Separation of As\textsuperscript{V} from aqueous solutions using chelating polymers containing Fe\textsuperscript{III} -loaded phosphorus groups

Abstract: As\textsuperscript{V} ions were removed by batch equilibrium with Fe\textsuperscript{III}-loaded chelating polymers containing aminophosphinic or aminophosphonic groups. It was effectively removed As\textsuperscript{V} from a synthetic wastewater as well as from a real drinking water containing 40 μg As per liter. Sorption is best described by pseudo-second order kinetics and a Langmuir isotherm.

Keywords: Arsenic removal, chelating polymers, aminophosphinic groups, aminophosphonic groups

1 Introduction

Arsenic-contaminated drinking water is a major environmental problem. The primary source of dissolved arsenic in ground water is oxidative weathering and geochemical reactions; uncontrolled industrial waste discharge is also a problem. Arsenic has been associated with cancerous and non-cancerous health effects [1-7]. Its toxicity strongly depends on the oxidation state. The distributions of the principal aqueous forms of inorganic arsenic (arsenate – As\textsuperscript{V} and arsenite - As\textsuperscript{III}) are influenced by pH and redox conditions [5,7,8]. At pH 6 - 9 As\textsuperscript{III} predominates; at pH above 9 the more toxic As\textsuperscript{V} (arsenic acid oxyanions: H\textsubscript{2}AsO\textsubscript{4}\textsuperscript{-} and HAsO\textsubscript{4}\textsuperscript{2-}) predominates [3,7,9-11]. The World Health Organization (WHO) limit in drinking water is 10 μg L\textsuperscript{-1} [4,8-10,12]. This stringent standard will require many utilities to upgrade their present system or consider new treatment options. Ion exchange is currently an EPA-identified best available technology (BAT) for As\textsuperscript{V} removal [13].

The use of chelating polymers for trace element preconcentration and separation is reasonably well understood and progress is mainly in improving resin specificity and application techniques. Chelating polymers comprise two components, (a) inert solid support and (b) chelating ligand. The attachment of functional groups to the polymer makes it capable of forming metal chelate rings [14-16]. The atoms capable of forming chelate rings include oxygen, nitrogen, phosphorus and sulfur. Ligand incorporation can be either by adsorption (impregnation) on the solid support or by chemical anchoring [17]. The polymer and chelating group structures and their interactions determine the applications.

Insoluble crosslinked polystyrene resins are preferred as support. If the functional group is selective for a target it can be isolated by simple filtration [18]. Polymers with immobilized phosphorus acid ligands are important due to their selectivity [19]. Dual mechanism bifunctional polymers (DMBPs) represent a new class of chelating ion exchange resins [20].

The polymers were loaded with Fe\textsuperscript{III} due to its high affinity for arsenic [1,4,5,7,10,12,213]. The As\textsuperscript{V} adsorption of Fe\textsuperscript{III}-loaded chelating polymers containing aminophosphinic or aminophosphonic groups was examined.
2 Experimental procedure

2.1 Materials

Styrene-1% divinylbenzene copolymer grafted with amine groups (Fluka, 2 mmol amine /g polymer, N = 2.8%), phenylphosphonic acid (Fluka, techn. 97%), phosphorous acid (Aldrich, 99%), benzaldehyde (Merck, p.a.), propionaldehyde (Merck, p.a.), methanol, acetone and diethyl ether (Chimreactiv, p.a), \( \text{Fe(NO}_3\text{)}_3 \) in 0.5 M HNO\(_3\) (Merck Standard Solution), \( \text{H}_3\text{AsO}_4 \) in 0.5 M HNO\(_3\) (Merck Standard Solutions) were used.

The stock arsenic solution was prepared by diluting \( \text{H}_3\text{AsO}_4 \) in 0.5 M HNO\(_3\) (Merck Standard Solutions). Other As\(^{v}\) solutions were prepared by dilution of the stock solution. All other chemicals were of analytical reagent grade and used as received. Distilled water was used in all experiments.

2.2 Instruments

The polymeric resins were characterized using a Shimadzu Prestige-21 FTIR spectrophotometer from 4000–400 cm\(^{-1}\) (KBr pellets). Thermal properties were characterized by thermogravimetric analysis (TGA) and differential thermal analysis (DTA), performed on a Mettler 851-LF1100 TGA/SDTA from 25 to 900\(^\circ\)C at 10\(^\circ\)C min\(^{-1}\) under nitrogen. Phosphorus was determined by a modified Schoniger method [24]. Energy dispersive X-ray analysis (EDX) was performed using an Inspect S scanning electron microscope, which also provided images. The pH was measured by a CRISON MultiMeter MM41 with a calibrated glass electrode. Arsenic was determined using a Varian SpectrAA 110 atomic absorption spectrometer with a Varian VQA 77 hydride generation system. For batch experiments an MTA (Kutesz, Hungary) mechanical shaker bath was used.

2.3 Preparation of aminophosphinic acid (AP1, AP2) and aminophosphonic acid (AP3, AP4) grafted on styrene divinylbenzene copolymer

6 g of styrene-1% divinylbenzene copolymer grafted with amine groups were mixed with benzaldehyde (or propionaldehyde), phenylphosphinic acid (or phosphorous acid) and 50 mL tetrahydrofuran and stirred for 24 h at 55\(^\circ\)C. The molar ratio of amine : benzaldehyde (or propionaldehyde) : phenylphosphinic acid (or phosphorous acid) was 1 : 1 : 1.5. The polymer beads were separated by filtration, washed with methanol, acetone and diethyl ether. Washing was repeated three times using 20 mL of each solvent. The products were dried at 50\(^\circ\)C for 24 hours.

2.4 Preparation of chelating polymers loaded with Fe\(^{iii}\) ions

The polymers with aminophosphinic (AP1, AP2) and aminophosphonic (AP3, AP4) acid groups were loaded with Fe\(^{iii}\). To determine the maximum iron loading, 0.1 g of each polymer was placed in 25 mL of Fe\(^{iii}\) solution (10-200 mg L\(^{-1}\)) for 24 h. The pH was adjusted to 3 to avoid Fe\(^{iii}\) precipitation. The solutions were filtered and the residual iron concentrations determined by AA. The dependence of the Fe\(^{iii}\) adsorption on the initial solution Fe\(^{iii}\) concentration was established.

2.5 Experimental separation methods

Adsorption experiments were performed with aminophosphinic (AP1, AP2) and aminophosphonic (AP3, AP4) acid containing polymers loaded with Fe\(^{iii}\) at pH 9.00. Solution pH was adjusted with 1 M NaOH. The effects of initial arsenic concentration and contact time were studied. 0.1 g of adsorbent were placed in 25 mL of As\(^{v}\) solution (10-300 µg L\(^{-1}\)) for 48 h at 25 ± 1\(^\circ\)C. The solutions were filtered and arsenic concentrations were determined. To examine the effect of contact time, 0.1 g of each adsorbent in 25 mL of 100 µg L\(^{-1}\) As\(^{v}\) solutions stood for 1, 2, 4, 6, 8, 10, 14, 24 and 48 h. The solutions were filtered and arsenic concentrations determined.

2.6 As\(^{v}\) adsorption of from a real drinking water

The real drinking water sample had the composition: NO\(_3\)^- : 22 mg L\(^{-1}\); NO\(_2\)^- : 0.3 mg L\(^{-1}\); P\(_2\)O\(_5\) : 46.7 mg L\(^{-1}\); SO\(_4\)^2- : 11.1 mg L\(^{-1}\); NH\(_4\)^+ : 6.6 mg L\(^{-1}\); Fe\(^{ii}\) : 2 mg L\(^{-1}\); Mn\(^{ii}\) : 0.51 mg L\(^{-1}\); Na\(^+\) : 118 mg L\(^{-1}\); K\(^+\) : 1.67 mg L\(^{-1}\); Ca\(^{ii}\) : 30.8 mg L\(^{-1}\); Mg\(^{ii}\) : 18.2 mg L\(^{-1}\); As\(^{iii}\) : 40 µg L\(^{-1}\) and pH = 6.64.

0.1 g of adsorbent was placed in 25 mL of drinking water for 24 hours. Ion concentrations were analyzed before and after adsorption to examine the effects of foreign ions on arsenic adsorption. Fe\(^{ii}\), Mn\(^{ii}\), Na\(^+\), K\(^+\), Ca\(^{ii}\), and Mg\(^{ii}\)
were determined by AA. Nitrite, nitrate, phosphate and ammonium ions were determined using a Cary 50 VARIAN UV-VIS spectrophotometer. Sulfate was determined with barium chloride using a WTW Turb 555 IR turbidimeter. The pH was measured using a Denver pH meter.

2.7 Sorption performance

Sorption is quantified in terms of metal uptake, $q_e$ (µg g⁻¹). The material balance can be expressed by [3,6,7,9,24,25]:

$$q = \frac{(C_0 - C_e)V}{m}$$  \hspace{1cm} (1)

where: $C_0$ - initial solution arsenic concentration, µg L⁻¹; $C_e$ - equilibrium solution arsenic concentration, µg L⁻¹; V - solution volume, L; m - amount of the adsorbent, g.

Freundlich and Langmuir isotherms were used to model the adsorption [2-7,9,22,24-26]. The linear form of the Freundlich isotherm can be written:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$  \hspace{1cm} (2)

and the Langmuir isotherm as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$$  \hspace{1cm} (3)

$K_f$ and $1/n$ are constants characteristic of the adsorption; $q_m$ is a measure of monolayer adsorption capacity [mg g⁻¹]; $K_L$ is a constant related to the free energy of adsorption.

Pseudo-first order [3-7,9,23,26], pseudo-second order [3-7,9,23,26] and intra-particle diffusion [3,4,9,27] models were used to determine the adsorption kinetics.

3 Results and discussion

3.1 Characterization of polymers with aminophosphinic or aminophosphonic groups

Aminophosphonic acids and their derivatives belong to an important group of organophosphorus compounds [28,29]. Preparations of aminophosphinic acid groups and aminophosphonic acid groups grafted on styrene–divinylbenzene copolymer (Schemes 1 and 2) have been reported [30,31].

The characteristics of chelating polymers with aminophosphinic (AP1, AP2) and aminophosphonic (AP3, AP4) acid groups are given in Table 1.

FTIR spectra are in Fig. 1. The intense bands between 2950-2800 cm⁻¹ are CH₃ and CH₂ stretching vibrations; $\nu$(CH₂) = 750 cm⁻¹; the bands around 980 cm⁻¹, 1035 cm⁻¹ and 1380 cm⁻¹ are attributed to the P-OH, P-O-alkyl and P=O vibrations. The band at 535 cm⁻¹ is attributed to the group $\nu$(Fe-O) + $\nu$(C-C) [32,33].

Fig. 2 shows a SEM micrograph of aminophosphinic acid grafted polymeric resin. The particles ranged from 30 to 60 µm.

TGA thermograms are in Fig. 3. The copolymer with aminophosphonic acid (AP3, AP4) showed higher thermal stability than the plain copolymer with amino groups (support), showing that the aminophosphonic acid group modified the thermal decomposition pathways. The total weight loss for the plain copolymer was 94% and for the copolymer with aminophosphonic acid (AP3, AP4) 86% and 85%.
3.2 Establishment of the optimum Fe\textsuperscript{III} loading

To determine the maximum iron loading the Fe\textsuperscript{III} uptake was plotted against the initial iron concentration (Fig. 4). Fe\textsuperscript{III} uptake increased with initial iron concentration up to a limiting value. For polymer grafted with aminophosphonic acid (AP3 and AP4) the maximum was loaded at 50 mg Fe\textsuperscript{III} L\textsuperscript{-1}, for polymer grafted with aminophosphinic acid (AP1 and AP2) the maximum occurred at 80 mg L\textsuperscript{-1}. These concentrations were used for subsequent experiments. Fe\textsuperscript{III} uptake by aminophosphinic acid grafted polymer was higher than that of aminophosphonic acid grafted polymer.

3.3 Effect of initial arsenic concentration and sorption modelling

The adsorption isotherms are presented in Fig. 5. The equilibrium uptake increases with As\textsuperscript{V} concentration. The heterogeneous distribution of binding sites predicts that all sites are not equally effective. The sites with higher As\textsuperscript{V} affinity contribute more to sorption.

The equilibrium data have been compared with Freundlich and Langmuir isotherms over the entire concentration range. The Freundlich plots (Fig. 6) have very low regression coefficients suggesting limited validity of the Freundlich isotherm. The constants...
Separation of As\textsuperscript{V} using chelating polymers with phosphorus groups

K\textsubscript{F} and 1/n computed from the plot are presented in Table 2. K\textsubscript{F} can be defined as an adsorption coefficient which gives the quantity of adsorbed metal for unit equilibrium concentration. The slope 1/n is a measure of surface heterogeneity. For 1/n = 1, the partition between the two phases is independent of concentration. The situation 1/n < 1 is the most common and corresponds to a normal L-type Langmuir isotherm, while 1/n > 1 indicates cooperative adsorption involving strong interactions between adsorbate molecules. The observed 1/n < 1 implies favorable As\textsuperscript{V} adsorption.

The Langmuir model parameters estimated from the slope and intercept of the linear plot (Fig. 7) are given in Table 2. This model better describes the sorption data with correlation coefficients closer to 1. The isotherm follows the sorption over the entire concentration range for all four materials, and the maximum sorption capacities are very close to those experimentally obtained. The dimensionless separation factor (R\textsubscript{L}) describes the essential characteristics of a Langmuir isotherm. It measures the adsorbent capacity (Eq. 4). Its value decreases with increasing K\textsubscript{L} and initial concentration.

\[
R_L = \frac{1}{1 + K_L \cdot C_0}
\]

R\textsubscript{L} relates to the equilibrium isotherm as follows: unfavourable, R\textsubscript{L} >1; linear, R\textsubscript{L} = 1; favourable 0<R\textsubscript{L}<1; and irreversible, R\textsubscript{L}=0 [2-4,34-36]. The values for the entire concentration range lie between 0 and 1 in all cases, demonstrating favourable sorption.

AP1 and AP2 resins, which contain more Fe\textsuperscript{III} than the AP3 and AP4 resins, are more effective in As\textsuperscript{V} removal, in agreement with the results in section 3.2.

3.4 Effect of contact time and sorption dynamics

The effect of contact time on As\textsuperscript{V} sorption is shown in Fig. 8. Adsorption by all adsorbents increased with time up to 10 h, then remained constant. Application of the different kinetic models revealed some interesting features of the mechanism and rate-controlling step. First, the Lagergren pseudo-first order kinetic model was applied (Fig. 9). The plots show low correlation coefficients and the equilibrium metal uptakes (q\textsubscript{e}) deviated much from the experimental value. This model does not describe the sorption kinetics well.
It was then applied the pseudo-second order model. The plots of \( \frac{t}{q} \) against \( t \) (Fig. 10) showed better linearity with correlation coefficients higher than 0.99. The equilibrium sorption capacity \( q_e \) and the rate constant \( k_2 \) from the slope and intercept are reported in Table 3. The predicted equilibrium adsorption capacities were close to the experimental values. This model describes the As\(^{V}\) adsorption kinetics adequately.

Sorption by porous sorbents takes place by three consecutive mass transport steps: (1) film diffusion - the sorbate is transported from solution to the active part of the sorbent external surface; (2) intraparticle diffusion - sorbate is transported through the sorbent pores; and (3) sorption - adherence of the sorbate to the sorbent. The slowest (rate limiting) step is either boundary layer diffusion or intraparticle diffusion. A plot of \( q_e \) versus the square root of time was used to identify the slowest step \([3,4,7,9,27]\). If the plot is a straight line through the origin intra-particle diffusion is rate-limiting. A nonlinear plot shows that boundary layer diffusion is rate-limiting. In Fig. 11 the plots do not pass through the origin and contain two linear sections instead of one. Intra particle diffusion is excluded as the rate limiting step for all the adsorbents. Therefore the adsorption of

<table>
<thead>
<tr>
<th>Material</th>
<th>( q_{m, exp} ) µg g(^{-1} )</th>
<th>( q_{m, calc} ) µg g(^{-1} )</th>
<th>( K_F ) µg g(^{-1} )</th>
<th>( 1/n )</th>
<th>( R^2 )</th>
<th>( k_L ) L µg(^{-1} )</th>
<th>( q_{m, calc} ) µg g(^{-1} )</th>
<th>( R^2 )</th>
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<td>AP1</td>
<td>10.5</td>
<td>3.271</td>
<td>0.2538</td>
<td>0.8453</td>
<td>0.3096</td>
<td>10.6</td>
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<td>10</td>
<td>2.508</td>
<td>0.2907</td>
<td>0.9182</td>
<td>0.1405</td>
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<td>AP3</td>
<td>6.3</td>
<td>1.582</td>
<td>0.2762</td>
<td>0.8892</td>
<td>0.0872</td>
<td>6.6</td>
<td>0.9995</td>
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<td>AP4</td>
<td>5</td>
<td>1.262</td>
<td>0.2707</td>
<td>0.9041</td>
<td>0.0735</td>
<td>5.3</td>
<td>0.9952</td>
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</table>

Figure 5: Adsorption isotherms of As\(^{V}\) onto the polymeric adsorbents. \( C_0 = 10-300 \) µg L\(^{-1} \); \( m=0.1 \) g; \( V=0.025 \) L; \( t=24 \) h; \( T=25 \pm 1\)°C; pH = 9.

Figure 6: Freundlich plot for As\(^{V}\) adsorption onto polymeric adsorbents.

Figure 7: Langmuir plot for As\(^{V}\) adsorption onto polymeric adsorbents.

Figure 8: Effect of contact time on adsorption capacity. \( C_0 = 100 \) µg L\(^{-1} \); \( m=0.1 \) g; \( V=0.025 \) L; pH = 9.
Separation of AsV using chelating polymers with phosphorus groups

AsV occurs by two processes. At the beginning of the process AsV is rapidly uptaken though film diffusion, and at the end it is transported inside the adsorbent particle. [3,4,7,9,27].

3.5 Adsorption of AsV from a real drinking water

The real drinking water sample had the composition: NO₃⁻: 22 mg L⁻¹; NO₂⁻: 0.3 mg L⁻¹; P₂O₅: 46.7 mg L⁻¹; SO₄²⁻: 11.1 mg L⁻¹; NH₄⁺: 6.6 mg L⁻¹; Fe³⁺: 2 mg L⁻¹; Mn²⁺: 0.51 mg L⁻¹; Na⁺: 118 mg L⁻¹; K⁺: 1.67 mg L⁻¹; Ca²⁺: 30.8 mg L⁻¹; Mg²⁺: 18.2 mg L⁻¹; As³⁺: 40 μg L⁻¹ and pH = 6. Its composition after adsorption by the resins is in Table 4.

AsV adsorption takes place with complete iron adsorption because arsenic has a high affinity for iron ions. The amounts of calcium and magnesium decrease although these ions do not influence arsenic adsorption. Arsenic content after adsorption is lower than the WHO limit of 10 μg L⁻¹. These resins effectively remove arsenic from drinking water.

Table 3: Kinetic parameters for AsV sorption.

<table>
<thead>
<tr>
<th>Model/parameters</th>
<th>AP1</th>
<th>AP2</th>
<th>AP3</th>
<th>AP4</th>
</tr>
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<tbody>
<tr>
<td>qₑ,exp, μg g⁻¹</td>
<td>10.5</td>
<td>10</td>
<td>6.3</td>
<td>5</td>
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<tr>
<td>Pseudo-first order model</td>
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<td></td>
<td></td>
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<tr>
<td>qₑ,calc, μg g⁻¹</td>
<td>3.83</td>
<td>4.05</td>
<td>3.65</td>
<td>2.44</td>
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<tr>
<td>k₁, min⁻¹</td>
<td>0.0015</td>
<td>0.002</td>
<td>0.0016</td>
<td>0.002</td>
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<tr>
<td>R²</td>
<td>0.8845</td>
<td>0.9343</td>
<td>0.8338</td>
<td>0.6976</td>
</tr>
<tr>
<td>Pseudo-second order model</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>qₑ,calc, μg g⁻¹</td>
<td>1.002×10⁻³</td>
<td>1.03×10⁻³</td>
<td>5.5×10⁻⁴</td>
<td>7.5×10⁻⁴</td>
</tr>
<tr>
<td>k₂, min⁻¹(μg g⁻¹)²</td>
<td>10.8</td>
<td>10.4</td>
<td>6.9</td>
<td>5.5</td>
</tr>
<tr>
<td>R²</td>
<td>0.9996</td>
<td>0.9996</td>
<td>0.9941</td>
<td>0.9907</td>
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<tr>
<td>Intraparticle diffusion model</td>
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<tr>
<td>kₜ, μg (g min⁻⁰.⁵)⁻¹</td>
<td>0.2556</td>
<td>0.2918</td>
<td>0.2595</td>
<td>0.2295</td>
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Table 4: Drinking water composition after adsorption.

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<th>Composition</th>
<th>Adsorbents</th>
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<td></td>
<td>AP1</td>
</tr>
<tr>
<td>NO₃⁻, mg L⁻¹</td>
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</tr>
<tr>
<td>NO₂⁻, mg L⁻¹</td>
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<tr>
<td>P₂O₅, mg L⁻¹</td>
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</tr>
<tr>
<td>SO₄²⁻, mg L⁻¹</td>
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</tr>
<tr>
<td>NH₄⁺, mg L⁻¹</td>
<td>6.5</td>
</tr>
<tr>
<td>Fe³⁺, mg L⁻¹</td>
<td>BDL’</td>
</tr>
<tr>
<td>Mn²⁺, mg L⁻¹</td>
<td>0.5</td>
</tr>
<tr>
<td>Na⁺, mg L⁻¹</td>
<td>118</td>
</tr>
<tr>
<td>K⁺, mg L⁻¹</td>
<td>1.67</td>
</tr>
<tr>
<td>Ca²⁺, mg L⁻¹</td>
<td>18.9</td>
</tr>
<tr>
<td>Mg²⁺, mg L⁻¹</td>
<td>11.3</td>
</tr>
<tr>
<td>As³⁺, μg L⁻¹</td>
<td>BDL’</td>
</tr>
<tr>
<td>pH</td>
<td>7.1</td>
</tr>
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</table>

BDL – below detection limit

Figure 9: Pseudo-first order kinetic plot for AsV adsorption.

Figure 10: Pseudo-second order kinetic plot for AsV adsorption.

Figure 11: Weber-Morris plots for intra-particle diffusion.
4 Conclusions

As$^\text{V}$ sorption by aminophosphinic and aminophosphonic acids grafted on styrene-1% divinylbenzene copolymer loaded with Fe$^{III}$ was evaluated. Aminophosphinic acid grafted polymer is more efficient than aminophosphonic acid grafting in removing As$^\text{V}$ from aqueous solutions. More Fe$^{III}$ can be loaded onto aminophosphinic acid, giving a higher adsorption capacity.

As$^\text{V}$ adsorption was better described by the Langmuir model and follows pseudo-second order kinetics. The adsorption process is complex and involves multiple steps.

All four resins were very efficient in removing arsenic from a real drinking water containing 40 μg L$^{-1}$. The residual arsenic was less than the WHO limit of 10 μg L$^{-1}$.

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