

Removal of trace As(V) from aqueous solution by Fe(III)-loaded porous amidoximated polyacrylonitrile

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ABSTRACT

A Fe(III)-loaded chelating resin named Fe(III) AO PAN was prepared by immobilizing Fe(III) onto porous amidoximated polyacrylonitrile (AO PAN) obtained by modification of hydroxylamine with polyacrylonitrile (PAN), which was synthesized by suspended emulsion polymerization. The structures of PAN, AO PAN, and Fe(III)-AO PAN were characterized by infrared spectrometry and scanning electron microscopy. The performance of Fe(III)-AO PAN as the ligand exchange adsorbent to remove As(V) from aqueous solution was investigated using static equilibrium and dynamic adsorption experiments. The adsorption experiments showed that Fe(III)-AO PAN had higher adsorption selectivity for As(V) than other ubiquitous anions in nature water body such as Cl^- , SO_4^{2-} , HCO_3^- , PO_4^{3-} , and SiO_3^{2-} . The optimal pH for adsorption of As(V) on Fe(III) AO PAN was 2.0, with the maximum adsorption capacity of 0.55 mg/g. The As(V) adsorbed on Fe(III) AO PAN could be easily eluted with 10 BV of 5% NaCl solution (at pH = 9.0).

Key words | adsorption, amidoximated polyacrylonitrile, arsenic(V), Fe(III), ligand exchange adsorbent

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INTRODUCTION

Arsenic is a ubiquitous contaminant in nature, and primarily exists in the main form of arsenate (As(V)) or arsenite (As(III)) (Mohan & Pittman 2007). It may cause cardiovascular disease and cancers of liver, bladder and lungs to human beings (Smith *et al.* 1992; Chen & Ahsan 2004). Thus, the removal of arsenic from ground and drinking water has received increased attention because of its toxicity. Many kinds of methods including precipitation (Meng *et al.* 2001), ion exchange (Kim & Benjamin 2004), coagulation-precipitation (Jia & Demopoulos 2008), membrane (Waypa *et al.* 1997) and adsorption (Daus *et al.* 2004) have so far been proposed and used for this purpose. Among these methods, ion exchange is currently an Environmental Protection Agency (EPA)-identified best available technology for removing arsenic owing to the high removal efficiency from aqueous solution (EPA 2000). However, the adsorbed amount and selectivity of traditional anion exchange resins for arsenic is

severely retarded due to the competition from the other anions such as sulfate ions that are ubiquitously abundant in natural water body (Zhao & Sengupta 1998; An *et al.* 2005). To overcome the drawback of the ion exchange resins, many researchers have devoted their efforts in developing metal-loaded ligand exchange adsorbents, which are composed of a chelating resin and a transition metal cation (Lewis acid) as its terminal functional groups (Helfferich 1962; Henry *et al.* 2004). Metal-loaded ligand exchange adsorbent has been found to be high selectivity for arsenic even in the presence of ubiquitous anions such as sulfates and others. Many metal ions such as Fe(III), Al(III), La(III), Zr(IV), and Cu(II) are immobilized onto chelating resins to attain ligand exchange adsorbents (Matsunaga *et al.* 1996; Ohki *et al.* 1996; An *et al.* 2005). More recently, it has been shown that Fe(III)-loaded ligand exchange adsorbent shows greater selectivity for arsenate (Matsunaga *et al.* 1996; Jia & Demopoulos

2008). Furthermore, the properties of the metal-hosting chelating resins are of critical importance in the preparation of ligand exchange adsorbents. The chelating resins should possess stable physical, chemical properties, high metal-loading capacity, porous structure, as well as strong bonding force to metal ions (Henry *et al.* 2004; An *et al.* 2010). It is well known that the chelating resins bearing amidoxime group have high affinity for metal ions (Shaaban *et al.* 2014; Deng *et al.* 2015). The chelating resins, especially, which are based on acrylonitrile (AN) are easy to prepare and present a reactive pendant cyano group, which can be modified by different kinds of reagent through nucleophilic addition and cycloaddition reactions (Pervova *et al.* 2003; Dedkova *et al.* 2005).

In this study, polyacrylonitrile (PAN) was prepared by suspended emulsion polymerization and subsequently modified with hydroxylamine hydrochloride, and Fe(III)-loaded ligand exchange adsorbent (Fe(III)-AO PAN) was obtained by immobilizing Fe(III) onto AO PAN. The structures of AO PAN and Fe(III)-AO PAN were characterized by infrared (IR) and scanning electron microscopy (SEM). Furthermore, the batch and column experiments including adsorption kinetic and dynamic properties of Fe(III)-AO PAN for As(V) were investigated in details.

EXPERIMENTAL

Materials and methods

Acrylonitrile (AN, Tianjin Kermel Chemical Reagent Co., A.R. grade, China) was distilled to get 76–78 °C distillation just before polymerization. Potassium peroxydisulfate (KPS), Span-80, hydroxylamine hydrochloride (NH₂OH·HCl) and ferric chloride (FeCl₃·6H₂O) were purchased from Tianjin Reagent Chemical Co. (China). Sodium arsenic (Na₂HAsO₄·7H₂O) (A.R.), NaAsO₂ (purity >99.0%), and Poly (vinyl alcohol)(PVA, polymerization degree = 1,750 ± 50) were purchased from Aldrich Sigma (Shanghai, China). The stock solutions of 1,000.0 mg/L As(V) and As(III) were prepared by dissolving Na₂HAsO₄·7H₂O and NaAsO₂ in deionized water, respectively. The pH of arsenic solution was adjusted by dilute hydrochloric acid or sodium hydroxide. All other chemicals in this study were reagent grade and used without further purification.

The morphology was determined using a SEM (JSM-5610LV, JEOL, Tokyo, Japan), in which the samples were sputter-coated with Pt film before SEM examination. IR spectra were recorded on a Nicolet MAGNA-IR550 (series II) spectrometer (Madison, WI); test conditions: potassium bromide pellets, scanning 32 times, resolution 4 cm⁻¹. A pH meter (Mettler-Toledo, LE438pH, China) was used for the measurement of pH values. The concentration of Fe(III) was determined on a flame atomic absorption spectrophotometer (FAAS) (Model 932A, Australia), equipped with an air-acetylene flame. The concentrations of arsenic were measured using a double channel atomic fluorescence spectrometer (AFS-920, China). The experimental data of kinetics and isotherms were fitted by the software of OriginPro 8.0.

Preparation of PAN

PAN was prepared by suspended emulsion polymerization. A typical procedure was as follows: 0.06 g KPS was added to a mixture containing 22.6 mL of AN, 0.25 g of Span-80, 3.0 mL of 2% PVA solution, and 20 mL deionized water. The system was sparged 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, extracted with ethanol for 24 h. Finally, PAN was dried under vacuum at 50 °C for 48 h.

Preparation of AO PAN

In total, 3 g of NH₂OH·HCl was added to 100 mL of methanol solution containing 2 g of PAN. After the mixture was stirred for 30 min, the pH of the mixture was adjusted to 8 with 10% NaOH aqueous solution. The reaction was performed at 70 °C for 12 h under stirring. The mixture was filtered, and then washed with deionized water and acetone, respectively. Finally, AO PAN was extracted in ethanol for 24 h, dried at 50 °C under vacuum for 48 h.

Preparation of Fe(III)-AO PAN

In total, 400 mg of AO PAN was equilibrated with 400 mL of FeCl₃ solution (4 mM) at pH 3 for 24 h. After filtration, Fe (III)-AO PAN was thoroughly washed with deionized water

and dried at 50 °C under vacuum for 48 h. The loaded Fe(III) on AO PAN was determined by measuring the difference of Fe(III) concentration before and after adsorption.

Adsorption procedure

Batch adsorption

The pH effect on equilibrium uptake of As(V) was examined by adding 50 mg of Fe(III)-AO PAN into a flask containing 20 mL of 5 mg/L arsenic solution with varying pH in the range of 1.0–6.0. The mixture was then shaken on a rotating tumbler for 12 h at 25 °C. At equilibrium, the residual concentration of arsenic was determined via atomic fluorescence spectrometry (AFS). The adsorbed amount was then calculated according to Equation (1):

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

where Q is the adsorption amount (mg/g); C_0 and C are the initial concentration and the concentration of arsenic in solution when the contact time is t , respectively (mg/mL); V is the solution volume (mL); and W is the dry weight of the adsorbent (g).

A kinetic experiment was conducted to test the As(V) adsorption rate and determine the time needed for equilibrium. The experiment was initiated by adding 0.5 g of Fe(III)-AO PAN into 200 mL of 5 mg/L As(V) solution. During the experiment, the mixture was shaken at 120 rpm on a rotating tumbler. At predetermined time intervals, an aliquot of 1 mL solution was taken and analyzed for As(V). The As(V) uptake at various times were then calculated according to Equation (1).

Adsorption isotherms were carried out at different initial arsenic concentrations at pH 2.0 in flasks. The flasks were shaken on a rotating tumbler at 120 rpm for 24 h.

The effects of coexisting anions such as chloride, sulfate, bicarbonate, silicate, and phosphate on the removal of arsenic were investigated using the following experiment. 0.05 g of Fe(III)-AO PAN was introduced to flasks containing 20 ml of 100 µg/L arsenic solution and coexisting ions. The concentrations of the coexisting ions in nature water were evaluated at three levels (0.1, 1.0 and 10 mM) and pH 6.0. The mixtures were equilibrated at 25 °C for 24 h

with shaking at 120 rpm, and then the concentration of residual arsenic was analyzed.

Regeneration of Fe(III)-AO PAN

To evaluate the reusability of Fe(III)-AO PAN, the adsorption-desorption cycles of the adsorbent were repeated five times using the same adsorbent. The adsorbed adsorbent was placed into 20 mL of desorbent and stirred for 10 h at room temperature. The residual concentration of As(V) was determined by AFS.

Fix-bed column experiment

The breakthrough behaviors of As(V) as well as various competing anions were tested for Fe(III)-AO PAN in a fixed-bed configuration. This experiment was carried out with a glass column (11 mm in diameter and 200 mm in length) equipped with a water bath to maintain a constant temperature. 5 mL Fe(III)-AO PAN was packed in the column for test use. Simulates contaminated water was introduced in the resin bed in a down-flow mode. A peristaltic pump (HL-2, China) was employed to assure a constant flow rate. The major compositions in the influent water were as follows: As(V) = 400 µg/L, Cl⁻ = 25 mg/L, SO₄²⁻ = 80 mg/L, PO₄³⁻ = 1 mg/L, SiO₃²⁻ = 5 mg/L, HCO₃⁻ = 80 mg/L, and pH = 6.0. A constant flow rate of 3 BV/h was maintained. The exhausted Fe(III)-AO PAN was regenerated using 5% NaCl solution at pH 9.0.

RESULTS AND DISCUSSION

Characterization of PAN, AO PAN and Fe(III)-AO PAN

The IR spectra of PAN, AO PAN, and Fe(III)-AO PAN are presented in Figure 1. By comparison of the IR spectra of PAN, the adsorption peaks of C≡N at 2,244 cm⁻¹ almost disappear in the curve of AO PAN, and the characteristic peaks of C=N and =N-O- groups at 1,654 and 918 cm⁻¹ are observed, indicating that the modification reaction was successful. From Figure 1, it also can be seen that, a clear shift of the absorption peaks of C=N and =N-O- groups in Fe(III)-AO PAN samples, in comparison with that of

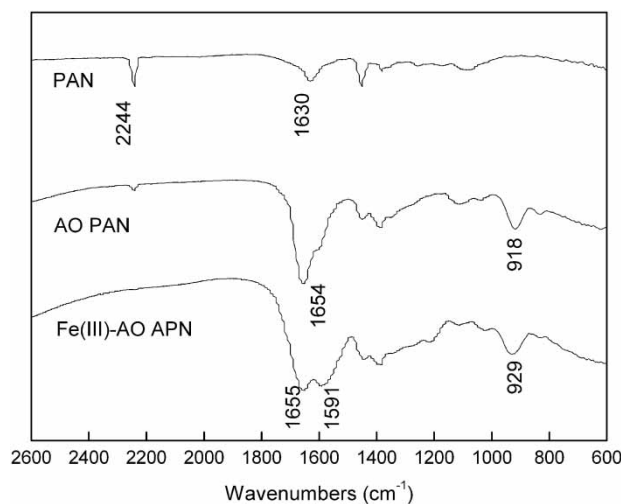


Figure 1 | The IR spectra of PAN, AO PAN and Fe(III)-AO PAN.

AO PAN, and Fe(III)-AO PAN shows a new absorption peak at $1,591\text{ cm}^{-1}$, which may due to the coordination of the amidoxime groups with Fe(III).

To observe the morphology of PAN and AO PAN and Fe(III)-AO PAN, scanning electron micrographs of the platinum-coated samples were performed. The photographs are shown in [Figure 2](#). Obviously, there are abundant loose pores distributed on the surface of AN, AO PAN, and Fe(III)-AO PAN, indicating that Fe(III)-AO PAN remains the porous structures after hydroxylamine modification. In addition, the loading amount of Fe(III) on AO PAN determined by FAAS were 69.4 mg/g , which is desirable for efficient removal of As(V).

Effect of pH on As(V) adsorption

To clarify the effect of the pH on the uptake of arsenate, the adsorption capacities of Fe(III)-AO PAN for As(V) were determined in the range of 1–6 and the results are depicted in [Figure 3](#). Obviously, the pH have an important effect on As(V) sorption on Fe(III)-AO PAN, and the optimal As(V) uptake (0.43 mg/g) are reached at pH 2. The adsorbed amounts of As(V) decrease with increasing solution pH in the pH range of 2.0–6.0. This phenomenon was also observed in previous reports ([Matsunaga *et al.* 1996](#); [Anirudhan *et al.* 2011](#)). The decrease of the adsorbed amounts of As(V) in the pH range of 2.0–6.0 may be attributed to the competition from OH^- in aqueous solution ([Tao *et al.*](#)

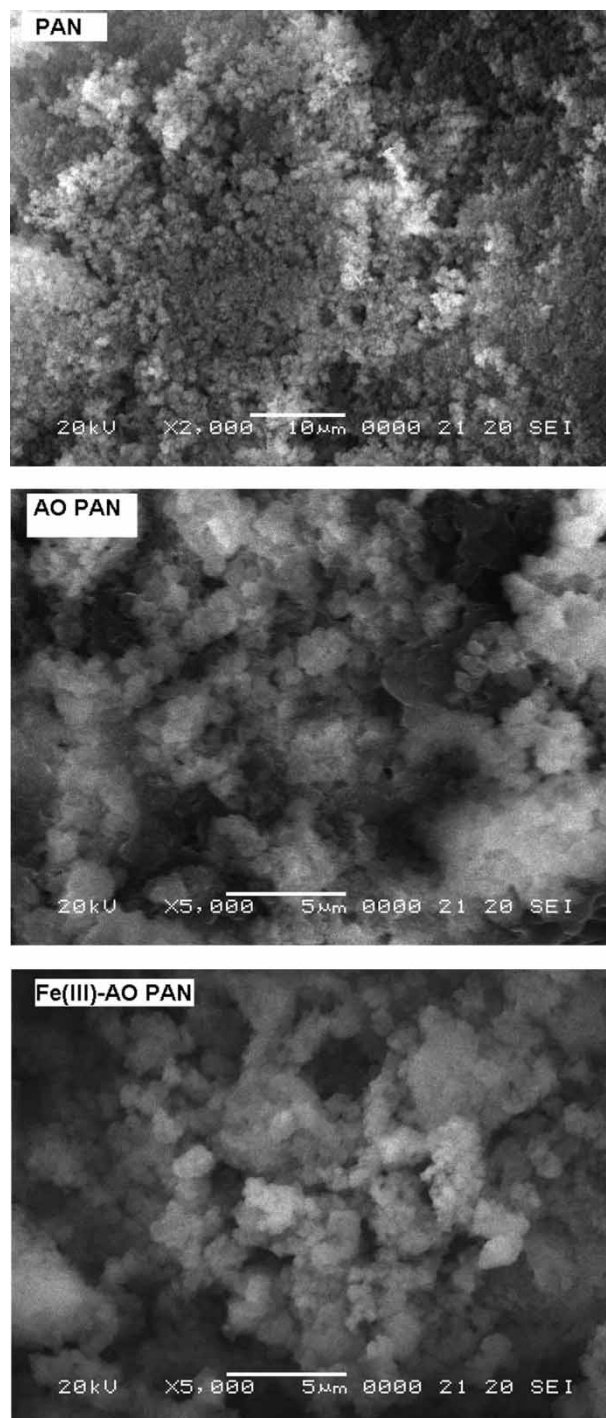


Figure 2 | The SEM images of PAN, AO PAN, and Fe(III)-AO PAN.

[2011](#)). On the other hand, lower pH is preferable for As(V) adsorption by ligand exchanger adsorbents, such as Fe(III)-loaded resins ([Matsunaga *et al.* 1996](#); [Gu *et al.*](#)

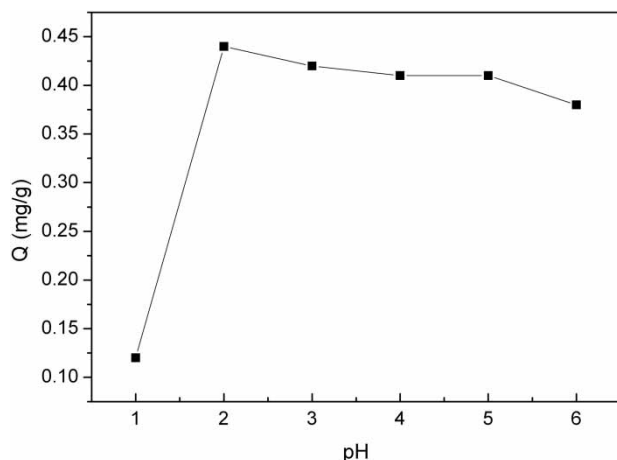


Figure 3 | Effect of pH on the adsorbed amounts of As(V) on Fe(III)-AO PAN (As(V) concentration: 5 mg/L; dosage of Fe(III)-AO PAN: 50 mg; temp.: 25 °C).

2005). At low pH, the main species of arsenic are H_3AsO_4 and H_2AsO_4^- , the corresponding reaction conducted in an As(V) adsorption can be shown in Figure 4 (Matsunaga *et al.* 1996; Dzombak & Morel 1987).

Furthermore, the dissociation of ferric ion from Fe(III)-AO PAN was checked as a function of pH. The result is shown in Figure 5. A considerable amount of ferric ion is released from the resin at a pH below 1, while no ferric ion is liberated from the adsorbent in the wide pH range from 2 to 11. This means the adsorbent can be used in a wide pH range.

Based on this, Fe(III)-AO PAN has highest adsorbed amount for As(V). Thus, the experiments of adsorption kinetics, adsorption isotherms were conducted at pH 2.

Adsorption kinetics

Figure 6 shows the effect of contact time on the adsorption of As(V) at different temperatures. As shown in Figure 6, the

adsorption rates of As(V) onto Fe(III)-AO PAN are fast within the first 30 min, and the adsorption equilibrium can be reached within 180 min. Generally, the adsorption rate found in the literatures mainly depends on the characteristics of the hosting chelating resins (Lezzi *et al.* 1994; Sanchez *et al.* 2000). Suzuki *et al.* synthesized Zr-loaded porous spherical resin and investigated the adsorption properties for As(V). The adsorption equilibrium was attained in 6 h (Suzuki *et al.* 1997), while for a titanium dioxide-loaded Amberlite XAD-7 resin it took 4 h and for a Cu(II) loaded WH-425 resin 7 h were necessary (Tatineni & Hideyuki 2002; Tao *et al.* 2011). Comparing with the above-mentioned polystyrene backbone resins, the faster adsorption rate of Fe(III)-AO PAN for As(V) may be attributed to the higher hydrophilicity of the polymeric backbone of AO PAN, which results in increase in the diffusivity and accessibility of As(V) to the polymeric ligand in the adsorbent. Furthermore, the results show that the adsorption rates increase with the increasing temperature.

The adsorption kinetics data were treated according to the pseudo first-order and pseudo second-order non-linear models given below as Equations (2) and (3), respectively (Ho & McKay 2000).

$$q_t = q_e - q_e e^{-k_1 t} \quad (2)$$

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

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/min); and q_e and q_t are the adsorption amount at equilibrium and at time t , respectively (mg/g).

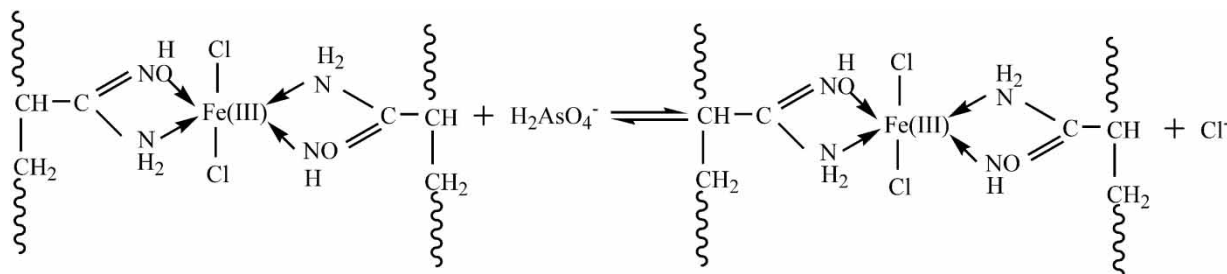


Figure 4 | Schematic illustration of As(V) adsorption by Fe(III)-AO PAN.

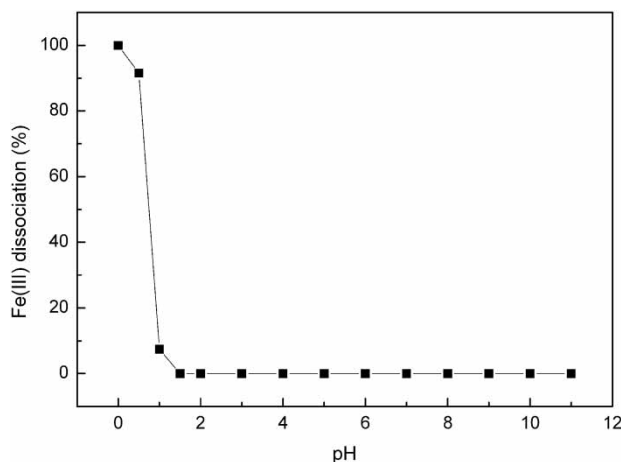


Figure 5 | Effect of pH on dissociation of Fe(III) from Fe(III)-AO PAN (Fe(III)-AO PAN weight: 20 mg; volume of solution: 20 mL; temp.: 25 °C).

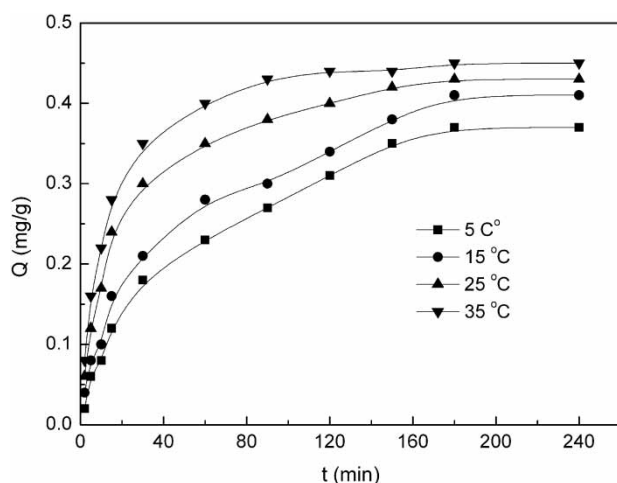


Figure 6 | Adsorption kinetics of at different temperatures (As(V) concentration: 5 mg/L; dosage of Fe(III)-AO PAN: 20 mg; pH 2).

The results and corresponding kinetic parameters including the correlation coefficients (R^2) and standard error are shown in Figure 7 and Table 1, respectively. Comparing the regression coefficients (R^2) of pseudo first-order kinetic model, the R^2 values of pseudo second-order kinetic model are higher and close to 1, indicating that the pseudo second-order kinetic model is quite useful to elaborate the adsorption of As(V) on Fe(III)-AO PAN compared with the pseudo first-order model.

Adsorption isotherms

The Langmuir isotherm describes the monolayer adsorption on the solid surface with a finite number of identical sites,

and the non-linear model can be expressed as follows (Limousin *et al.* 2007):

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (4)$$

where C_e is the equilibrium concentration of metal ions (mg/L), q_e is the amount of adsorbed material at equilibrium (mg/L), q_{\max} is the maximum adsorption capacity, and K_L is Langmuir constant (L/mg), which reflects the free energy of adsorption.

Another model, 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 and can be elucidated as follows (Limousin *et al.* 2007):

$$q_e = K_F C_e^b \quad (5)$$

where K_F is a Freundlich constant (mg/L) and b is an empirical parameter relating the adsorption intensity, which varies with the heterogeneity of the material.

The adsorption isotherms of As(V) at four different temperatures on Fe(III)-AO PAN are shown in Figure 8. The data were analyzed with the Langmuir (Equation (4)) and Freundlich (Equation (5)) equations and the parameters for the two isotherms obtained from experimental data are presented in Figure 9 and Table 2, respectively. It is apparent that the regression coefficient (R^2) values of Langmuir model are higher than the R^2 values of Freundlich model, indicating that the Langmuir model describes the observed data much better than the Freundlich alternative.

Furthermore, a summary of the adsorption behavior of various ligand exchanger adsorbents, which were obtained by loading different transition metal cations such as Zr(IV), Cu(II), Ti(IV), and Fe(III) onto polystyrene-supported chelating resins is given in Table 3. In general, the adsorbed amounts found in the literature depend on the type of adsorbents, contact time for adsorption, initial concentration, etc. Although Fe(III)-AO PAN has lower adsorption capacities than the majority of the above-mentioned adsorbents listed in Table 3, the faster adsorption rate of Fe(III)-AO PAN for As(V) indicates

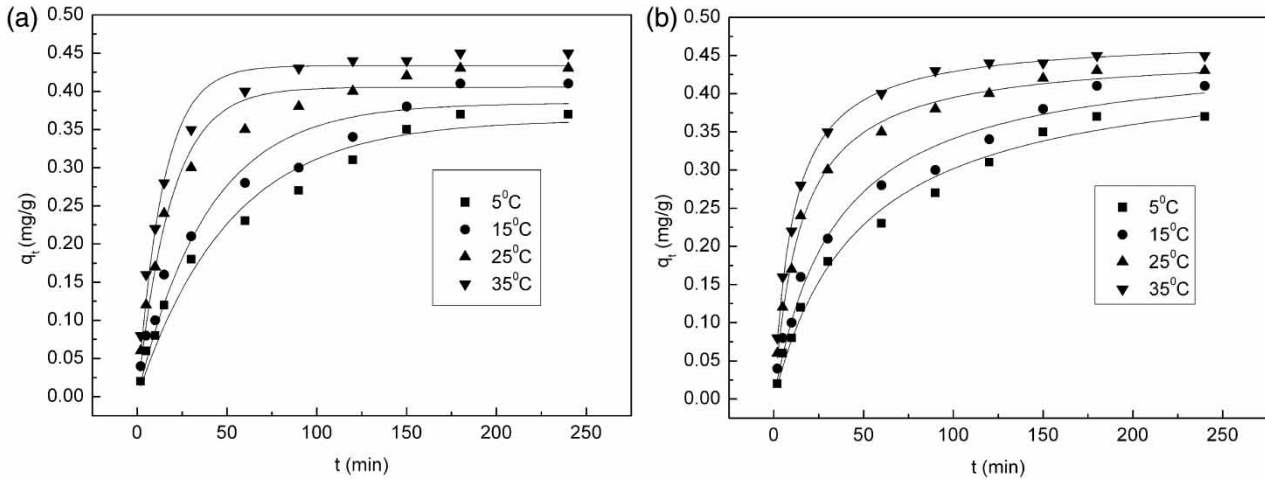


Figure 7 | Adsorption kinetics curves fitted with the non-linear pseudo first-order (a) and pseudo second-order (b) models.

Table 1 | The kinetic parameters of adsorption for As(V) at different temperatures

| Temperature (°C) | Pseudo first-order kinetics | | | | Pseudo second-order kinetics | | | |
|------------------|-----------------------------|----------------|--------------|--------|------------------------------|----------------|--------------|--------|
| | k_1 (min ⁻¹) | Standard error | q_e (mg/g) | R^2 | k_2 (g/mg/min) | Standard error | q_e (mg/g) | R^2 |
| 5 | 0.0140 | 0.0026 | 0.32 | 0.9851 | 0.0927 | 0.0078 | 0.36 | 0.9883 |
| 15 | 0.0134 | 0.0040 | 0.33 | 0.9657 | 0.1251 | 0.0115 | 0.38 | 0.9930 |
| 25 | 0.0203 | 0.0058 | 0.30 | 0.9622 | 0.1615 | 0.0104 | 0.44 | 0.9988 |
| 35 | 0.0296 | 0.0060 | 0.31 | 0.9839 | 0.1949 | 0.0075 | 0.47 | 0.9997 |

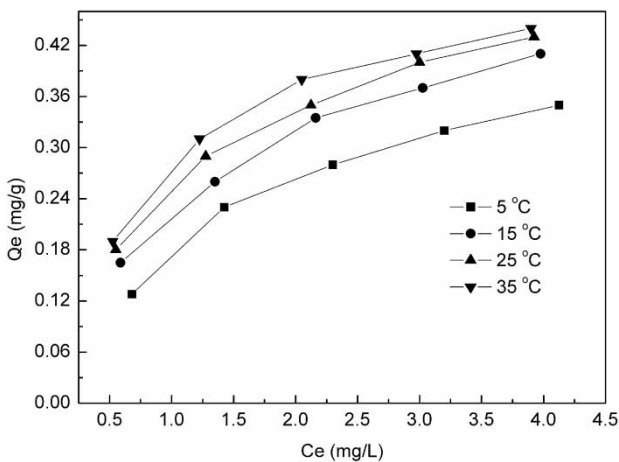


Figure 8 | Adsorption isotherms of As(V) on Fe(III)-AO PAN at different temperatures (dosage of Fe(III)-AO PAN: 20 mg; pH 2).

that the higher hydrophilicity of the polymeric backbone of AO PAN is beneficial to the adsorption of As(V) in aqueous solution.

Competitive adsorption

Generally, arsenic contaminated water contains abundant amounts of various anions, which may compete with arsenic for active sites on Fe(III)-AO PAN. In this study, several kinds of anions commonly abounding in natural water such as Cl^- , SO_4^{2-} , HCO_3^- , PO_4^{3-} , and SiO_3^{2-} were chosen as foreign ions. Considering the practical treatment conditions of the ground and drinking water, the pH value of arsenic containing wastewater was adjusted to pH 6. The concentrations of the foreign ions were set at three levels (0.2, 1.0, and 5.0 mM) (Hang et al. 2012). Arsenic solution (100 $\mu\text{g/L}$; 20 mL) with added foreign ions was used as simulated contaminated water. As shown in Figure 10, Cl^- , SO_4^{2-} , and HCO_3^- anions have slightly negative effect on the As(III) and As(V) removal at lower concentration. The removal of As(III) and As(V) was obviously hindered by PO_4^{3-} and SiO_3^{2-} as compared with Cl^- , SO_4^{2-} , and HCO_3^- . The decrease in removal efficiency in the presence

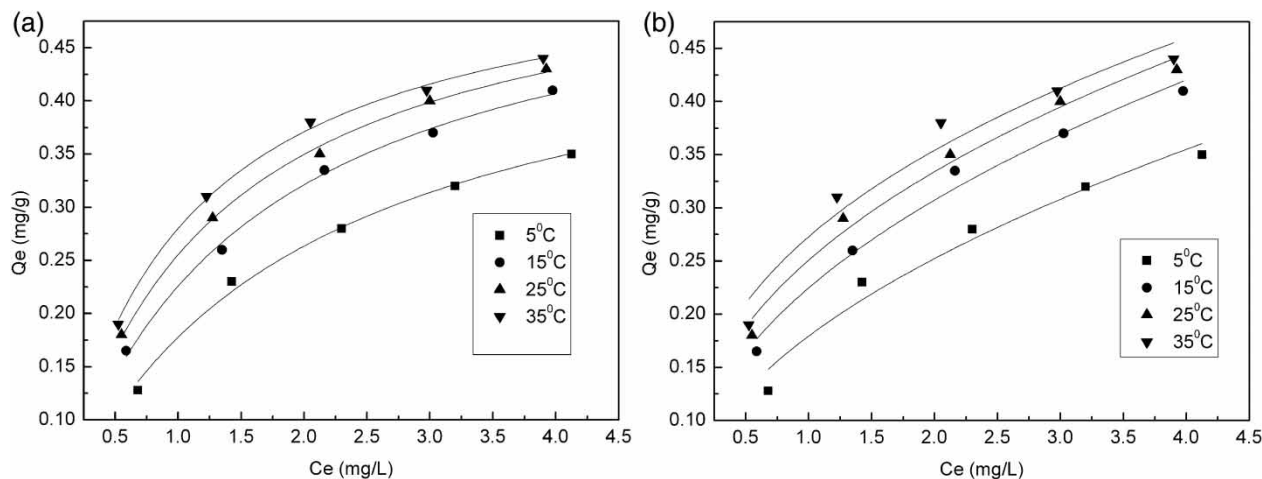


Figure 9 | Adsorption isotherms curves fitted with the non-linear Langmuir (a) and Freundlich (b) models.

Table 2 | Isotherm parameters for the adsorption of As(V) onto Fe(III)-AO PAN

| T (°C) | Langmuir isotherm model | | | | Freundlich isotherm model | | | |
|--------|----------------------------------|----------------|-----------------------------|---------|---------------------------|----------------|-----------------------------|---------|
| | q_{\max} (mg g ⁻¹) | Standard error | K_L (L mg ⁻¹) | R_L^2 | b | Standard error | K_F (mg g ⁻¹) | R_F^2 |
| 5 | 0.50 | 0.0232 | 0.5369 | 0.9930 | 0.49 | 0.0579 | 0.1793 | 0.9610 |
| 15 | 0.55 | 0.0171 | 0.6843 | 0.9955 | 0.45 | 0.0352 | 0.2247 | 0.9822 |
| 25 | 0.55 | 0.0109 | 0.8539 | 0.9975 | 0.41 | 0.0350 | 0.2508 | 0.9789 |
| 35 | 0.54 | 0.0099 | 1.0423 | 0.9972 | 0.38 | 0.0501 | 0.2728 | 0.9474 |

Table 3 | Comparison of adsorption capacities (Q) of different adsorbent systems for As(V)

| Adsorbents | pH | Q (mg/g) | Reference |
|---|-------|----------|----------------------------|
| Zr-loaded lysine diacetic acid chelating resin | 4 | 49.2 | Balaji et al. (2005) |
| Fe(III) loaded Lewatit TP 207 | 1.7 | 58.0 | Rau et al. (2000) |
| Cu(II) loaded DOW 3N | 7–7.5 | 92 | An et al. (2005) |
| Fe(III) loaded lysine diacetic acid chelating resin | 3.7 | 55.5 | Matsunaga et al. (1996) |
| Titanium dioxide-loaded Amberlite XAD-7 resin | 1–5 | 4.72 | Tatineni & Hideyuki (2002) |
| Cu(II) loaded WH-425 | 6–8 | 0.36 | Tao et al. (2011) |
| Fe(III) loaded amidoximated polyacrylonitrile | 2 | 0.55 | Present study |

of PO_4^{3-} and SiO_3^{2-} is due to the significant competition for adsorption sites with arsenic. This can be explained by the chemical similarity between the two foreign ions and arsenic, which leads to a significant competition (Pan et al. 2014).

Desorption and reusability

Based on the previous reports about desorption experiments (An et al. 2005; Tao et al. 2011), 5% (w/w) NaCl aqueous solution at pH 9.0 was chosen as the eluant to regenerate the

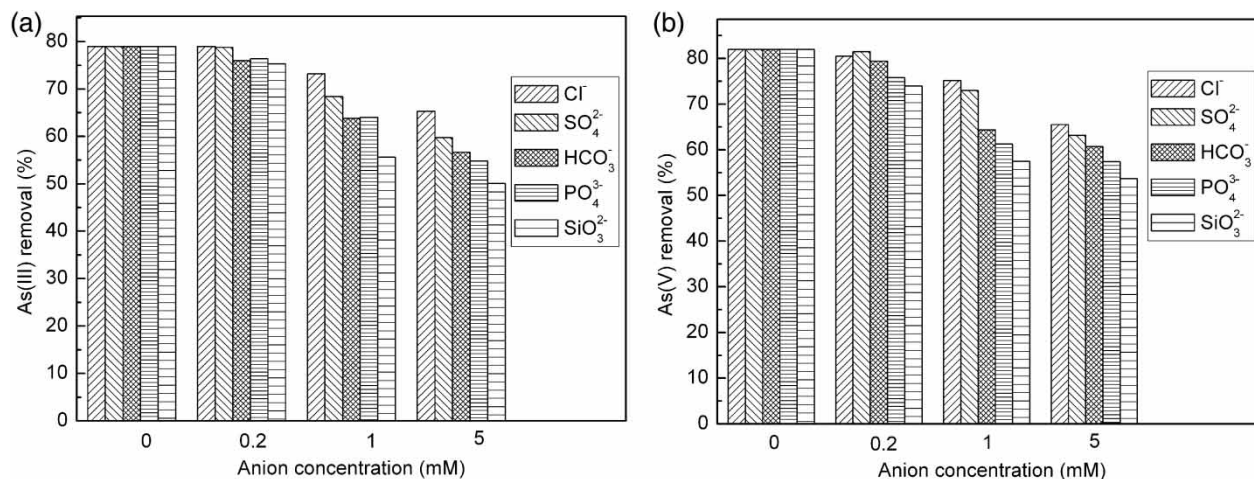


Figure 10 | Effect of foreign ions on the removal of As(III) (a) and As(V) (b) on Fe(III)-AO PAN (arsenic concentration: 100 µg/L; dosage of Fe(III)-AO PAN: 50 mg; pH 6).

adsorbent. Five adsorption-desorption cycles were conducted for investigating the reusability of Fe(III)-AO PAN. The adsorbed amounts of the reused Fe(III)-AO PAN for As(V) from the first to the fifth adsorption-desorption cycle are 0.43, 0.42, 0.40, 0.39, and 0.38 mg/g, respectively. There is a little decrease in adsorbed amounts after five adsorption-desorption cycles, meaning that Fe(III)-AO PAN exhibits good reusability.

Fixed-bed adsorption

To investigate the potential performance of Fe(III)-AO PAN in practical use, the column sorption runs were carried out with a single-component arsenate solution or a multicomponent feeding solution through two separate columns filled with 5 mL of Fe(III)-AO PAN, respectively.

Their breakthrough curves are shown in Figure 11. The breakthrough point is set as 10 µg/L (the horizontal dashed line in Figure 11), which is the maximum contaminant level for arsenic in drinking water promulgated by World Health Organization (WHO). It can be noted that, As(V) removal from the multi-component feeding solution onto Fe(III)-AO PAN breaks through quickly, and the effective treatment volume is less than 110 bed volumes (BV), whereas that for the single-component arsenic solution is around 150 BV under otherwise identical conditions.

Effectively regenerating the As(V) saturated Fe(III)-AO PAN to reuse the ligand exchanger is quite important for

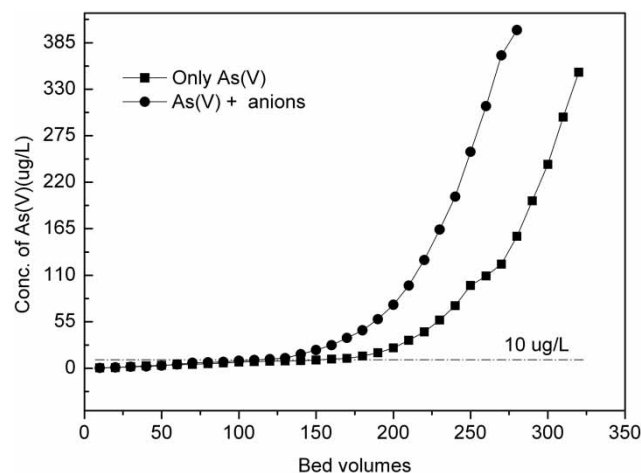


Figure 11 | Breakthrough curves of As(V) onto Fe(III)-AO PAN.

field applications. Figure 12 shows the As(V) desorption profiles during regeneration with 6% NaCl at 9.0 of pH value. The As(V) loaded on Fe(III)-AO PAN can be completely rinsed within seven BVs of regenerate. The column experiments results show that Fe(III)-AO PAN is effective for As(V) removal from solution.

CONCLUSIONS

A Fe(III)-loaded chelating resin named Fe(III) AO PAN was prepared by immobilizing Fe(III) onto porous amidoximated polyacrylonitrile (AO PAN) obtained by modification of

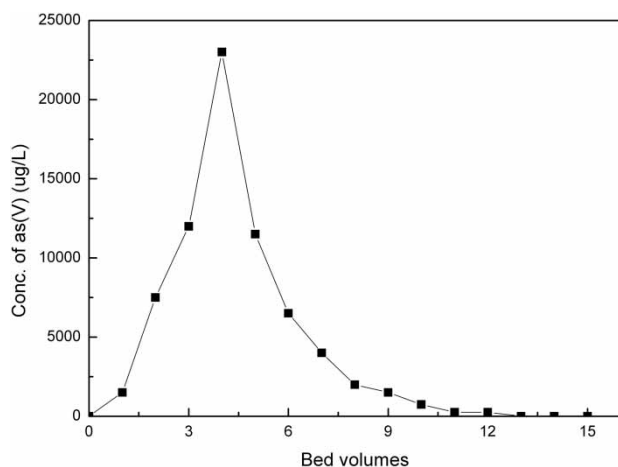


Figure 12 | Column dynamic desorption and desorption efficiency curve of As(V) on Fe(III)-AO PAN.

hydroxylamine with polyacrylonitrile (PAN), which was synthesized by suspended emulsion polymerization. The obtained adsorbent was characterized by IR spectra and SEM, and can be used to selectively remove As(V) from aqueous solutions. The adsorption capacity of Fe(III)-AO PAN is 0.55 mg/g, and the adsorption kinetics follows a pseudo second-order rate model. The isotherm adsorption equilibrium can be well described by the Langmuir isotherm model. Fe(III)-AO PAN had higher selectivity for As(V) under competitive conditions. Meanwhile, the adsorbed As(V) could be effectively desorbed in 6% NaCl solution (pH = 9).

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