_2 have very little adsorption

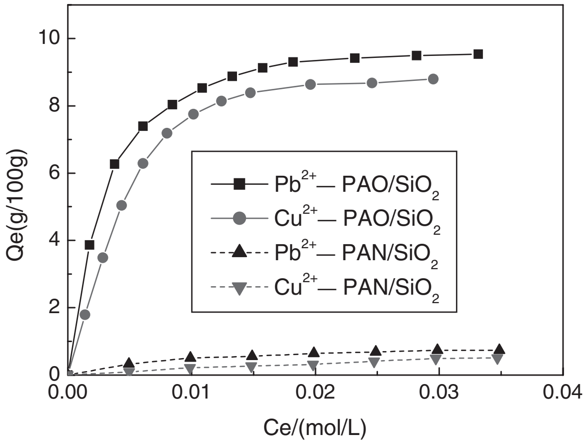
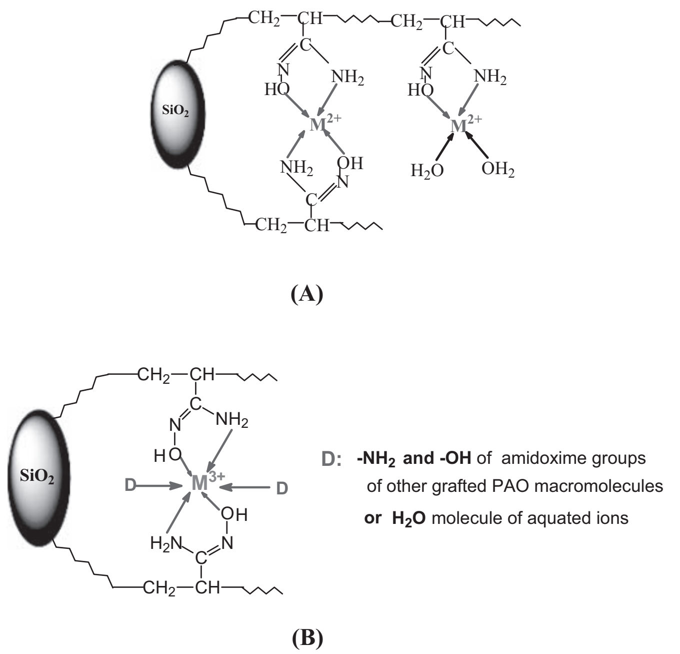


Fig. 10. Adsorption isotherms of PAO/SiO_2 and PAN/SiO_2 particles for Pb^{2+} and Cu^{2+}ions. Temperature: 30°C; pH=4.



Sch. 2. Possible model of chelating adsorption of PAO/SiO$_2$for metal ion. (A) Towards heavy metal ions; (B) Towards rare earth ions.

ability for Pb^{2+} and Cu^{2+}ions, whereas the functional particles PAO/SiO$_2$ possess a strong adsorption ability for Pb^{2+} and Cu^{2+}ions, displaying the chelating function of PAO/SiO$_2$ particles. The maximum adsorption capacity can reach 9.5 g/100g for Pb^{2+} ion and 9.0 g/100 g for Cu^{2+} ion, respectively, and the adsorption isotherms are very precipitous. The precipitous adsorption isotherms imply a strong adsorption action. The powerful adsorption action of PAO/SiO2 for Pb^{2+}and Cu^{2+} ions originated from the strong chelating action of amidoxime groups towards heavy metal ions. The amidoxime group is a bidentate ligand, and a stable five-membered chelating ring can form between one amidoxime group and one heavy metal ion. The possible combining mode of PAO/SiO$_2$ with Pb^{2+}ion or Cu^{2+} ion is shown in Scheme 2 (A), indicating the possible co-chelating effect of the adjacent PAO macromolecules on PAO/SiO$_2$ for heavy metal ion. Just the chelation of the amodoxime group enables PAO/SiO$_2$ particles to have strong chelating adsorption ability for heavy metal ions.

Similarly, the adsorption isotherms of PAO/SiO$_2$ and PAN/SiO$_2$ particles for two rare earth ions, Sm^{3+} and Eu^{3+}ions are shown in Figure 11. It is can be clearly seen that the grafted particles PAN/SiO$_2$ nearly have no adsorption ability for Sm^{3+} and Eu^{3+}ions, whereas the functional particles PAO/SiO$_2$ possess strong adsorption ability for Sm^{3+} and Eu^{3+}ions, displaying the chelating function of PAO/SiO$_2$ particles. It can be found that the adsorption amounts of Sm^{3+} and Eu^{3+}ions on the particles PAO/SiO$_2$ are almost completely identical, and it is due to that the fact that the two elements, Sm and Eu, are two adjacent elements in lanthanide series, so they have nearly identical physicochemistry property. The possible combining mode of PAO/SiO$_2$ with Sm^{3+} and Eu^{3+}ions is shown in Scheme 2 (B), indicating the possible co-chelating effect of the adjacent PAO macromolecules on PAO/SiO$_2$ for rare earth ion. Just the chelating action of the amodoxime group enables PAO/SiO$_2$ particles to have strong chelating adsorption ability for rare earth ions.

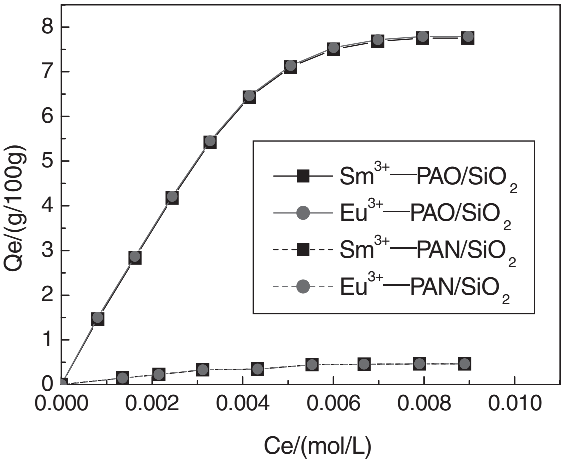


Fig. 11. Adsorption isotherms of PAO/SiO$_2$ and PAN/SiO$_2$ particles for Sm^{3+} and Eu^{3+}ions. Temperature: 30°C; pH=4.

4 Conclusions

By using a two-step chemical process, graft-polymerization and polymer reaction (aminoximation transformation reaction), composite chelating material PAO/SiO$_2$ on which poly(amidoxime) was grafted were successfully prepared. For the graft polymerization of acrylonitrile, only the reaction temperature and the used amount of initiator are controlled to be suitable, the grafted particles PAN/SiO$_2$ with a high grafting degree can be obtained. In the aminoximation transformation reaction, in order to make the conversion of the nitrile groups to reach a higher extent, the reaction temperature and the pH value of the medium should effectively are controlled. The composite chelating material PAO/SiO$_2$ has very strong chelating adsorption ability for heavy metal ions and rare earth ions. The composite chelating material PAO/SiO$_2$ is a promising a adsorption material in the environmental protection and the recovery of important metal ions from water medium.

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