Hg(II) adsorption using amidoximated porous acrylonitrile/itaconic copolymers prepared by suspended emulsion polymerization

Chunnuan Ji, Rongjun Qu, Hou Chen, Xiguang Liu, Changmei Sun and Caixia Ma

ABSTRACT

Initially, porous acrylonitrile/itaconic acid copolymers (AN/IA) were prepared by suspended emulsion polymerization. Successively, the cyano groups in AN/IA copolymers were converted to amidoxime (AO) groups by the reaction with hydroxylamine hydrochloride. The structures of the AN/IA and amidoximated AN/IA (AO AN/IA) were characterized by infrared spectroscopy, scanning electron microscopy, and porous structural analysis. The adsorption properties of AO AN/IA for Hg(II) were investigated. The results show that AO AN/IA has mesopores and macropores, and surface area of 11.71 m² g⁻¹. It was found that AO AN/IA has higher affinity for Hg(II), with the maximum adsorption capacity of 84.25 mg g⁻¹. The AO AN/IA also can effectively remove Hg(II) from different binary metal ion mixture systems. Furthermore, the adsorption kinetics and thermodynamics were studied in detail. The adsorption equilibrium can quickly be achieved in 4 h determined by an adsorption kinetics study. The adsorption process is found to belong to the second-order model, and can be described by the Freundlich model.

Key words | adsorption, amidoxime, chelating polymers, metal ions, suspended emulsion polymerization

INTRODUCTION

The presence of potentially toxic metals in the environment has been of great concern due to their persistence and harmful effects upon aquatic life and human health (Wan Nga & Hanafiah 2008; Wang et al. 2012). Such potentially toxic metals as mercury, cadmium, lead, chromium, and copper can be distinguished from other pollutants, since they cannot be biodegraded but accumulate in living organisms, thus causing various diseases and harmful effects on proteins, enzymes and human life (Martín-González et al. 2006). Thus, it is critical to remove potentially toxic metals from waste water (Shaaban et al. 2014).

Nowadays, various methods have been developed and used to remove potentially toxic metals in polluted water, including chemical precipitation (González-Muñoz et al. 2006), ion exchange (Dabrowski et al. 2004), adsorption (Ge et al. 2012), membrane filtration (Borbély & Nagy 2009), and electrochemical treatment (Chen 2004). Among these treatment methods, the selective adsorption by chelating polymers is considered to be a promising one due to its remarkable simplicity, high efficiency and low cost. Chelating polymers based on polyacrylonitrile (PAN) are easy to be prepared and present a reactive pendant group (nitrile group), which can be modified by different kinds of reagent through nucleophilic addition. Some authors have carried out modifications of PAN with NaOH to obtain amidino and carboxylic groups (Deng et al. 2005; Zhang et al. 2010). Several articles have been devoted to PAN modifications with hydroxylamine to form amidoxime (AO) groups (Kavakli & Güven 2004; Saeed et al. 2008). Among these functional groups, AO groups have been found to be one of the most efficient functional groups for removal of potentially toxic metals, and various chelating polymers with AO groups have been designed for removing potentially toxic metals from aqueous solutions (Godjevargova et al. 2002; Riqueza et al. 2002). Their metal absorption rates, however, are usually limited owing to the hydrophobic characteristic of the supporting matrix.
Furthermore, the hydrophobicity of the polymeric backbone can limit the intrinsic chelating properties of the functional groups (Lezzi et al. 1994; Sanchez et al. 2000). To increase the hydrophilicity of chelating polymers, a lot of chelating polymers have been synthesized by the copolymerization of acrylonitrile with hydrophilic monomers, such as methyl acrylate (Liu et al. 2010), and acrylic acid (Hu & Chou 1996). In our previous paper, porous PAN/itaconic acid (IA) copolymers were prepared by suspended emulsion polymerization and the effect of the process variables, including the water/monomer mass ratio, agitation conditions, potassium persulphate (KPS) concentration, IA concentration, poly(vinyl alcohol) (PVA) concentration, and Span80 concentration, on the average particle size and particle size distribution, particle morphology, and porosity of acrylonitrile/IA (AN/IA) copolymers were investigated in detail (Yu et al. 2009). As a subsequent work, the objective of the present work is to modify the porous PAN/IA copolymers and investigate the adsorption equilibrium, kinetics and thermodynamics of the resins for Hg(II) in aqueous solution.

MATERIALS AND METHODS

AN (Tianjin Kermel Chemical Reagent Co., analytical reagent grade, China) was distilled to get 76–78 °C distillation just before polymerization. IA (chemically pure grade, Shanghai Yingyuanka Chemical Co., Shanghai, China) was recrystallized from acetone. All other chemicals in this study were reagent grade and used without further purification. Span-80, hydroxylamine hydrochloride (NH₂OH · HCl), KPS, and PVA (polymerization degree = 1,750 ± 50) were purchased from Tianjin Reagent Chemical Co. (China). Stock solution of Hg(II) was prepared by dissolving appropriate amounts of HgCl₂ in distilled water. Stock solution of other metals was prepared by dissolving analytical grade nitrate in distilled water. Buffer solutions were prepared by addition of dilute nitric acid or liquid ammonia to 0.1 M ammonium acetate solution.

The morphology was determined using scanning electron microscopy (SEM; JSM-5610LV, JEOL, Tokyo, Japan), in which the samples were sputter-coated with Pt film before SEM examination. Infrared (IR) spectra were recorded on a Nicolet MAGNA-IR550 (serious II) spectrometer (Madison, WI, USA); test conditions: potassium bromide pellets, scanning 32 times, resolution 4 cm⁻¹. A pH meter (Mettler-Toledo, LE438 pH, China) was used for the measurement of pH values. Porous structure parameters were characterized using an automatic physisorption analyzer (ASAP 2020) by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods through N₂ adsorption at 77 K. Potentiometric method was carried out to determine the surface charge (pH_{PZC}) (Malvern Nano Zs 90, UK). The concentrations of metal ions were measured on a flame atomic absorption spectrophotometer (FAAS) (Model 932A, Australia), equipped with an air-acetylene flame. The operating parameters such as lamp current, slit width, and wavelength used for recording FAAS for Hg(II) were 3.0 mA, 0.5 nm, and 253.7 nm, respectively. Each determination in the adsorption procedure was repeated three times, and the results are given as average values. Error bars are also indicated wherever necessary.

Preparation of AN/IA and AO AN/IA

The synthetic route and the structures of AN/IA and AO AN/IA are shown in Figure 1.

AN/IA was prepared according to our previous paper (Yu et al. 2009). A typical procedure was as follows: 0.06 g KPS was added to a mixture containing 22.6 mL of AN, 2.24 g of IA, 0.25 g of Span-80, 3.0 mL of 2% PVA solution, and 20 mL deionized water. The system was charged with N₂ for
5 min and was sealed under N2. The mixture was stirred at room temperature until the solid dissolved completely. The resulting mixture was kept at 70 °C to start the polymerization for 7 h. The polymerization product was collected by filtration and extracted with ethanol for 24 h. Finally, AN/IA was dried under vacuum at 50 °C for 48 h.

Three grams of NH2OH · HCl was added to 100 mL of methanol solution containing 2 g of AN/IA copolymers. After the mixture was stirred for 2 h, the pH of mixture was adjusted to 8 with 10% NaOH aqueous solution. The reaction was performed at 70 °C for 12 h under stirring. AO AN/IA was filtered, and then washed with distilled water and acetone, respectively. Finally, AO AN/IA was extracted in ethanol for 24 h and dried at 50 °C under vacuum for 48 h.

Effect of pH on metal ion removal

The effect of pH on mercury removal was examined by placing 50 mg of AO AN/IA in a series of flasks containing 20 mL of 100 mg L⁻¹ Hg(II) with varying pH in the range of 1.0 – 6.0. The mixtures were equilibrated in a shaker for 12 h at 25 °C. After adsorption, the residual concentration of Hg(II) was determined via FAAS. The percentage of mercury removal was calculated according to Equation (1):

\[
\text{Hg(II) removal (\%)} = \frac{(C_0 - C)}{C_0} \times 100
\]

where \( C_0 \) and \( C \) are the initial and equilibrium concentration, respectively.

Adsorption kinetics

To obtain the data of adsorption kinetics, 20 mg of AO AN/IA was added to 20.0 mL of 100 mg L⁻¹ metal ion solution (pH 6.0). Then the mixture was shaken continuously in a thermostat-cum-shaking assembly at a predetermined temperature. An aliquot of 1 mL solution was removed at predetermined intervals for analysis by FAAS and the adsorption capacity of AO AN/IA for Hg(II) was calculated according to Equation (2):

\[
Q = \frac{(C_0 - C)V}{W}
\]

where \( Q \) is the adsorption capacity (mg g⁻¹); \( C_0 \) and \( C \) are the initial concentration and the concentration at any time \( t \), respectively, of metal ion in solution (mg L⁻¹); \( V \) is the solution volume (L); \( W \) is the dry weight of AO AN/IA (g). The time taken for 50% uptake of maximum capacity for metal ions \( (T_{1/2}) \) was determined.

Adsorption isotherms

Adsorption isotherms were obtained with different initial concentrations of metal ion while holding AO AN/IA amount at a constant value (20 mg) at different temperatures. After a shaking time of 24 h, the solution was separated from the adsorbent and the residual concentrations of the metal ions in solutions were measured by FAAS. The adsorption capacities were calculated also according to Equation (2), where \( C \) is the equilibrium concentration of metal ion in solution.

Separation of Hg(II) from several binary mixtures

In order to check the effect of foreign ions on the removal of Hg(II) by AO AN/IA, the performances were tested in 5 mg L⁻¹ Hg(II) solutions containing Na(I), K(I), Ca(II), Mg(II), Zn(II), Cu(II) or Ni(II) in the range of 10–5,000 mg L⁻¹ at pH 6.0. A typical procedure was as follows: 300 mg of AO AN/IA was shaken with a solution of the binary mixture system at 25 °C for 24 h. Then AO AN/IA was separated by filtration and the concentration of Hg(II) in the binary mixture was determined by FAAS.

Regeneration of AO AN/IA

To investigate the reusability of AO AN/IA, adsorption–desorption cycles of the resin were repeated five times using the same resin. In this paper, 0.1 M HNO₃, 5% thiourea in 0.1 M HNO₃, and 10% thiourea in 0.1 M HNO₃ were used for the desorbents of Hg(II). The resins containing adsorbed Hg(II) were placed in 20 mL of desorbent and stirred for 10 h at room temperature. The final concentrations of Hg(II) were determined by FAAS.

RESULTS AND DISCUSSION

Characterization of AO AN/IA

The IR spectra of AN/IA and AO AN/IA are presented in Figure 2. AN/IA was confirmed by the adsorption peaks at 2,244 and 1,727 cm⁻¹, which are caused by the stretching vibration of nitrile and carbonyl groups, respectively. After modification of the nitrile group with hydroxylamine
hydrochloride, the characteristic peaks of C\(=\)N and =N–O– groups at 1,650 and 933 cm\(^{-1}\) were observed, indicating that the modification reaction was successfully done.

To observe morphology of AN/IA and AO AN/IA, scanning electron micrographs of the platinum-coated samples were obtained. The photographs are shown in Figure 3. Obviously, there are abundant loose pores distributed on the surface of AN/IA and AO AN/IA, indicating AO AN/IA retains the porous structures after hydroxylamine modification.

Figure 4 shows the adsorption–desorption isotherms of nitrogen at 77 K on AN/IA and AO AN/IA. All isotherms exhibit a Type IV profile according to the IUPAC classification, with remarkable hysteresis loops in relative pressure higher than 0.8 (Sing et al. 1985). This implies that the pores of AN/IA and AO AN/IA are mostly mesoporous and macroporous. As seen in Figure 4, almost no nitrogen is adsorbed by AN/IA and AO AN/IA at lower relative pressure (P/P\(_0\)), indicating that there are few micropores in AN/IA and AO AN/IA. Furthermore, Figure 4 shows BJH desorption pore size distributions of AN/IA and AO AN/IA. It can be noted that the pores between 10 and 60 nm were dominant for all the copolymers; that is, both mesopores and macropores are present in AN/IA and AO AN/IA, which is in accordance with the results of SEM analysis. After the reaction of AN/IA with NH\(_2\)OH · HCl, the pores between 10 and 75 nm in AO AN/IA decrease and the amount of those between 75 and 95 nm increase slightly. The porous structure parameters of AN/IA and AO AN/IA from the basis of the nitrogen adsorption data are summarized in Table 1. It is found that a BET surface area of 15.78 m\(^2\) g\(^{-1}\) and a BJH desorption volume of 0.079 cm\(^3\) g\(^{-1}\) are obtained for AN/IA, which decrease to 11.71 m\(^2\) g\(^{-1}\) and 0.048 cm\(^3\) g\(^{-1}\), respectively, after modification with NH\(_2\)OH · HCl. These results might be attributed to the formation of an organic layer in the pores, which blocks the adsorption of nitrogen molecules. In addition, the slight increase of pore size for AO AN/IA is probably because sodium hydroxide, which is utilized to remove HCl to make NH\(_2\)OH free, partially destroys the framework of AN/IA and makes the pore size increase. This phenomenon was also observed in our previous work (Liu et al. 2010).

The zeta potential of AO AN/IA in the pH range 2–9 was determined. The result is presented in Figure 5. It is found that the pH of point of zero charge (pH\(_{\text{PZC}}\)) for AO AN/IA is 3.9. This indicates that, at this pH, the change of the positive surface sites is equal to that of the negative ones. The pH\(_{\text{PZC}}\) is usually used to hypothesize on the ionization of functional groups and their interaction with metal species in solution (Fiol & Villaescusa 2009).
Effect of pH on adsorption

The pH of the metal ion solution has a significant impact on the uptake of potentially toxic metals, since it determines the existence form of the functional group in the adsorbent, the degree of ionization and speciation of the adsorbate (Denizli et al. 2004). The effect of pH on the removal of Hg(II) was determined in the range of 3–7 and the results are depicted in Figure 6. Obviously, the removal percentage of Hg(II) increases as pH value increased from 1.0 to 6.0. The maximum removal of Hg(II) was observed at pH 6. According to the previous reports, the dominant mercury species at pH > 4 is Hg(OH)$_2$ in the presence of Cl$^-$ (Knocke & Hemphill 1981). The species such as HgCl$_2$, Hg(OH)$_2^+$, and HgOHCl are also present in small concentration. The existence of dimeric HgCl$_2$ in aqueous solutions has been reported by many authors (Biscarini et al. 1971). In this paper, maximum adsorption efficiency at pH 6 may be explained as follows: at higher pH values, the dominant mercury species are neutral molecules. These species are softer acids than the metal cations of Hg(II) and have stronger interaction with AO functional groups. In acidic medium particularly below the pH$_{PZC}$, there is competitive adsorption between metal cations and hydrogen ions for the binding sites on the surface of AO AN/IA. Also, AO AN/IA cannot effectively chelate with the metal ions owing to the protonation of AO groups. It has been shown that there is no change in the final pH of

### Table 1 Parameters of porous structure of AN/IA and AO AN/IA

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$/g$^{-1}$)</th>
<th>BJH desorption cumulative volume of pores (cm$^3$/g$^{-1}$)$^*$</th>
<th>BJH desorption average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN/IA</td>
<td>15.78</td>
<td>0.079</td>
<td>78.89</td>
</tr>
<tr>
<td>AO AN/IA</td>
<td>11.71</td>
<td>0.048</td>
<td>80.98</td>
</tr>
</tbody>
</table>

$^*$The total volume of pores between 1.7 and 300 nm diameter

Figure 4 | Nitrogen adsorption-desorption isotherms and BJH desorption pore size distributions of AN/IA and AO AN/IA.

Figure 5 | The zeta potential (ZP) of AO AN/IA in the pH range 2–9.
the solution between 1 and point of zero charge. Hence, the following experiments were carried out in solution pH 6.

**Effect of adsorbent amount on adsorption**

The effect of AO AN/IA dosage on the removal was studied by varying the adsorbent amount from 10 to 50 mg in 20 mL metal ion solution. The results are shown in Figure 7. It is evident that the removal increases with adsorbent amount from a given initial solute concentration, due to the number of active sites in unit volume of solution increasing with the increase in adsorbent amount. The removal percentages increase sharply for amount from 10.0 to 30.0 mg and reach up to 99.1%. However, no further increase of removal is observed for dosage increasing from 40.0 to 50.0 mg. Therefore, the dosage of AO AN/IA was selected as 20 mg in 20 mL metal ion solution for further experiments.

**Adsorption kinetics**

Figure 8 shows the effect of contact time on the adsorption of Hg(II) at different temperatures. As shown in Figure 8, the adsorption of Hg(II) onto AO AN/IA is fast within the first 30 min, and \( T_{1/2} \) is less than 5 minutes. The adsorption equilibrium can be reached within 240 min. Many publications have reported on the adsorption of Hg(II) with different adsorbents. Liu et al. synthesized amidoximated poly acrylonitrile/methyl acrylate; the \( T_{1/2} \) for Hg(II) was about 180 min (Liu et al. 2010). Hassan & El-Wakil (2003) introduced AO groups into bagasse constituents, and the \( T_{1/2} \) of the amidoximated bagasse for Hg(II) was about 15 min. Comparing with the amidoximated poly acrylonitrile/methyl acrylate and bagasse, the faster adsorption rate of AO AN/IA for Hg(II) may be attributed to the high hydrophilicity of AO AN/IA, which results in increase in the diffusivity and accessibility of Hg(II) to the AO group in the adsorbent (Kawai et al. 2000). Furthermore, the results show that the adsorption rates increase with the increasing temperature. The reason for this may that there was sufficient swelling of AO AN/IA at higher temperature, which made it easier for Hg(II) to diffuse into the interior of AO AN/IA.

The adsorption kinetics data were treated according to the pseudo-first-order and pseudo-second-order models.

![Figure 6](image-url)  
**Figure 6** | Effect of pH on the removal of Hg(II) on AO AN/IA (metal concentration: 100 mg L\(^{-1}\); dosage of AO AN/IA: 50 mg; temp: 25 °C).

![Figure 7](image-url)  
**Figure 7** | Effect of dosage on the removal of Hg(II) on AO AN/IA (metal concentration: 100 mg L\(^{-1}\); pH 6; temp: 25 °C).

![Figure 8](image-url)  
**Figure 8** | Adsorption kinetics of Hg(II) on AO AN/IA at different temperatures (metal concentration: 100 mg L\(^{-1}\); dosage of AO AN/IA: 20 mg; pH 6).
given below as Equations (3) and (4), respectively (Ho & Mckay 2000).

\[ q_t = q_e - q_e \cdot e^{-k_1t} \]  \hspace{1cm} (3)

\[ q_t = \frac{k_2q_e^2t}{1 + k_2q_e t} \]  \hspace{1cm} (4)

where \( k_1 \) is the rate constant of pseudo-first-order adsorption (min\(^{-1}\)); \( k_2 \) is the rate constant of pseudo-second-order adsorption (g mg\(^{-1}\) min\(^{-1}\)); \( q_e \) and \( q \) are the adsorption amount at equilibrium and at time \( t \), respectively (mg g\(^{-1}\)).

The results along with the correlation coefficients \( R^2 \) are listed in Table 2. Comparing the correlation coefficients \( R^2 \) values of the pseudo-first-order kinetic model, the \( R^2 \) values of the pseudo-second-order kinetic model are higher, indicating that the pseudo-second-order kinetic model is more useful to elaborate the adsorption of Hg(II) on the AO AN/IA than the pseudo-first-order model.

Figure 9 is the curve of ln\( K_c \) vs. 1/\( T \), where \( K_c \) is the distribution constant, ln\( K_c = q_e/c_e \). The result revealed that the distribution constant increases with the increase of temperature. This indicates the adsorption process was an endothermal process. From Figure 9, it can be concluded that the linear slope was -615 and the correlation coefficient was 0.9670.

The changes in Gibbs free energy (\( \Delta G \)), enthalpy (\( \Delta H \)) and entropy (\( \Delta S \)) of the adsorption process were determined according to Equations (5) and (6):

\[ \ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \]  \hspace{1cm} (5)

\[ \Delta G^0 = -RT \ln K_c \]  \hspace{1cm} (6)

where \( R \) is the gas constant (J mg\(^{-1}\) K\(^{-1}\)) and \( T \) is the temperature (K).

The \( \Delta G \) value was calculated to be -3.43, -3.69, and -4.03 kJ mol\(^{-1}\) at 15, 25, and 35 °C, respectively. The negative \( \Delta G \) values indicate the thermodynamically feasible and spontaneous nature of the adsorption process. The \( \Delta H \) and \( \Delta S \) parameters were found to be 5.12 kJ mol\(^{-1}\) and 29.74 J mol\(^{-1}\) K\(^{-1}\), respectively. The positive \( \Delta H \) value indicates the adsorption of AO AN/IA for Hg(II) is an endothermal process, which is fitted to the deduction obtained from the adsorption kinetics.

### Adsorption isotherms

The Langmuir adsorption isotherm has been successfully applied to the sorption process of potentially toxic metals. The basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent. This model can be expressed in non-linear form (Limousin et al. 2007):

\[ q_e = \frac{qK_Lc_e}{1 + K_Lc_e} \]  \hspace{1cm} (7)

where \( C_e \) is the equilibrium concentration of metal ions in the solution (mg L\(^{-1}\)), \( q_e \) is the amount of adsorbed material at equilibrium (mg g\(^{-1}\)), \( q \) is the maximum adsorption capacity (mg g\(^{-1}\)) and \( K_L \) is the Langmuir constant (L mg\(^{-1}\)), which reflects the free energy of adsorption.

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**Table 2** | The kinetic parameters of adsorption for Hg(II) obtained by using non-linear least squares method

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Pseudo-first-order kinetics</th>
<th>Pseudo-second-order kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k_1 ) (min(^{-1}))</td>
<td>( q_e ) (mg g(^{-1}))</td>
</tr>
<tr>
<td>15</td>
<td>0.1841</td>
<td>76.21</td>
</tr>
<tr>
<td>25</td>
<td>0.1918</td>
<td>77.76</td>
</tr>
<tr>
<td>35</td>
<td>0.1969</td>
<td>79.14</td>
</tr>
</tbody>
</table>

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**Figure 9** | Plot of ln\( K_c \) vs 1/\( T \) for the adsorption of AO AN/IA for Hg(II).
Another model, the Freundlich isotherm, describes the reversibility of the adsorption which is not limited to the monolayer adsorption. It is mainly dependent on the adsorption of solute in the heterogeneous binding sites. The non-linear form of the Freundlich equation can be elucidated as follows (Limousin et al. 2007):

\[ q_e = K_F C_0^b \]  

(8)

where \( K_F \) is a constant relating to the adsorption capacity (mg L\(^{-1}\)) and \( b \) is an empirical parameter relating to the adsorption intensity, which varies with the heterogeneity of the material.

Figure 10 shows the adsorption isotherms of AO AN/IA for Hg(II) at three different temperatures. The experimental data were analyzed with the Langmuir (Equation (7)) and Freundlich (Equation (8)) equations. The parameters for the two isotherms obtained from experimental data are presented in Table 3. The non-linear plots of the Langmuir and Freundlich models are shown in Figure 11(a) and 11(b), respectively. It is apparent that the \( R^2 \) values of the Freundlich model are higher than the \( R^2 \) values of the Langmuir model, indicating that the Freundlich model describes the observed data much better than the Langmuir alternative.

### Separation of Hg(II) from several binary mixtures

The ability to remove metal ions selectively from aqueous solution under competitive condition is of utmost importance in designing chelating polymers for environmental remediation applications. In this study, several kinds of foreign ions existing in natural water, such as Na(I), K(I), Ca(II), Mg(II), Zn(II), Cu(II), and Ni(II), were chosen as foreign ions (Daşbaşı et al. 2013; Colaço et al. 2014). The concentrations of these foreign ions are tabulated in Table 4. Table 4 shows the removal of Hg\(^{2+}\) in the presence of macro amounts of

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**Table 3 | Isotherm parameters for the adsorption of Hg(II) obtained by using non-linear least squares method**

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>q (mg g(^{-1}))</th>
<th>( K_L ) (L mg(^{-1}))</th>
<th>( R^2 )</th>
<th>b</th>
<th>( K_F ) (mg g(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>155.06</td>
<td>0.0096</td>
<td>0.9571</td>
<td>0.56</td>
<td>5.51</td>
<td>0.9814</td>
</tr>
<tr>
<td>25</td>
<td>169.18</td>
<td>0.0159</td>
<td>0.9802</td>
<td>0.51</td>
<td>9.52</td>
<td>0.9827</td>
</tr>
<tr>
<td>35</td>
<td>193.09</td>
<td>0.0199</td>
<td>0.9679</td>
<td>0.50</td>
<td>12.79</td>
<td>0.9791</td>
</tr>
</tbody>
</table>

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Figure 10 | Adsorption isotherms of Hg(II) on AO AN/IA at different temperatures (dosage of AO AN/IA: 20 mg; pH 6).

Figure 11 | The Langmuir isotherms (a) and Freundlich isotherms (b) of Hg(II) on AO AN/IA.
foreign ions. In the systems of Hg(II)–Na(I), Hg(II)–K(I), Hg(II)–Ca(II), and Hg(II)–Mg(II), the foreign ions such as Na(I), K(I) and Ca(II) do not affect the removal of AO AN/IA for Hg(II). For other binary systems, the removals of Hg(II) are 85.7% for Hg(II)–Na(I), 98.3% for Hg(II)–K(I), 96.0% for Hg(II)–Ca(II), and 88.4% for Hg(II)–Mg(II). This indicated that AO AN/IA exhibits high adsorption selectivity for Hg(II) over the above-mentioned foreign ions, thus making them promising candidates as Hg(II) absorbent materials.

Desorption and reusability

Such solutions as 0.1 M HNO₃, 2% thiourea in 0.1 M HNO₃, and 5% thiourea in 0.1 M HNO₃ (Qu et al. 2013) were chosen to desorb the metal ions adsorbed on AO AN/IA. The experimental results showed that rate of elution using the above-mentioned solutions were 89.1, 94.6, and 98.7%, respectively. Therefore, a solution of 5% thiourea in 0.1 M HNO₃ was employed as eluant to regenerate the resins. The adsorption capacities of the reused AO AN/IA for Hg(II) from the first adsorption–desorption cycle to the fifth one were 87.65, 83.5, 82.2, 82.4 and 80.7 mg g⁻¹, respectively. There is little decrease in adsorption capacities after five adsorption–desorption cycles, indicating that AO AN/IA exhibits good reusability.

CONCLUSIONS

In this study, a novel chelating polymer bearing the AO group containing mesopores and macropores, with a surface area of 11.71 m² g⁻¹, was prepared through the hydroxylamine modification of AN/IA copolymer. Its adsorption properties for Hg(II) were studied. The adsorption capacity was determined as 84.25 mg g⁻¹ at pH 6. The kinetic data indicated that the adsorption process followed the pseudo-second-order rate model. The Freundlich model was better than the Langmuir model to describe the isotherm process. The calculated thermodynamic parameters showed that the adsorption was an endothermal and spontaneous process. The separation tests indicated that AO AN/IA had higher selectivity for Hg(II) in binary mixture systems. AO AN/IA could be regenerated by 5% thiourea in 0.1 M HNO₃ with higher effectiveness. Five adsorption–desorption cycles demonstrated that AO AN/IA could be used repeatedly without considerable changes in adsorption capacity.

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