Zirconium(IV) Loaded Bifunctional Fiber Containing Both Phosphonate and Sulfonate as Arsenate Adsorbent

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Abstract
Fibrous arsenate adsorbent was prepared by loading Zr(IV) onto a bifunctional cation exchange fiber containing both phosphonate and sulfonate. This bifunctional cation exchange fiber was prepared by phosphorylation and sulfonation of the precursory fiber, which was obtained by co-graft polymerization of chloromethylstyrene and styrene onto polyethylene coated polypropylene fiber. Performances of the Zr(IV) loaded fiber as arsenate adsorbent was studied in columnar mode. The column packed with Zr(IV) loaded fiber removed arsenate from a weakly acidic pH solution containing 0.016 mM arsenate (1.2 mg of As dm\(^{-3}\)) even at a flow rate of 200 h\(^{-1}\) in space velocity. Sodium salts of chloride, nitrate and sulfate did not interfere with uptake of arsenate but they slightly enhanced arsenate uptake. Adsorbed arsenate was quantitatively eluted with aqueous sodium hydroxide, and then the column was able to be regenerated by contact with dilute sulfuric acid for the next arsenate adsorption operation.

Key words: arsenate removal, bifunctional cation exchange fiber, zirconium

1 Introduction
In many countries, high arsenic (As) concentrations in alluvial aquifers become problem, and in particular, both alluvial and deltaic aquifers in Ganges delta area contain As at the most serious concentration levels [1]. Several arsenic adsorbents have been proposed to purify water contaminated with As. Ferric oxides and alumina were not able to use repeatedly and generate secondary problems from sludge containing As. Ligand exchangers based on metal ion loaded chelating resins can adsorb arsenate selectively and the adsorbed arsenate can be eluted with some pertinent eluents. For instance, Zhu and one of the present authors (A. J.) proposed a ligand exchange adsorbent for arsenate and arsenite on the basis of Zr(IV) loaded cation exchange resins having phosphoric acid and phosphonic acid groups [2,3]. Several groups have also proposed arsenate adsorbents by loading metal ions such as Fe(III), Zr(IV), Mo(VI) and Cu(II) onto chelating resins such as iminodiacetic acid resins and their homologs [4-9]. However, one of the most serious drawback of granular arsenic adsorbents is low kinetic performances in uptake of arsenate. Opposed to granular adsorbents, fibrous adsorbents have excellent...
kinetic performances in uptake of a target ion. Indeed, Seko et al. have reported a fibrous arsenate adsorbent, which was obtained by loading Zr(IV) onto a monofunctional cation exchange fiber prepared by graft polymerization of vinyl monomers containing phosphoric acid groups [6]. This fibrous adsorbent exhibits excellent kinetic performances but unfortunately its columnar uptake of arsenate was tested in relatively high concentration levels of 5 – 10 mM (M = mol dm$^{-3}$) of arsenate (370 – 750 mg dm$^{-3}$ of As). However, concentrations of arsenate are not so high in arsenic contaminated groundwater even in Ganges delta area and are less than 2 mg dm$^{-3}$. In this connection, we have already developed a bifunctional cation exchange fiber containing both phosphonic and sulfonic acids (named FPS, Scheme 1) [10]. This work was planned in order to clarify the behavior of Zr(IV) loaded FPS in column mode uptake of arsenate in the lower concentration levels of 0.016 – 0.15 mM (1.2 – 11 mg of As dm$^{-3}$).

2 Experimental

2.1 Materials

Polyethylene coated polypropylene staple fiber (0.9 denier, length 3.8 cm) was provided by Kurashiki Textile MFG Co., Osaka, Japan. Chloromethylstyrene (CMS) was provided from Seimi Chemical Co. Chigasaki, Japan. Styrene (ST) was purchased from Wako Pure Chemical Co. Reagents were of guaranteed grade and ultra-pure water was used unless otherwise noted. CMS and ST were co-grafted onto polyethylene coated polypropylene fibers by means of electron irradiation induced liquid phase graft polymerization in which equimolar mixture of CMS and ST was used in their liquid phase graft co-polymerization onto the trunk fiber. The detailed procedures for the graft polymerization and preparation of FPS were described elsewhere [10]. Weight increase in graft polymerization was 1.3 times that of the trunk fiber. The acid capacity, phosphorus and sulfur contents were determined by reported methods [11,12]. The acid capacity of FPS is 4.9 meq/g and its phosphorus and sulfur contents were 0.99 and 2.1 mmol/g, respectively.

2.2 Preparation of Zr(IV) Loaded Bifunctional Fiber

Loading of Zr(IV) onto FPS was conducted by column method. A dried sample of FPS (0.4 g) was packed into polyethylene column (i. d. 1.3 cm) and FPS was swollen for 24 h in water. Then the FPS bed in the column was pressed with a glass rod with a flat end until the bed height became constant. The volume of the wet fiber bed in the column was 2.0 cm$^3$. The Zr(IV) solution was prepared by dissolving Zr(SO$_4$)$_2$$\cdot$4H$_2$O into an aqueous H$_2$SO$_4$ (0.5 M). Then, acidic 0.01 M Zr(IV) solution (0.5 M H$_2$SO$_4$) (96 cm$^3$) was fed to the column. After washing the column with 0.5 M H$_2$SO$_4$ (30 cm$^3$) and with water (20 cm$^3$) in successive, 0.2 M NaOH solution (40 cm$^3$) was fed to the column. After the column was washed with water (20 cm$^3$) and then with 0.5 M H$_2$SO$_4$ (30 cm$^3$), acidic 0.01 M Zr(IV) solution (0.5 M H$_2$SO$_4$) (96 cm$^3$) was fed to the column for more loading of Zr(IV). This series of operations were repeated three times. Flow rate of all solutions and water was 3 h$^{-1}$ in space velocity ($SV$), which is designated by the ratio $F/V_{bed}$, here $F$ is flow rates of solutions or water in cm$^3$ h$^{-1}$ and $V_{bed}$ is a volume of the fiber bed. All column effluents were collected on a fraction collector, and concentration of Zr(IV) in each fraction was measured by ICP-AES. Amount of immobilized Zr(IV) was calculated from the concentration difference between feeding solution and column effluents.

2.3 Column Mode Adsorption and Elution of Arsenate
Arsenate feed solutions were prepared by dissolving Na$_2$HAsO$_4$·7H$_2$O in water. The pH of feed solutions was adjusted by spiking a dilute H$_2$SO$_4$. Before adsorption operation of arsenate, the Zr(IV) loaded fiber packed column was conditioned to be the same pH as that of arsenate feed solutions. Arsenate feed solutions were fed to the column at a given flow rate. After the column was washed with water, adsorbed arsenate was eluted by feeding 0.1 M NaOH to the column at a flow rate of 5 h$^{-1}$ in SV. After washing the column with water, the column was regenerated by feeding 0.5 M H$_2$SO$_4$ for the next use. All effluents were collected on a fraction collector and arsenic and zirconium concentrations in each fraction were determined by ICP-AES. Arsine hydride generation method was used when the concentration of As in feed solutions was 1.2 mg dm$^{-3}$. The 1% breakthrough point was designated as the feed volume supplied to the column up to $C/C_0 = 0.01$, where $C_0$ and $C$ represent concentrations of As in feeds and in column effluents, respectively. Volumes of solutions or water supplied to the columns in adsorption-elution-regeneration operations are expressed by unit of bed volumes (BV), which is designated by the ratio, $V_{supplied}/V_{bed}$; here $V_{supplied}$ is volumes of solutions or water in cm$^3$.

3 Results and Discussion

3.1 Zirconium (IV) Loading onto FPS

The pKa$_1$ of phosphonic acid is 2 – 3. Then dissociation of phosphonic acid group on the grafted polymer chains will be depressed below pH 1, resulting in folding of grafted chains on which phosphonate groups are fixed in the case of the monofunctional phosphonate fiber. In case of the bifunctional phosphonate/sulfonate fiber, on the other hand, sulfonic acid groups completely dissociate even in strongly acidic solutions, resulting in elongation of the grafted polymer chains because of electrostatic repulsion between negatively charged sulfonate groups. The uptake of Zr(IV) by FPS in the first run was 0.57 mmol/g, which is a half of its phosphorus content. The loading procedures of Zr(IV) on FPS were repeated three times. The total amount of Zr(IV) on FPS after 3 runs increased up to 1.19 mmol/g. Scheme 2 shows one of possible structures around the loaded Zr(IV). As ligand exchanger, Zr(IV) should be retained on FPS without any leakage at wide pH range. In this regard, the column packed with the Zr(IV) loaded FPS was treated with 0.5 M H$_2$SO$_4$ or 0.2 M NaOH at the flow rate of 3 h$^{-1}$ in SV and no measurable Zr(IV) was found in the effluents.

3.2 Effect of Flow Rate on Arsenate Adsorption

In case of columns packed with Zr(IV) loaded phosphonic acid and phosphoric acid resins, flow rates of feeds for arsenate removal were around 10 h$^{-1}$ in SV. Fibrous adsorbents generally take up ionic species much faster than granular resins. Then, the effect of flow rate of a feed on breakthrough profiles of arsenate was tested by changing the flow rates of the feed from 10 to 100 h$^{-1}$ in SV. Here, the feed was 0.13 mM arsenate solution of pH 3.0. Figure 1 shows

![Scheme 2. Possible bonding of Zr(IV) with FPS](image)

![Flow rate of feed](image)

![Fig. 1 Effect of flow rate of feed on breakthrough profiles of arsenate. Feed: 0.13 mM of arsenate, pH 3.](image)
breakthrough profiles of arsenate. One percent breakthrough points of arsenate decrease with an increase in the flow rate of the feed. The 1% breakthrough capacity for arsenate was 0.035 mmol/g at the flow rate of 10 h⁻¹ in SV but it decreased down to 0.027 mmol/g at the flow rate of 100 h⁻¹ in SV. However, the 1% breakthrough capacity for arsenate was not significantly affected up to the flow rate of 50 h⁻¹ in SV. Indeed, the 1% breakthrough capacities for arsenate at flow rates of 20 and 50 h⁻¹ in SV were 0.032 and 0.030 mmol/g, respectively. If the adsorption of arsenate is controlled by diffusion of arsenate in fiber phases, breakthrough profiles of arsenate must be flow-rate independent up to flow rates of 1000 h⁻¹ as in the case of uptake of heavy metal ion by several chelating fibers [6]. However, breakthrough profiles of arsenate is flow rate dependent. This means that the ligand exchange reaction is not so fast or the diffusion of arsenate is not as fast as those for uptake of the metal ions by the chelating fibers. At the present, it is difficult to judge which is the real cause of the flow rate dependent breakthrough profiles.

3.3 Elution of Adsorbed Arsenate

Since hydroxide is the hardest Lewis base among common inorganic anions, it is expected that aqueous NaOH behave the effective eluting reagent for adsorbed arsenate as already reported [2]. Figure 2 illustratively shows an elution profile of arsenate in the elution operation with 0.1 M aqueous NaOH. The adsorbed arsenate was quantitatively eluted within 30 BV of the eluent. During elution, no measurable Zr(IV) was found in the column effluents. After the elution of arsenate, the column was regenerated by feeding 0.5 M H₂SO₄. The regenerated column was further conditioned by contacting the blank solution, which had the same composition as that of the feed except for arsenate, and then next adsorption-elution-regeneration operations were started.

3.4 Effect of Inorganic Anions on Arsenate Adsorption

The most frequently encountered anions in groundwater are chloride and sulfate and less frequently one is nitrate. It is important to check the effect of these anions on uptake of arsenate. Then, solutions containing arsenate (0.13 mM) and a sodium salt of each anion (0.30 mM) were prepared and supplied to the column at the flow rate of 50 h⁻¹ in SV. The pH of solutions was kept at 3.0. Figure 3 shows breakthrough profiles of arsenate and suggests that the adsorption of arsenate is not interfered with these anions but breakthrough points are slightly increased by sodium chloride and sodium sulfate. Similar trends were reported by several researchers on arsenate adsorption by metal ion loaded chelating resins [2,4,7]. The Zr(IV) binds with arsenate so strongly that increased concentration of sodium ion from added salts will promote the invasion of arsenate through ion pair formation of arsenate with sodium ion according to reactions (1) and (2).
### 3.5 Effect of pH on Arsenate Adsorption

Zr(IV) prefers hydroxide to arsenate. This predicts that uptake of arsenate by the present adsorbent decreases with an increase in pH. Then, the pH effect on arsenate adsorption was tested in the pH range between 2.0 and 5.6. The results are summarized in Table 1 with experimental conditions.

Table 1: Summary of pH effect on columnar uptake of arsenate

<table>
<thead>
<tr>
<th>pH of feed</th>
<th>C\text{\textsubscript{o}} of arsenate in feed\textsuperscript{a)} (mM)</th>
<th>BP\textsuperscript{b)} point (cm\textsuperscript{3}\ cm\textsuperscript{-3}-F)</th>
<th>BP\textsuperscript{b)} capacity (mmol/g)</th>
<th>Total uptake (mmol/g)</th>
<th>Eluted amount (mmol/g)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>0.13</td>
<td>40</td>
<td>0.026</td>
<td>0.038</td>
<td>0.036</td>
<td>95</td>
</tr>
<tr>
<td>2nd</td>
<td>0.13</td>
<td>40</td>
<td>0.026</td>
<td>0.043</td>
<td>0.042</td>
<td>98</td>
</tr>
<tr>
<td>3.0</td>
<td>0.13</td>
<td>45</td>
<td>0.029</td>
<td>0.034</td>
<td>0.033</td>
<td>97</td>
</tr>
<tr>
<td>2nd</td>
<td>0.13</td>
<td>47</td>
<td>0.031</td>
<td>0.039</td>
<td>0.040</td>
<td>103</td>
</tr>
<tr>
<td>4.0</td>
<td>0.15</td>
<td>31</td>
<td>0.022</td>
<td>0.034</td>
<td>0.033</td>
<td>97</td>
</tr>
<tr>
<td>2nd</td>
<td>0.15</td>
<td>31</td>
<td>0.023</td>
<td>0.035</td>
<td>0.034</td>
<td>97</td>
</tr>
<tr>
<td>5.0</td>
<td>0.15</td>
<td>28</td>
<td>0.021</td>
<td>0.026</td>
<td>0.025</td>
<td>96</td>
</tr>
<tr>
<td>2nd</td>
<td>0.15</td>
<td>29</td>
<td>0.021</td>
<td>0.029</td>
<td>0.029</td>
<td>100</td>
</tr>
<tr>
<td>5.6</td>
<td>0.14</td>
<td>20</td>
<td>0.014</td>
<td>0.027</td>
<td>0.025</td>
<td>93</td>
</tr>
<tr>
<td>2nd</td>
<td>0.14</td>
<td>20</td>
<td>0.014</td>
<td>0.036</td>
<td>0.036</td>
<td>100</td>
</tr>
</tbody>
</table>

\textsuperscript{a)} Feed (160 BV) was supplied to the column at the flow rate of 50 h\textsuperscript{-1} in SV.

\textsuperscript{b)} BP means 1% breakthrough.

Results in Table 1 suggest that the 1% breakthrough capacity for arsenate was not changed so greatly below pH 3 but gradually decreases with an increase in the pH of the feed between pH 3 and pH 5.6. Arsenate will be adsorbed by Zr(IV) loaded FPS through their coordination to Zr(IV). The anion of weak Lewis base like sulfate is coordinated to Zr(IV) after the regeneration operation with treatment of aqueous H\textsubscript{2}SO\textsubscript{4}. The weak Lewis base sulfate is easily replaced with arsenate species such as H\textsubscript{2}AsO\textsubscript{4}\textsuperscript{-} and HAsO\textsubscript{4}\textsuperscript{2-}. For instance, exchange of sulfate with H\textsubscript{2}AsO\textsubscript{4}\textsuperscript{-} can be expressed by the reaction (3).

\[ R(SO_3^-)(PO_3^{2-})Zr^{4+} + S O_4^{2-} \rightleftharpoons R(SO_3^-)(PO_3^{2-})Zr^{4+}(H_2AsO_4^-) + 1/2(SO_4^{2-}) \]  

Since hydroxide OH\textsuperscript{-} is the hardest Lewis base among the anions of interest here, the following ligand exchange reaction (4) shifts to right hand side with an increase in pH:

\[ R(SO_3^-)(PO_3^{2-})Zr^{4+}(H_2AsO_4^-) + OH^- \rightleftharpoons R(SO_3^-)(PO_3^{2-})Zr^{4+}(OH^-) + H_2AsO_4^- \]

Then, uptake of arsenate decreased with an increase in pH. Above pH 5, however scattering in total uptake of arsenate became marked compared with those below pH 4. This is probably due to that the buffer capacity of the feed is the minimum around ca. pH 4.6. Low buffer capacity will bring unstable pH of the feed leading to rather marked scattering of total uptake of arsenate above pH 4.
3.6 Rapid Adsorption of Arsenate from Its Highly Diluted Solution

Although arsenic concentrations in groundwater are less than 2 mg dm$^{-3}$ [1], volumes of arsenic contaminated groundwater are huge. The higher the adsorption rate of arsenate, the shorter the time required for purification of the given volume of contaminated groundwater. Then, the purification of water contaminated with arsenate was tested by feeding a solution containing 0.016 mM arsenate (1.2 mg of As dm$^{-3}$, pH 3) to the column at a flow rate of 200 h$^{-1}$ in SV. Figure 4 shows the breakthrough profile of arsenate during adsorption operation. The 1% breakthrough point was 302 BV, which correspond to the breakthrough capacity 0.024 mmol of As/g of dried FPS. Even though the concentration of arsenate was as low as 1.2 mg of As dm$^{-3}$ and the flow rate was as high as 200 h$^{-1}$ in SV, the 1% breakthrough capacity was not decreased in appreciable amounts.

All experimental results given in this paper were obtained using the same column for 4 months without change of Zr(IV) loaded FPS and reloading of Zr(IV) as well. During repeated adsorption-elution-regeneration operations, no measurable Zr(IV) was found in the column effluents. This means that the Zr(IV) was strongly retained on FPS. Concentrations of arsenate in groundwater is usually less than 2 mg dm$^{-3}$, it is very important to investigate the behavior of the proposed adsorbent in such dilute arsenic concentration levels comparable to those in real groundwater, because breakthrough capacities are affected by kinetic aspects of ligand exchange reactions. The present work clarified that the Zr(IV) loaded FPS fiber is able to purify 300 BV of water contaminated with 1.2 mg dm$^{-3}$ of arsenic as arsenate for 1.5 h.

**References**