

Synthesis of Crosslinked Polyacrylonitrile via Atom Transfer Radical Polymerization with Activators Regenerated by Electron Transfer and Use of the Resin in Mercury Removal After Modification

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ABSTRACT: Crosslinked polyacrylonitrile (PAN) was synthesized with divinylbenzene as the crosslinker with an iron(III)-mediated atom transfer radical polymerization method with activators regenerated by electron transfer. The polymerization exhibited first-order kinetics with respect to the polymerization time. Hydroxylamine hydrochloride (NH₂OH·HCl) was used to modify the cyano groups of the crosslinked PAN to obtain amidoxime (AO)

groups. The AO-crosslinked PAN was used to remove Hg(II). The optimum pH, adsorption kinetics, and adsorption isotherms were investigated. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2179–2186, 2012

Key words: adsorption; atom transfer radical polymerization (ATRP); kinetics (polym.)

INTRODUCTION

Heavy-metal contamination, which can cause dangerous consequences for human beings, exists in the aqueous wastewater of many industries.¹ Mercury is one of the most toxic heavy metals present in the environment, and it poses a potential threat to human health even at very low concentrations. Many techniques have been developed to remove mercury from aquatic systems.² There are several treatment processes for metal-contaminated wastewater, such as ion exchange, carbon adsorption, and adsorption. In recent years, great attention has been paid to the adsorption methodology for its efficacy and selectivity. Polymeric materials have been synthesized or modified to remove metal ions.^{3,4} Numerous adsorbents with various chelating

groups for the removal and recovery of metal ions have been reported.^{5,6}

Polyacrylonitrile (PAN) is an important precursor for polymer materials because of its unique and well-known properties. Also, PAN can be easily chemically modified to contain pendant cyano groups to obtain adsorbent-containing amidoxime (AO) groups, which can be successfully used for the treatment of metals from aqueous solutions for its high complex-forming capability with metal ions.^{7,8} However, difficulties are sometimes encountered in the isolation of the adsorption products because of the solubility in wastewater within a low pH range.⁹ So, it is necessary to synthesize predetermined polymers.

Atom transfer radical polymerization (ATRP)¹⁰ can be successfully used for the synthesis of polymers with complex architectures, such as pure linear, branched, and starlike polymers,^{11–13} and crosslinked polymers because of the availability and facile preparation of many multifunctional initiators.¹⁴ A number of authors have reported the synthesis of crosslinked polymers with ATRP.^{15,16}

Although normal ATRP has made great advances in the synthesis of polymers, the high concentration and sometimes difficult removal of metal catalysts limit its widespread use in industry. Recently, Matyjaszewski et al.¹⁷ reported the activators regenerated by electron transfer (ARGET) ATRP, which allows a polymerization to be established at parts per million level of catalyst concentration. In the ARGET system, a parts per million level of metal catalyst is used,

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together with a sufficiently large excess of reducing agent; this not only reduces excess M_t^{n+1} (metal catalyst with higher oxidation state) deactivator formed in the termination reactions to the original active M_t^n (metal catalyst with lower oxidation state) but is also responsible for the scavenging of oxygen and suppression of side reactions between the chain end and the catalyst. A large number of studies have reported to have synthesized well-defined pure linear polymers by ARGET ATRP.^{18,19} A few ARGET ATRP systems have been reported to synthesize branched polymers^{20,21} and crosslinked polymers.

In this article, we reported a novel ARGET ATRP system used to prepare crosslinked PAN with CCl_4 as the initiator, anhydrous ferric trichloride (FeCl_3)/iminodiacetic acid (IDA) as the catalyst system, L-ascorbic acid (VC) as the reducing agent, divinylbenzene (DVB) as the crosslinker, and *N,N*-dimethylformamide (DMF) as the solvent. The crosslinked product was modified with hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$), which modified the cyano groups into AO groups to yield the adsorbent. The adsorbent-containing AO groups were used for the extraction of Hg(II) from aqueous solutions. The adsorption capacity for Hg(II) was also investigated.

EXPERIMENTAL

Materials

Acrylonitrile (AN; 98%, Tianjin Fuchen Chemical Reagents Co., Tianjin, China) was distilled under normal pressure and stored at 5°C. Carbon tetrachloride (CCl_4 ; Tianjin Regent Chemical Co. Tianjin, China), anhydrous ferric trichloride (FeCl_3 ; 97 wt %, Sinopharm Chemical Reagent Co., Shanghai, China), IDA (98 wt %, Sinopharm Chemical Reagent Co.), VC (99.7 wt %, Tianjin Regent Chemical Co.), DVB (Aldrich, Saint Louis, Missouri), analytical-reagent-grade hydrated mercurous nitrate [$\text{Hg}(\text{NO}_3)_2\cdot\text{H}_2\text{O}$; Tianjin East Regent Chemical Co., Tianjin, China], and DMF (99.5%, Tianjin Fuchen Chemical Reagents Co.) were used as received. All other chemical reagents were used as received.

ARGET ATRP polymerization procedure

The procedure was prepared according to the literature.²² In a typical experiment, AN (19.8 mL, 0.3 mol), CCl_4 (0.14 mL, 1.5 mmol), FeCl_3 (1.5×10^{-5} mol), IDA (1.5×10^{-4} mol), DVB (5 mL), and VC (1.5×10^{-4} mol) were mixed in a dry two-necked round-bottom flask, which was bathed in ice water. The mixture was degassed *in vacuo*, charged with N_2 (three times), and finally sealed with N_2 . The mixture was immersed in a thermostated oil bath held at the desired temperature. At timed intervals, the

reaction was terminated by cooling of the flask in the ice water. The product was dissolved with DMF and precipitated by methanol–water (1 : 1 v/v). Then, the product was dried 24 h *in vacuo*.

Characterization

Infrared spectra were recorded on a PerkinElmer Spectrum 2000 FTIR spectrometer (Perkin Elmer, Inc., Shelton, CT). The conversion of the polymerization reaction was calculated according to the following equation:

$$\text{Conversion (\%)} = \frac{\text{Crosslinked polymer (g)}}{\text{DVB (g)} + \text{AN (g)}} \times 100$$

Modification of the crosslinked PAN with hydroxylamine hydrochloride

The modification of the crosslinked PAN (AO-crosslinked PAN) resin was performed by the reaction of the resin samples with hydroxylamine hydrochloride in an aqueous solution (pH = 9.0) at 70°C for 24 h, as described by De Santa Maria et al.²³ The modified resin was characterized by infrared spectra and SEM.

Adsorption characteristics

Optimum sorption uptake

The adsorption experiments were performed on a rotating shaker. The AO-crosslinked PAN sorbent (10 mg) was immersed in 1 mL of 0.1 mol/L Hg(II) and 19 mL of acetic acid/ammonium acetate buffer solution at different pH values in a 100-mL Erlenmeyer flask and stirred 24 h at 25°C. The metal uptake was calculated by eq. (1):

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

where q is the adsorption amount (mmol/g), C_0 and C are the initial and the final concentrations of metal ions in solution, respectively (mmol/mL), V is the volume (mL), and W is the weight of AO-crosslinked PAN sorbent (mg).

Adsorption kinetics

The modified crosslinked PAN sorbent (10 mg) was added to 20 mL of a 5.0×10^{-3} mol/L Hg(II) 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(II) were analyzed by atomic absorption spectroscopy.

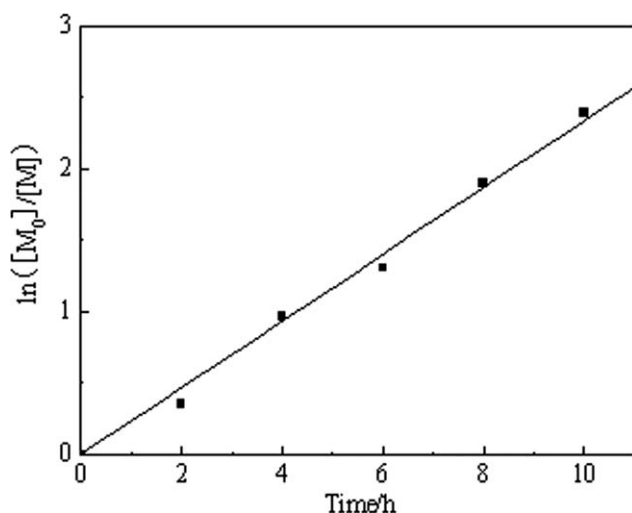


Figure 1 First-order kinetics plots for the ARGET ATRP of AN and DVB.

Adsorption isotherms

The adsorption isotherms were obtained by the mixture of 10 mg of dry adsorbent in a series of flasks containing 20 mL of different initial metal ion concentrations, which varied from 0.25 to 5 mmol/L, for 12 h. The initial pH was adjusted to 2.0 for Hg(II). Also, the concentration variations of Hg(II) were determined via atomic absorption spectroscopy.

RESULTS AND DISCUSSION

Synthesis of the AO-crosslinked PAN adsorbent

ARGET ATRP of AN mediated by an iron catalyst was conducted in a DMF solution with FeCl_3/IDA as the catalyst system, VC as the reducing agent, CCl_4 as the initiator, and DVB as the crosslinker at 65°C . Kinetic plots of the variation of $\ln([M]_0/[M])$ ($[M]$ is the concentration of the monomer at different times; and $[M]_0$ is the initial concentration of the monomer) versus the polymerization time for ARGET ATRP of AN are shown in Figure 1. As can be seen from Figure 1, there was a linear increase in the variation of $\ln([M]_0/[M])$ versus the polymerization time. The linear kinetic plot of the monomer conversion suggested that the polymerization was also consistent with a controlled process. The product was determined by FTIR spectra [Fig. 2(a)]. There was a peak at 2200 cm^{-1} , which was characterized as the CN stretching vibration. The peaks at 3080 , 1600 , and 900 cm^{-1} were attributed to the benzene ring of DVB. These indicated that crosslinked PAN was successfully synthesized.

The product was modified with hydroxylamine hydrochloride, as reported by De Santa Maria et al.²³ The modification product was also determined by FTIR spectra [Fig. 2(b)]. Compared to the

unmodified resins [Fig. 2(a)], the band at 2241 cm^{-1} related to the CN group in the spectrum in Figure 2(b) almost disappeared. The increase in the absorption band around 3500 cm^{-1} in the spectrum in Figure 2(b) compared to the FTIR spectrum of the unmodified polymers in the spectrum in Figure 2(a) indicated the presence of $-\text{OH}$ bonds that belonged to AO groups. These indicated that the modification reaction was successful.

SEM was used to observe the morphologies of the crosslinked PAN and AO-crosslinked PAN, as shown in Figure 3. From Figure 3, we can see that compared with the morphology of the crosslinked PAN [Fig. 3(a)], the morphology of the AO-crosslinked PAN [Fig. 3(b)] did not significantly change. This indicated that the modification reaction did not change the morphology of the polymer.

Hg uptake

pH effect on the adsorption of AO-crosslinked PAN resin for Hg(II)

pH is one of the most important factors influencing the adsorption behavior, for not only affecting the surface structure of the sorbents and the formation of metal ions but also influencing the interaction between the sorbents and metal ions. Figure 4 shows the effect of pH on the adsorption of Hg(II) from aqueous solution with AO-crosslinked PAN. The pH values were varied between 1.0 and 6.0. From Figure 4, it can be seen that the amounts of the adsorbed metal ions were higher than 2.0 mmol/g , and the maximum adsorption capacity achieved was 3.0 mmol/g at pH 2.0 in the range 1.0–6.0. The adsorption capacity was better than those available in the literature. Consequently, all of the following experiments were performed at pH 2.0. Compared with other polymers containing AO groups,^{7,8} the AO-crosslinked PAN had a higher amount of adsorption for Hg(II).

Adsorption kinetics

The kinetics of adsorption are one of the important characteristics that define the efficiency of sorption.

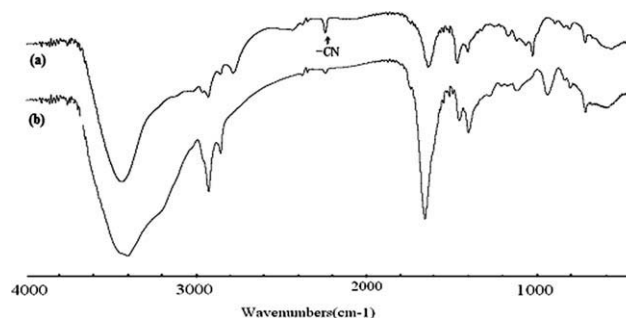


Figure 2 FTIR spectra of (a) crosslinked PAN and (b) AO-crosslinked PAN.

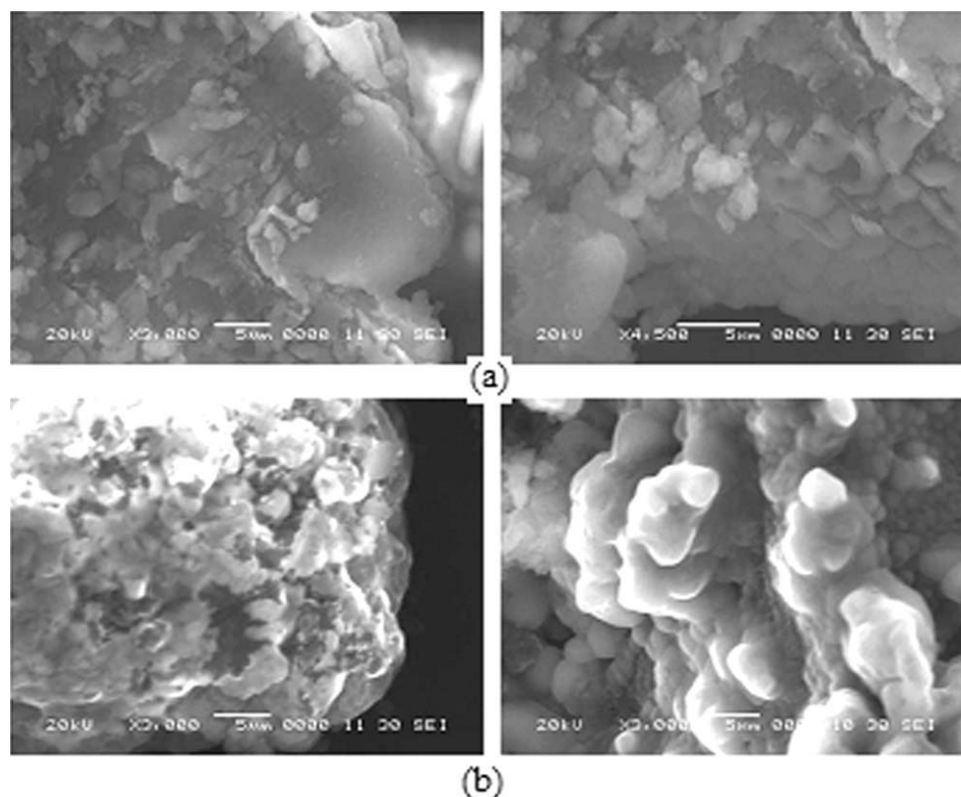


Figure 3 SEM photographs of (a) crosslinked PAN and (b) AO-crosslinked PAN.

The adsorption kinetics describe the uptake rate of metal ions, which controls the contact time of adsorbate uptake at the solid–solution interface. Figure 5 shows the kinetics of the adsorption of metal ions Hg(II). As shown in Figure 5, the adsorption capacities at different temperatures all increased rapidly at the beginning (in 60 min). Also it can be seen in Figure 5 that the adsorption capacities increased with increasing temperature, especially at 45°C. A possi-

ble explanation was that higher temperature made Hg(II) diffuse more easily, and the adsorption was an endothermic process.²⁴

To evaluate the kinetic mechanism, pseudo-first-order and pseudo-second-order models were employed to interpret the experimental data. The pseudo-first-order and pseudo-second-order equations are represented by eqs. (2) and (3), respectively:^{25,26}

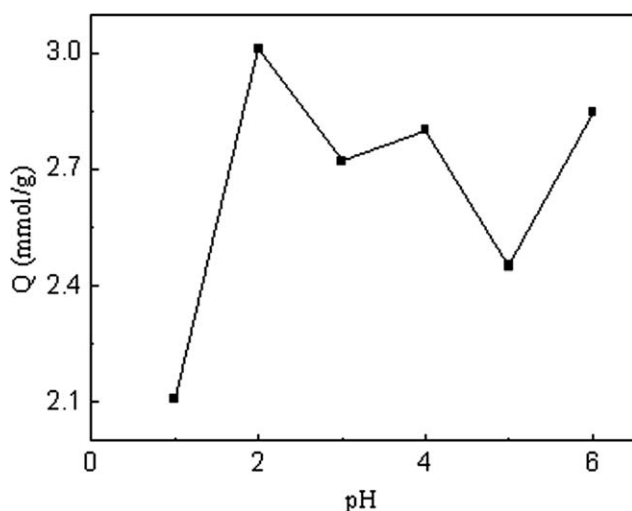


Figure 4 Effect of pH on the adsorption of AO-crosslinked PAN for Hg(II) (initial concentration = 5 mM, 25°C, adsorbent dose = 0.01 g).

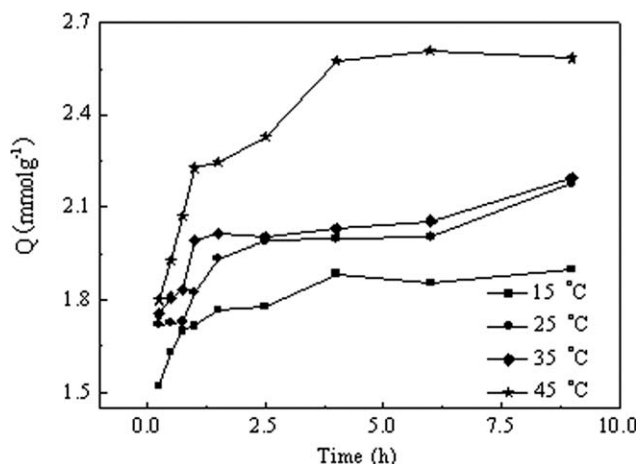


Figure 5 Adsorption kinetics of AO-crosslinked PAN for Hg(II) (initial concentration = 5 mM, pH 2.0, adsorbent dose = 0.01 g).

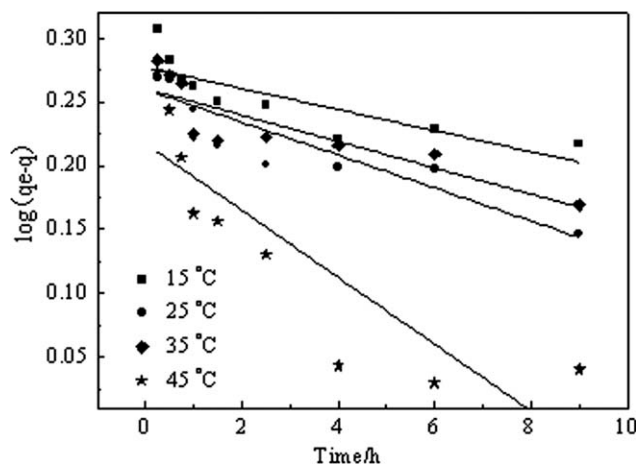


Figure 6 Plot of the pseudo first-order adsorption kinetics of Hg(II) on puresorbe at different temperatures.

$$\ln \left[\frac{(q_e - q_t)}{q_e} \right] = -k_1 t \quad (2)$$

$$\frac{t}{q_1} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where k_1 is the pseudo-first-order adsorption rate constant (min^{-1}), q_t (mmol/g) is the amount adsorbed at time t (min), q_e (mmol/g) denotes the amount adsorbed at equilibrium, and k_2 ($\text{g mol}^{-1} \text{min}^{-1}$) is the adsorption rate constant of pseudo-second-order.

Plots of $\log(q_e - q_t)$ versus t and t/q_t versus t were employed to test the pseudo-first-order and pseudo-second-order models, respectively. The results of model testing are shown in Figures 6 and 7, respectively. The fitting results are given in Table I.

As can be seen from Table I, the pseudo-second-order model provided better correlation coefficients (R^2 's) than the pseudo-first-order model for the AO-crosslinked PAN at any temperature studied; this suggested that the pseudo-second-order model was more suitable to describe the adsorption kinetics of the AO-crosslinked PAN for Hg(II). Furthermore, the calculated equilibrium adsorption capacities ($q_{e,cal}$'s), depending on the pseudo-second-order

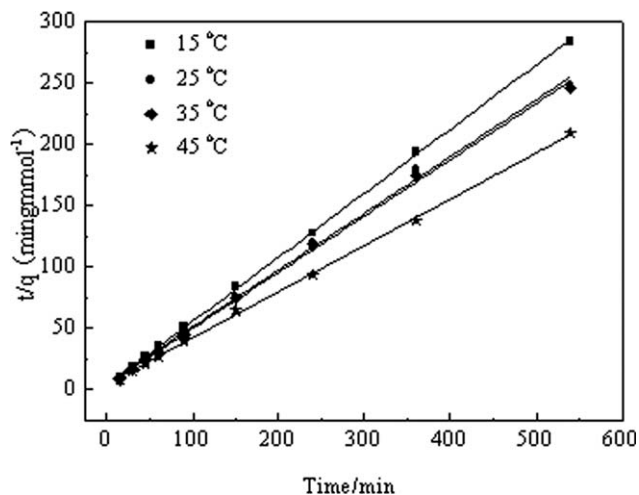


Figure 7 Plot of pseudo second-order adsorption kinetics of Hg(II) on puresorbe at different temperatures.

model much closer to the experimental equilibrium adsorption capacities ($q_{e,exp}$), also suggested the suitability of the pseudo-second-order model.

Data from the kinetic adsorption experiments were used to determine the values of ΔH and ΔS (ΔH and ΔS are represented enthalpies and entropies of reaction, respectively). According to Van't Hoff eqs. (4) and (5):

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4)$$

$$\Delta G = -RT \ln K_c \quad (5)$$

where T is the temperature and R is the gas constant. The plot of $1/T$ versus $\ln K_c$ (K_c is the equilibrium constant of reaction) is given in Figure 8. ΔS and ΔH were calculated from the slope and intercept of the plot (shown in Table II). The negative value of ΔG (ΔG stands for Gibbs free energy) suggested that adsorption was spontaneous. The positive value of ΔH suggested an endothermic process of adsorption. The positive value of ΔS showed the feasibility of adsorption and the increased randomness at the sorbent/solution interface during the adsorption of metal ions onto puresorbe.

TABLE I
Adsorption Kinetic Rate Constants for the AO-Crosslinked PAN at Different Temperatures

Temperature (°C)	Pseudo-first-order model				Pseudo-second-order model		
	$q_{e,exp}$ (mmol/g)	$q_{e,cal}$ (mmol/g)	k_1 (h^{-1})	R^2	$q_{e,cal}$ (mmol/g)	k_2 ($\text{g}\cdot\text{mmol}^{-1}\cdot\text{min}^{-1}$)	R^2
15	1.90	1.89	0.0143	0.6460	1.91	0.082	0.9997
25	2.18	1.82	0.0895	0.8148	2.16	0.040	0.9969
35	2.20	1.82	0.0223	0.7128	2.18	0.050	0.9997
45	2.58	1.65	0.0195	0.7108	2.65	0.033	0.9916

$q_{e,exp}$, amount of metal adsorbed at equilibrium per unit weight of adsorbent; $q_{e,cal}$, theoretical calculation of the amount of metal adsorbed per unit weight of adsorbent.

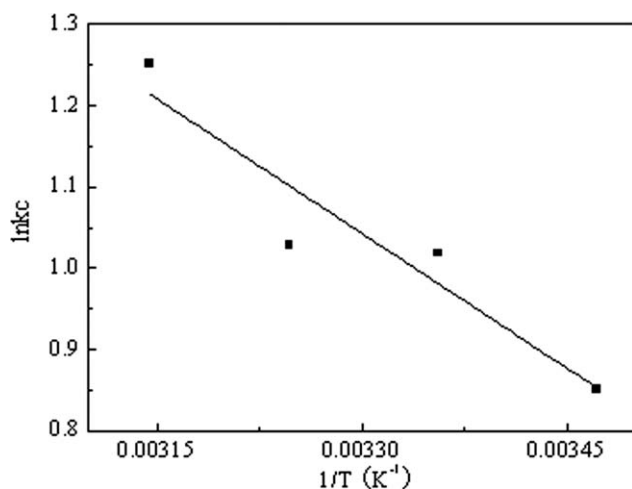


Figure 8 Figure $\ln K_c$ versus $1/T$ plot for Hg(II) adsorption on AO PAN.

Adsorption isotherms

The purpose of the adsorption isotherm is to relate the adsorbate concentration in the bulk solution to the adsorbed amount at the interface. Analysis of the isotherm data is important to develop an equation that accurately represents the results.²⁷ The adsorption isotherms of Hg(II) ion on the AO-crosslinked PAN are shown in Figure 9 at four different temperatures. It is shown that the adsorption amount increased with the equilibrium concentration of the metal ion in solution.

To better understand the adsorption behaviors, the Langmuir and Freundlich equations were employed to fit the experimental data. The Langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions; The Freundlich model assumes that the uptake or adsorption of metal ions occurs on a heterogeneous surface by monolayer adsorption.²⁸ The forms of Langmuir [eq. (6)] and Freundlich [eq. (7)] equations are expressed as follows:²⁸

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 K_L} \quad (6)$$

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

TABLE II
Thermodynamic Parameters for the Adsorption of Hg(II) by AO-Crosslinked PAN

Temperature (°C)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J mol ⁻¹ ·K ⁻¹)
288	-2.04	9.2	38.9
298	-2.52		
308	-2.63		
318	-3.31		

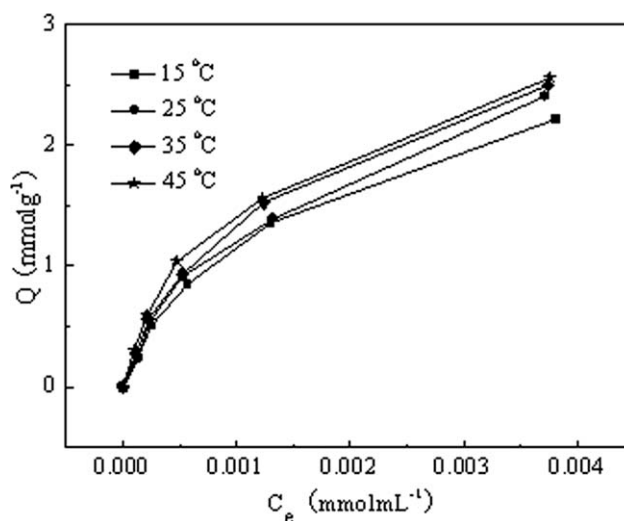


Figure 9 Adsorption isotherms of AO-crosslinked PAN for Hg(II) (pH 2.0, contact time = 12 h, adsorbent dose = 0.01 g). Q is the maximum adsorption capacity at different pH value.

where Q_e (mmol/g) is the adsorption capacity, C_e (mol/cm³) is the equilibrium concentration of Hg²⁺, Q_0 (mmol/g) is the saturated adsorption capacity, K_L is an empirical parameter (the Langmuir adsorption constant), n is the Freundlich constant, and K_F is the binding energy constant reflecting the affinity of the adsorbents to metal ions.

The experimental data fitted with Langmuir and Freundlich models are shown in Figures 10 and 11, respectively. Table III displays the coefficients of the Langmuir and Freundlich models along with the R^2 values. As shown in Table III, the Langmuir isotherm was a better fitting model than that of Freundlich as the former had a higher correlation regression coefficient; this indicated the applicability of a monolayer coverage of Hg(II) on the surface of the adsorbent.

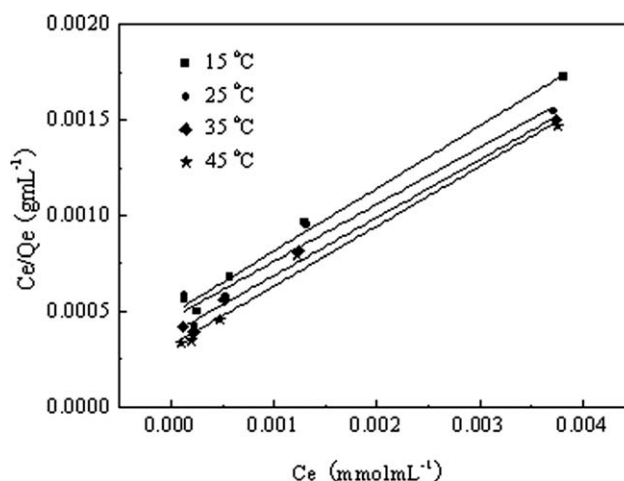


Figure 10 Langmuir isotherms of Hg(II) adsorbed on AO-crosslinked PAN at different temperatures.

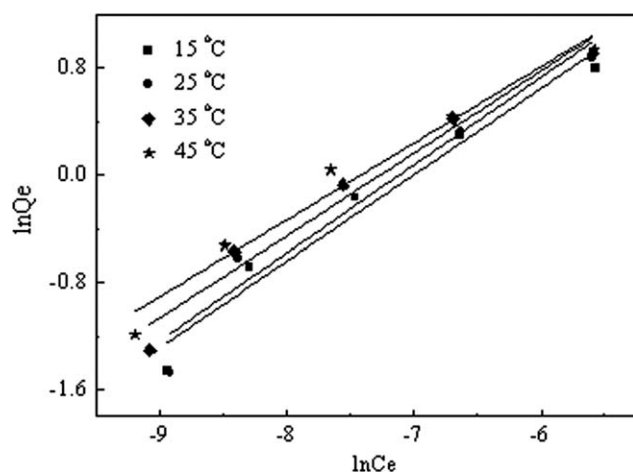


Figure 11 Freundlich isotherms of Hg(II) adsorbed on AO-crosslinked PAN at different temperatures.

Regeneration of AO-crosslinked PAN

The desorption of the adsorbed Hg(II) from the AO-crosslinked PAN was carried out with a 0.1 mol/L HNO₃ solution. To show the reusability of the AO-crosslinked PAN, an adsorption–desorption cycle of metal ions was repeated three times with the same preparation methods at 25°C, and the results are given in Table IV. As shown in Table IV, the results of the adsorption–desorption cycles showed that AO-crosslinked PAN could be used repeatedly at least three times without any detectable change in the adsorption capacity.

Adsorption mechanism

The adsorption mechanism for Hg(II) has been discussed in some reports.^{6,29} AO is supposed to be bidentate; two AOs may be used for chelate formation with a metal ion, which makes a square planer chelate. The mechanism is presented in Scheme 1.

CONCLUSIONS

In this article, crosslinked PAN was synthesized with DVB as the crosslinker with an iron (III)-medi-

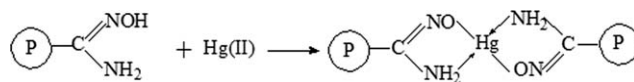
TABLE III
 K_L and n Values for Hg(II) Adsorption on AO-Crosslinked PAN at Different Temperatures

Temperature (°C)	Langmuir parameter			Freundlich parameter		
	Q_0 (mmol/g)	K_L	R_L^2	K_F	$1/n$	R_F^2
15	3.05	673	0.9884	91.3	0.6443	0.9557
25	3.36	641	0.9531	106	0.6554	0.9272
35	3.30	790	0.9882	87.4	0.6150	0.9614
45	3.20	979	0.9847	69.5	0.5716	0.9604

Both R_L^2 and R_F^2 are linear fitting parameters, 'L' and 'F' are the presentation of Langmuir Freundlich models.

TABLE IV
Desorption and Regeneration Data

Times reused	Adsorption capacity (mmol/g)
1	2.16
2	2.09
3	1.99



Scheme 1 Schematic diagram for complex formation between Hg(II) and AO-crosslinked PAN.

ated ARGET ATRP method. The polymerization exhibited first-order kinetics with respect to the polymerization time. Hydroxylamine hydrochloride (NH₂OH·HCl) was used to modify the cyano groups of the crosslinked PAN to obtain AO groups. AO-crosslinked PAN was shown to be an effective adsorbent for Hg(II) removal from aqueous solutions. The optimum pH corresponding to the maximum adsorption was found to be 2.0. The adsorption kinetics study indicated that pseudo-second-order rate model provided excellent fitting of the AO-crosslinked PAN for Hg(II) over the temperature range 15–45°C. The isotherm adsorption data of the Hg(II) on AO-crosslinked PAN at 25°C was well fitted by the Langmuir model; this indicated that the uptake of metal ions occurred on a homogeneous surface by monolayer adsorption. The regeneration experiments showed that the AO PAN-g-polystyrene (PS) could be used repeatedly.

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