Synthesis of polyacrylonitrile-grafted cross-linked N-chlorosulfonamidated polystyrene via surface-initiated ARGET ATRP, and use of the resin in mercury removal after modification

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ABSTRACT

A novel method of surface modification was developed via iron (III)-mediated atom transfer radical polymerization, with activators regenerated by electron transfer (ARGET ATRP) on the surfaces of polystyrene resin-supported N-chlorosulfonamide groups. The well-defined polyacrylonitrile (PAN) was grafted onto the surfaces of the polystyrene (PS). The graft reaction exhibited first-order kinetics with respect to the polymerization time in the low-monomer-conversion stage. The cyano group of PAN-g-PS was modified by $NH_2OH \cdot HCl$ to yield amidoxime (AO) groups. The AO groups had been demonstrated to be an efficient Hg-specific sorbent, which can remove Hg^{2+} from solutions. No interference arose from common metal ions, such as Pd^{2+}, Ag^+, and Cu^{2+}. Three adsorption–desorption cycles demonstrated that this resin is suitable for reuse without any considerable change in adsorption capacity.

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1. Introduction

The separation of heavy metal ions from industrial effluents has attracted much attention due to the hazardous effects of the heavy metal ions on different forms of life. Many researchers have studied the synthesis or modification of polymeric materials using different methods to overcome the difficulties involved in wastewater treatment processes [1,2]. In addition, many approaches based upon adsorption, solvent extraction and polymeric membranes have been used to remove metal ions from aqueous solutions [3–6]. Among all studied methods, the approach based upon adsorption is considered most attractive because it is an effective and relatively simple method for the removal of heavy metal ions. Furthermore, numerous adsorbents with various chelating groups for removing and recovering metal ions have been reported [7–10].

Polyacrylonitrile (PAN) is an important precursor to polymer materials because of its unique and well-known properties, including hardness and rigidity, chemical resistance, compatibility with certain polar substances, and low gas permeability [11]. In addition, PAN can be easily chemically modified to contain pendant cyano groups in order to obtain an adsorbent-containing amidoxime (AO) group, which has been applied in many areas, such as sewage disposal, metal recovery and so on. de Santa Mariaa et al. has reported some ways to chemically modify a resin-containing pendant cyano group [12]. A number of studies have shown that polymers containing AO groups can be successfully used for the treatment of metals from aqueous solutions due to the polymers' highly complex-forming capabilities with metal ions [13–16].

In order to take advantage of these properties on the macroscopic scale, the particles must be incorporated into a host material. Thus, much attention has been given to grafting linear polymers onto cross-linked polymer resin particles. As is well known, there are several methods for preparing grafting polymers, such as the chemisorption of a reactive polymer end group to the surface [17,18], grafting a polymer chain through a monomer covalently linked to the surface [19–21], and grafting a polymer chain from a surface modified with polymerization initiators [22,23]. Of these methods, maximum structural control can be achieved by the "grafting from" route. In addition, it is difficult to introduce linear polymer chains onto the matrix by the "grafting from" technique, using common radical initiation procedures without generating considerable amounts of wasteful non-grafted homopolymers as by-products. The emerging "controlled chain growth" technique, such as atom transfer radical polymerization (ATRP) [24,25], has been demonstrated to be applicable to the grafting of well-defined homopolymers [26,27], diblock copolymers [28–31], graft copolymers [32], star polymers [33], and hyperbranched polymers [34,35] from chloroalkylated solid surfaces, such as nanoparticles, nanotubes, nanowires, clays and polybutadiene microgels [36]. N-

chlorosulfonamidated polystyrene resin as a matrix has also been reported by Bicaka and co-workers [10]. Although the surface-initiated ATRP technique can control molecular weight, molecular weight distribution, and the structure of the resulting polymer [37], the color of the product is difficult to eliminate, and the catalyst is toxic. Recently, Matyjaszewski and co-workers [38] introduced the concept of the activator regenerated by electron transfer (ARGET), which has allowed the polymerizations to be established at the ppm level of catalyst concentration, making this approach more attractive for commercial use. Well-defined homopolymers of styrene [39–41] or acrylate [42,43] have been prepared by ARGET ATRP. However, to the best of our knowledge, only a few ARGET ATRP systems have been reported to modify the solid surfaces [44,45], and there have been no reports involving surface-initiated ARGET ATRP to modify polystyrene substrates until now.

In this work, we first report a novel method of surface modification of solids via iron (III)-mediated ARGET ATRP on the surfaces of N-chlorosulfonamidated polystyrene, using ferric trichloride anhydracs (FeCl$_3$)/iminodiacetic acid (IDA) as the catalyst system, L-ascorbic acid (VC) as the reducing agent, and N,N-dimethylformamide (DMF) as the solvent. The functional polymer-PAN was grafted onto modified polystyrene beads, and then modified the cyano groups into AO groups to yield adsorbent grafted to polystyrene beads. The modified resin-containing AO groups were used for the extraction of heavy metal ions (Hg^{2+}) from aqueous solutions. Then, the adsorption capacity of Hg^{2+} was investigated.

2. Experimental

2.1. Materials

Acrylonitrile (AN) (Tianjin FuChen Chemical Reagents Co., Tianjin, China) was distilled under normal pressure and stored at 5 °C. Styrene (St) (Tianjin Regent Chemical Co., Tianjin, China) was distilled under vacuum pressure and stored at 5 °C. Ferric trichloride anhydracs (FeCl$_3$) (Sinopharm Chemical Reagent Co., Shanghai, China), iminodiacetic acid (IDA) (Sinopharm Chemical Reagent Co., Shanghai, China), L-ascorbic acid (VC) (Tianjin Regent Chemical Co., Tianjin, China), N,N-dimethylformamide (DMF) (Tianjin FuChen Chemical Reagents Co., Tianjin, China), divinylbenzene (DVB) (Aldrich), chlorosulfonic acid (Merck), A1$_2$O$_3$ (Tianjin Regent Chemical Co., Tianjin, China), and Arabic Gum (Sinopharm Chemical Reagent Co., Shanghai, China) were used as received. All other chemical reagents were used as received.

2.2. Preparation of cross-linked styrene–divinylbenzene

The cross-linked styrene–divinylbenzene polymers were prepared according to the procedure described previously [46]. The resulting spherical beads were sieved, and the 210–420 nm fraction was used for further modifications.

2.3. Chlorosulfonation of the bead polymer

The bead polymer was chlorosulfonated using chlorosulfonic acid, as described previously [47].

2.4. Sulfamidation of the beads

Sulfamidation of the chlorosulfonated resins was performed by treating the resin samples with an excess of propyl amine (12 mL, 0.145 mol) in 2-methyl pyrrolidone (15 mL) at 0 °C, as described previously [10].

2.5. Chlorination with aqueous hypochloride

PS beads were placed in cold chlorosulfonic acid in a closed bottle and left in the refrigerator for 72 h. Then, the yellow beads were filtered and poured into crushed ice. After filtration, the beads were washed with acetone and ethyl acetate successively and dried at room temperature under a vacuum for 24 h. The process was also reported by Niyazi and Bahire [46].

2.6. Grafted polymerization of AN on modified PS beads using ARGET ATRP

The surface-initiated ARGET ATRP of AN on the modified PS beads surfaces was achieved by the following procedures. AN (13 mL, 0.2 mol), N-chlorosulfonamide PS beads (0.37 g, 1.1 mmol), FeCl$_3$ (1.5×10^{-5} mol), IDA (5×10^{-5} mol) and VC (8.5×10^{-5} mol) were mixed in a dry two-neck round-bottom flask, which was bathed in ice-water. Then the mixture was degassed in vacuo, charged with N$_2$ (three times) and sealed with N$_2$ finally. At timed intervals, the reaction was terminated by cooling the flask in ice water. The product was dissolved with DMF and was precipitated by methanol–water (v:v, 1:1). The production was dried 24 h under vacuum.

2.7. Characterization

Infrared spectra were recorded on a Perkin–Elmer Spectrum 2000 FTIR. The surface morphologies of the resins were observed using scanning electron microscopy (SEM), operating at 25 kV. The percentage of grafting (PG%) was calculated according to the following equation:

$$PG\,(\%) = \frac{PAN\,grafted\,(g)}{PS\,charged\,(g)} \times 100$$

2.8. Modification with hydroxylamine hydrochloride

Next, 4.8 g of hydroxylamine hydrochloride (NH$_2$OH·HCl) in 23 mL of methanol and 3.2 g of resin were added to a reactor equipped with a magnetic stirrer and reflux condensator. After 2 h, about 4.6 mL of NaOH (3.12 g) aqueous solution were added to this mixture, and the pH was maintained at 9.0. The reaction was performed for 24 h at 70 °C under stirring. The modified resin (AO PAN-g-PS) was washed thoroughly with hot water and ethanol and dried at 60 °C. The process was reported by de Santa Mariaa et al. [12].

2.9. Adsorption characteristics

2.9.1. pH optimum for sorption uptake

The adsorption experiments were performed on a rotating shaker. The AO PAN-g-PS sorbent (10 mg) was immersed in 1 mL of 0.1 mol L^{-1} Hg^{2+} and 19 mL of acetic acid/acetate buffer solution at different pH values in a 100 mL Erlenmeyer flask, and then stirred for 24 h at 25 °C. The metal uptake was calculated by the following equation:

$$q = \frac{(C_0 - C)V}{W},$$

where q is the adsorption amount (mmol g^{-1}); C_0 and C are the initial and the final concentrations of metal ions in solution, respectively (mmol mL^{-1}); V is the volume (mL); W is the weight of modified AN-g-PS sorbent (mg).
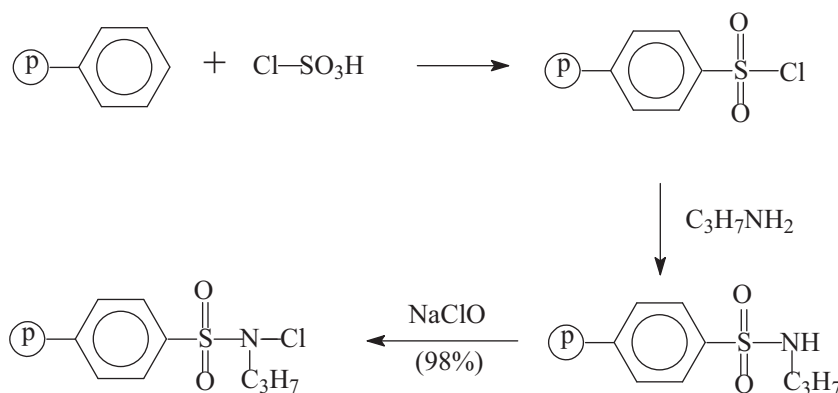
Scheme 1. Synthetic scheme for introducing N-chlorosulfonamide groups into PS resin.

2.9.2. Adsorption kinetics

The modified PAN-g-PS sorbent (10 mg each) was added to 20 mL of 5.0×10^{-3} mol L^{-1} Hg metal ion solution (pH = 2.0). The mixture was shaken continuously at a definite temperature. Aliquots of 1 mL solution were taken at different time intervals, and the concentration variations of Hg^{2+} were analyzed by AAS.

2.9.3. Adsorption isotherms

Adsorption isotherms were obtained by mixing 0.01 g of dry adsorbents in a series of flasks containing 20 mL of different initial metal ion concentrations, varying from 0.25 to 5 mmol L^{-1}, for 12 h. The initial pH was adjusted to 2.0 for Hg^{2+}. In addition, the concentration variations of Hg^{2+} were determined via AAS.

2.9.4. Adsorption selectivity

The adsorption selectivity of modified grafted resin was determined under competitive conditions, and approximately 0.01 g of the copolymers were contacted with a binary mixture system, in which the concentrations of each metal ion were equal (5×10^{-3} mol L^{-1}). The mixture was shaken for 24 h at 25 °C. The selectivity index was defined as the ratio of adsorption capacities of metal ions in the binary mixture.

2.9.5. The regeneration of AO PAN-g-PS

In order to determine the reusability of the AO PAN-g-PS, consecutive adsorption–desorption cycles were repeated three times using the same sorbent. Desorption of Hg^{2+} ions was performed with 0.1 mol L^{-1} HCl solution. The AO PAN-g-PS loaded with metal ions was placed in the desorption medium and stirred for 12 h at room temperature. The concentrations of Hg^{2+} in the aqueous solution were determined by AAS, as described above.

3. Results and discussion

3.1. Immobilization of the ARGET ATRP initiator on the microsphere surface

PAN-g-PS was successfully prepared by grafting from N-chlorosulfonamidated PS resin, and the latter was obtained via the following stepwise modifications, as shown in Scheme 1. The chlorine content of N-chlorosulfonamidated styrene–divinylbenzene resin is 3.0 mmol g^{-1}, as determined by a modified iodometric method [48].

3.2. Surface-initiated ARGET ATRP from the N-chlorosulfonamidated polystyrene bead surface

The surface-initiated ARGET ATRP of AN mediated by an iron catalyst was conducted in a DMF solution containing N-chlorosulfonamidated polystyrene beads, AN, FeCl$_3$, IDA, and VC at 65 °C. For the grafting PAN, the molecular weights of the grafted polymers were not obtained directly because it was difficult to obtain the samples for GPC analysis. It was found that the percentage of grafting (PG%) increased to 86% with the increase of polymerization time, as shown in Fig. 1. As can be seen from Fig. 1, there was a linear increase in the graft percentage with polymerization time. The result suggested that the chain growth from the functionalized N-chlorosulfonamidated polystyrene bead surfaces was also consistent with a "controlled" process.

Importantly, no free homopolymers of PAN were detected throughout the polymerization process. For the detection of any probable free homopolymer formation, the aqueous solution after the completion of ARGET ATRP was precipitated in methanol. No precipitate was observed. This observation clearly indicated that homopolymers were not present during the grafting procedure.

FTIR spectra were used as a powerful tool to verify the presence of certain functional groups in material modifications because an individual chemical bond often showed a unique energy adsorption band [49,50]. Fig. 2 shows the FTIR spectra of the (a) macroinitiator, (b) PAN-g-PS, and (c) AO PAN-g-PS. From Fig. 2, we can see that a sharp peak appeared [Fig. 2(b)] at 2241 cm^{-1}, corresponding to the stretching of the CN bond, as compared with Fig. 2(a). This indicated that PAN had been grafted onto the PS bead using ARGET ATRP.

In order to further verify the graft structures, SEM was used to observe the morphologies of bare PS and of PAN-g-PS. The pho-
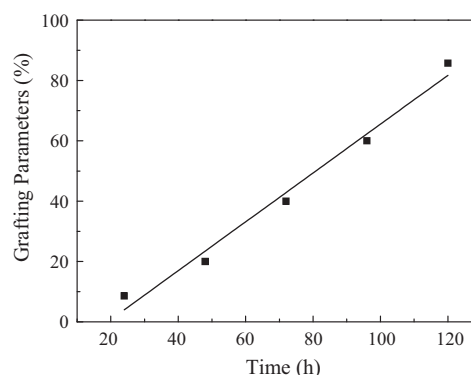

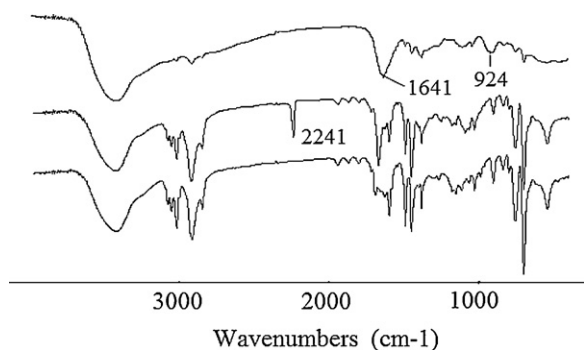**Fig. 1.** First-order kinetics plots for the surface-initiated ARGET ATRP of AN.

Fig. 2. FTIR spectrum of: (a) N-chlorosulfonamidated PS, (b) PAN-g-PS, and (c) AO PAN-g-PS.

tographs are displayed in Fig. 3. It can be seen that the surfaces of the PS beads changed significantly after the ARGET ATRP of AN (Fig. 3). In comparison with Fig. 3(a), the pore of grafted PS disappeared and was coated with film (Fig. 3(b)).

All of these results indicated that the PAN was grafted from the surfaces of PS beads successfully via the novel ARGET ATRP technique with the surface labile chlorines of PS.

The mechanism of the ARGET ATRP of AN from the surfaces of PS could be schematically shown in Scheme 2.

3.3. Chemical modification of PAN-g-PS with hydroxylamine

The modification of polymers containing cyano groups was reported by de Santa Mariaa et al. [12]. The schematic representation of conversion of CN groups to AO groups is shown in Scheme 3. The modification product was determined by FTIR spectra. Fig. 2(b) and (c) shows the FTIR analysis of unmodified and modified resins, respectively. Compared to the FTIR spectrum of the unmodified resins (Fig. 2(b)), the spectrum of the modified resins exhibited two absorption peaks at 1641 and 924 cm^{-1}, corresponding to the stretching vibration of C–N and N–O bonds of AO groups, respectively, and a band at 2241 cm^{-1} related to the CN group in Fig. 2(c) spectrum disappeared. In addition, the modification process was characterized by SEM, as shown in Fig. 3(c). From Fig. 3(c), we can see that the morphology of modified PAN-g-PS significantly changed, compared to the bare PS (Fig. 3(a)) and PAN-g-PS (Fig. 3(b)). These changes
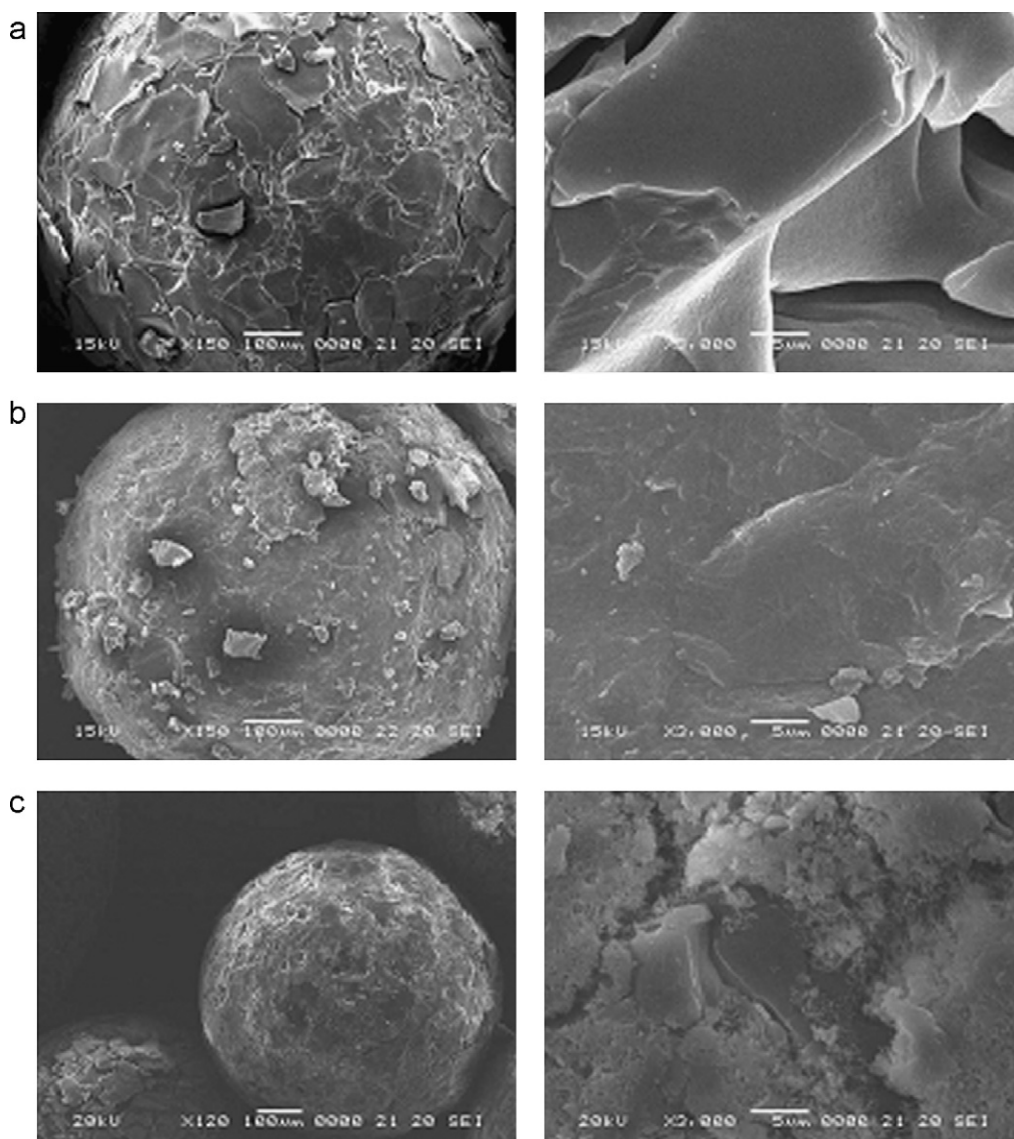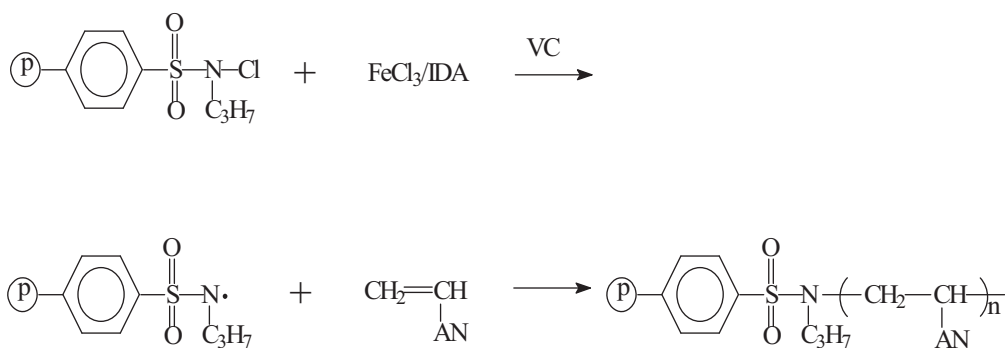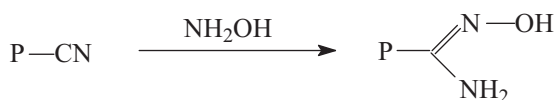

Fig. 3. SEM photographs of: (a) N-chlorosulfonamidated PS, (b) PAN-g-PS, and (c) AO PAN-g-PS.

Scheme 2. Proposed mechanism for ARGET ATRP grafting of polyacrylonitrile onto functional PS resin.

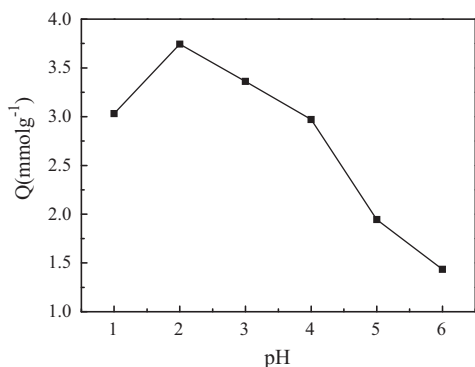**Scheme 3.** Modification of resin based on acrylonitrile.

Fig. 4. Effect of pH on the adsorption of AO PAN-g-PS beads for Hg^{2+} (initial concentration: 5 mM; 25 °C; adsorbent dose: 0.01 g).

Fig. 5. Adsorption kinetics of AO PAN-g-PS beads for Hg^{2+} (initial concentration: 5 mM; pH 2.0; adsorbent dose: 0.01 g).

indicated that the modification reaction was successfully completed.

3.4. Adsorption properties

This study examined Hg^{2+} ion adsorption from aqueous solution by AO PS-g-PAN under static conditions. According to previous literature [9,51], the adsorption mechanism of the polymer containing AO groups for Hg^{2+} is shown in Scheme 4.

3.4.1. Effect of pH on adsorption

The pH value of the metal ions solution is one of the most important factors influencing the adsorption behavior of metal ions on sorbents. It not only impacts the surface structure of sorbents and the formation of metal ions, but it may also influence the interaction between sorbents and metal ions. Fig. 4 shows the effect of pH on
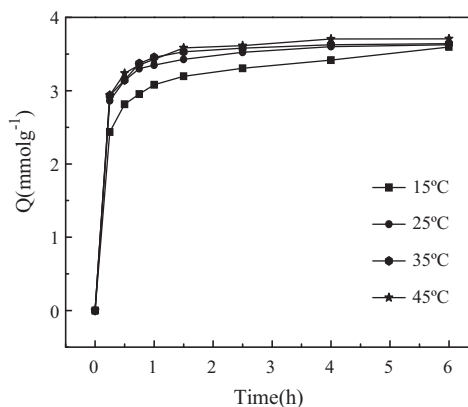
the adsorption of Hg^{2+} to the AO PAN-g-PS resins. From Fig. 4, it can be seen that the amount of adsorbed metal ions increases together with increase in the pH of the adsorption medium, until reaching a maximum (3.88 mmol g^{-1}) at pH = 2.0; the concentration of Hg^{2+} significantly decreased after adsorption. The amount of adsorbed metal ions showed a decreasing trend with increasing pH (2.0–6.0). The adsorption of AO PAN-g-PS maintained good adsorption for Hg^{2+} among a wide range of pH values 1.0–4.0 (>3.0 mmol g^{-1}). In addition, the adsorption was low at pH levels of 5.0 and 6.0. We chose pH = 2.0 to study the adsorption characteristics of AO PAN-g-PS beads for Hg^{2+} in the following study.

3.4.2. Adsorption kinetics

The adsorption kinetics that describe the solute uptake rate governing the contact time of the sorption reaction is one of the important characteristics that define the efficiency of sorption. The adsorption kinetics curves of AO PAN-g-PS for Hg^{2+} at different temperatures are shown in Fig. 5. As the figure indicates, the kinetics curves of sorbents showed sharp curves at the beginning (90 min), then the curves became gentle and turned into a straight line at the end. The adsorption amounts of Hg^{2+} exhibited only a slight change at different temperatures, particularly at 25 °C, 35 °C and 45 °C.
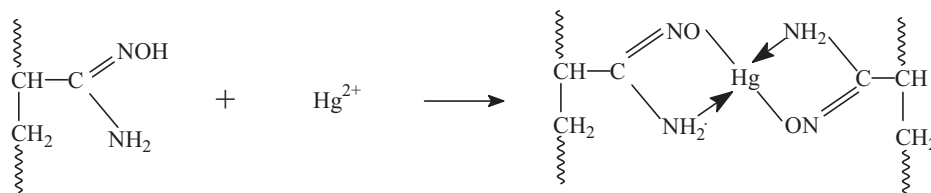
Scheme 4. Proposed schematic diagram for the complex formation between Hg^{2+} and AO PAN-g-PS.
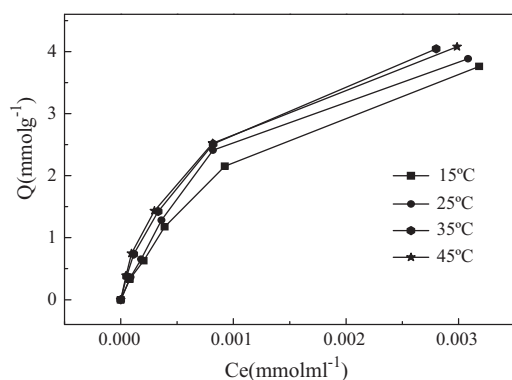
Fig. 6. Adsorption isotherms of AO PAN-g-PS beads for Hg^{2+} (pH 2.0; contact time: 12 h; adsorbent dose: 0.01 g).

This indicated that temperature had only a slight positive effect on adsorption capacity. As the kinetic data show, the adsorption process can be carried out perfectly with smaller reactor volumes, ensuring efficiency and economy at room temperature.

3.4.3. Adsorption isotherms

The adsorption isotherms of AO PAN-g-PS for Hg^{2+} at different temperatures are presented in Fig. 6. The Langmuir and Freundlich [52] isotherm models were used to interpret the isothermal adsorption experimental data. The Langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption, and the Freundlich model assumes that the uptake or adsorption of metal ions occurs on a heterogeneous surface. The adsorption experimental data were analyzed by Langmuir model (1) and Freundlich (2) model, respectively. The results are shown in Figs. 7 and 8.

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 K_t} \tag{1}$$

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{2}$$

where Q_e is the adsorption capacity, $mmol\,g^{-1}$; C_e is the equilibrium concentration of Hg^{2+}, $mol\,cm^{-3}$; Q_0 is the saturated adsorption capacity, $mmol\,g^{-1}$; K_L is an empirical parameter; n is the Freundlich constant; K_F is the binding energy constant reflecting the affinity of the adsorbents to metal ions.

Table 1 displays the coefficients of the Langmuir and Freundlich models, along with regression coefficients (R^2). As shown from Table 1, the R_L^2 values indicate that the Langmuir isotherm suits the experimental data better than the Freundlich, so the adsorption processes could be described by the Langmuir formula.
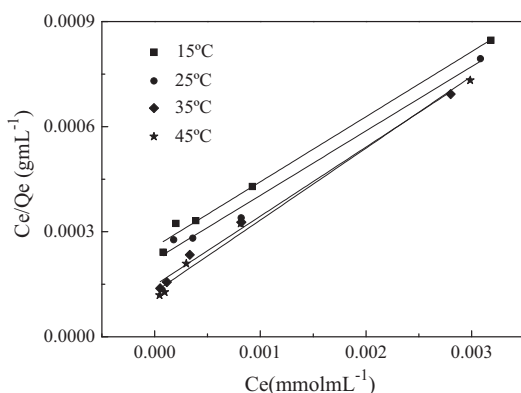

Fig. 7. Langmuir isotherms of Hg^{2+} adsorbed on AO PAN-g-PS beads at different temperatures.
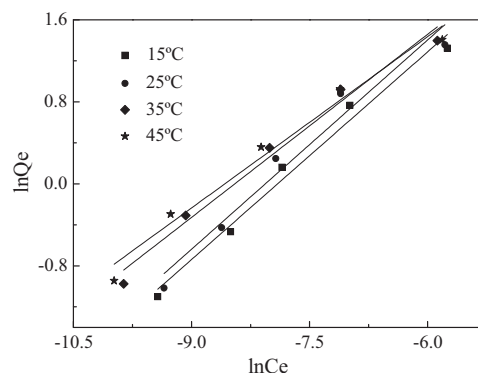

Fig. 8. Freundlich isotherms of Hg^{2+} adsorbed on AO PAN-g-PS beads at different temperatures.

Table 1
Langmuir and Freundlich constants for Hg^{2+} adsorption on AO PAN-g-PS beads at different temperatures.

Temperature (°C)	Langmuir parameters			Freundlich parameters		
	Q_0 ($mmol\,g^{-1}$)	K_L	R_L^2	K_F	$1/n$	R_F^2
15	5.38	718	0.9897	209	0.6757	0.9773
25	5.44	835	0.9899	242	0.6808	0.9500
35	5.07	1342	0.99105	153	0.5958	0.9768
45	4.87	1603	0.9898	119	0.5574	0.9719

Table 2
The adsorption selectivity of AO PAN-g-PS beads for Hg^{2+} in binary ions systems at 25 °C (initial metal ions concentration: 5 mM; adsorbent dose: 0.01 g; pH: 2.0).

System	Metal ion	Adsorption capacity ($mmol\,g^{-1}$)
$Hg^{2+}–Pb^{2+}$	Hg^{2+}	4.02
	Pb^{2+}	0
$Hg^{2+}–Ag^+$	Hg^{2+}	3.86
	Ag^+	0
$Hg^{2+}–Cu^{2+}$	Hg^{2+}	3.83
	Cu^{2+}	0

3.4.4. Adsorption selectivity

The adsorption selectivity is an indispensable factor for appreciating the capacities of an adsorbent, by which the chelating fiber can be used to adsorb a specific metal ion or to separate specific metal ions from a mixed metal ions solution. In this part, the coexistence of $Hg^{2+}–Pb^{2+}$, $Hg^{2+}–Ag^+$, $Hg^{2+}–Cu^{2+}$ systems was used to investigate the adsorption selectivity of AO PAN-g-PS beads. As shown in Table 2, the AO PS-g-PAN beads adsorbed Hg^{2+} only in all of the binary ions systems. This indicated that the resin exhibited excellent adsorption selectivity for Hg^{2+}. Moreover, the results shown in Table 2 could provide the possibility of separating Pb^{2+}, Ag^+, and Cu^{2+} from Hg^{2+} with the resin at pH = 2.0.

3.4.5. The regeneration of AO PAN-g-PS

Desorption of the adsorbed Hg^{2+} from the AO PAN-g-PS was carried out using $0.1\,mol\,L^{-1}$ HCl solution. In order to show the reusability of the AO PAN-g-PS, an adsorption–desorption cycle of metal ions was repeated three times using the same preparation methods. The results of the three adsorption–desorption cycles are shown in Table 3. The data in Table 3 suggest that

Table 3
Desorption and regeneration data.

Reuse time	Adsorption capacity ($mmol\,g^{-1}$)
1	3.83
2	3.76
3	3.72

the adsorption capacity did not significantly change during the repeated adsorption–desorption operations. These results show that AO PAN-g-PS could be repeatedly used in heavy-metal adsorption studies without any detectable change in adsorption capacity.

4. Conclusions

A new method for surface-initiated ARGET ATRP mediated by iron (III)/IDA as a catalyst system and VC as a reducing agent was developed. Well-defined PAN chains were grown from cross-linked polystyrene resin-supported N-chlorosulfonamide groups beads, with surface labile chlorides as initiating sites, by this new method and without the formation of homopolymers of AN. The PG% increased linearly with corresponding increases in polymerization time, and the proposed method showed the characteristics of a controlled/"living" polymerization. The PAN-g-PS beads can be modified by $NH_2OH \cdot HCl$ to yield AO PAN-g-PS beads, which had excellent adsorption selectivity for Hg^{2+}. The adsorption experiment showed that the AO PAN-g-PS beads have the highest adsorption for Hg^{2+} at pH = 2.0. Temperature had only a slight positive effect on adsorption capacities, and equilibrium could be achieved in 1.5 h. The adsorption processes could be described by the Langmuir isotherm, and the uptake of metal ions occurred on a homogeneous surface by monolayer adsorption. The selective adsorption indicated that this resin can be used to separate Pb^{2+}, Ag^+, and Cu^{2+} from Hg^{2+} at pH = 2.0. The regeneration experiment showed that AO PAN-g-PS could be repeatedly used in heavy-metal adsorption studies without any detectable change in adsorption capacity.

Acknowledgements

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