As(III) and As(V) removal from the aqueous phase via adsorption onto acid mine drainage sludge (AMDS) alginate beads and goethite alginate beads

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Abstract

Acid mine drainage sludge (AMDS) is a solid waste generated following the neutralization of acid mine drainage (AMD). This material entrapped in calcium alginate was investigated for the sorption of As(III) and As(V). Three different adsorbent materials were prepared: AMDS alginate beads (AABs), goethite alginate beads (GABs), and pure alginate beads. The effects of pH and the adsorption kinetics were investigated, and the adsorption isotherms were also evaluated. The optimal pH range using the AABs was determined to be within 2–10 for As(III) and 2–9 for As(V). Adsorption equilibrium data were evaluated using the Langmuir isotherm model, and the maximum adsorption capacity \( q_{\text{max}} \) was 18.25 and 4.97 mg g\(^{-1}\) for As(III) on AAB and GAB, respectively, and 21.79 and 10.92 mg g\(^{-1}\) for As(V) on AAB and GAB, respectively. The adsorption of As(III) and As(V) was observed to follow pseudo-second order kinetics. The As K-edge X-ray absorption near-edge structure (XANES) revealed that the adsorbed As(III) on the AABs was oxidized to As(V) by manganese oxide in the AMDS.

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1. Introduction

Arsenic (As) contaminated groundwater and wastewater treatment technologies for the removal of arsenic, such as co-precipitation, coagulation, membrane separation, ion exchange, nanotechnology, and adsorption, have been developed [1]. Among these treatment methods, adsorption using low-cost adsorbents has been widely used for As removal from the aqueous phase and can offer reliable and efficient performance [2].

Well-known iron materials are effective and cheap adsorbents for treating arsenic contaminated water [3]. Giles et al. [4] described the sorption capacity of iron oxides, iron hydroxides, and iron oxy- hydroxides for arsenite (As(III)) and arsenate (As(V)). Giménez et al. [5], meanwhile, investigated the use of natural hematite, magnetite, and goethite for arsenic removal. Lakshmipathiraj et al. [6] synthesized goethite for As(V) removal from aqueous solutions and observed good uptakes.

Recently, acid mine drainage sludge (AMDS), which contains a significant amount of iron and aluminum hydroxides, was used as an adsorbent [7]. AMDS is produced by the neutralization of AMD using alkaline materials, such as limestone, lime, caustic, or ammonia, and has been used as an alternative source of iron and aluminum oxide [8,9]. AMD is caused by accelerated oxidation of...
pyrite (FeS₂) and other sulfdic minerals due to their exposure to both oxygen and water in mining and processing of metal ores and coals, and it contains high concentrations of dissolved metals, such as Fe, Al, Mn, Pb, Cu, Zn, and As [10]. AMDS consists largely of amorphous micron- and submicron-sized metal oxide/hydroxide particles and has a high specific surface area and numerous functional groups [7,11–13]. AMDS from coal mine drainage sites is preferred because the concentration of impurities, such as As, Cd, Cu, and Zn, are generally lower in coal mine discharges than in those from metal mines [9]. The use of AMDS for arsenic adsorption has been investigated by Ko et al. [3] and Yang et al. [14]. Ko et al. [3] evaluated the adsorption of As(III) and As(V) by AMDS and found that the AMDS was effective for the removal of arsenic from the aqueous phase due to the presence of ferric oxide. Yang et al. [14], on the other hand, attempted to synthesize iron-oxide coated sand (IOC) using AMD as the iron source.

Particulate adsorbents should be anchored to solid supports using immobilization or coating techniques when used for the adsorption of metals or metalloids from wastewater and groundwater on the pilot or field scales. Alginate, which is extracted from brown seaweeds and consists of linear copolymers composed of α-L-guluronate and β-D-mannuronate, is a preferred material for the immobilization of particle-type adsorbents [15]. In fact, alginate beads are widely used for the removal of heavy metals from wastewater [16] and have been used to immobilize waste metal (hydr)oxides [17], activated carbon [1], and magnetic nanoparticles [18].

In the present study, three different adsorbent materials, including pure alginate beads (ABs), goethite alginate beads (GABs), and AMDS alginate beads (AABs), were used for the removal of arsenic. Batch tests were conducted in order to study the adsorption kinetics, isotherms, and the effect of pH on As(III) and As(V) removal from the aqueous phase. Moreover, K-edge X-ray absorption near-edge structure (XANES) analyses were performed in order to identify the oxidation state of the adsorbed arsenic on the surfaces of the AABs.

2. Materials and methods

2.1. Materials

All of the reagents used in the present study were of analytical grade and used as received without further purification. All of the solutions were prepared using Milli-Q water (<18 MΩ cm) (Barnstead Nanopure Diamond, USA). Sodium (meta) arsenite (NaAsO₂), sodium arsenate dibasic heptahydrate (Na₂H₂AsO₄·7H₂O), sodium alginic acid, calcium chloride (CaCl₂), ammonium oxalate monohydrate (C₂H₂N₂O₄·H₂O), and goethite were purchased from Sigma-Aldrich.

2.2. Preparation of AMDS

The AMDS used in the present study was collected from a coal mining site in Tae-Back, South Korea, where it had been generated from an active treatment system and collected as freshly generated sludge. AMDS particles were ground and sieved using a 200-mesh sieve (<75 μm) followed by drying at room temperature prior to use. The chemical constituents of the AMDS particles were determined by X-ray fluorescence spectrometry (XRF) (2SX 100e, Rigaku) and X-ray diffraction (XRD) analysis using Cu Kx filtered radiation (45 kV, 30 mA, 2θ range 5–50°, 2θ steps 0.04° and a scanning speed of 2° (X-pert PRO NPD). XRD patterns were compared to the Joint Committee on Powder Diffraction Standards (JCPDS) in order to identify crystal structures.

2.3. Synthesis and characterization of the ABBs and GABs

AABs and GABs were prepared using an encapsulation technique. Encapsulation of AMDS and goethite into alginate bead was achieved by dissolving alginic acid sodium salt (25 g) in distilled water (500 mL) to generate a 5% (w/v) viscous alginic acid solution. A given amount of prepared AMDS or goethite was dispersed into the alginate solution with agitation such that the ratio of AMDS or goethite to alginate was 1:9 (w/v). Each alginic acid solution mixed with AMDS or goethite was dropped into a 0.05 M CaCl₂ solution (1 L), and the beads formed immediately [19]. The formed beads were stirred for 24 h using a magnetic stirrer to ensure sufficient Ca²⁺ diffusion onto the alginate structure and then washed several times with distilled water in order to remove any unreacted calcium chloride. The washed beads were dried at 60 °C for 24 h. Pure alginate beads without AMDS or goethite were also prepared under similar experimental conditions.

Samples of the prepared beads were characterized using field emission scanning electron microscopy (FE-SEM) XRD analyses; point of zero charge (pHpzc) analyses; the nitrogen adsorption-desorption, Barrett–Joyner–Halenda (BJH), and Brunauer–Emmett–Teller (BET) methods; and atomic force microscopy (AFM). The XRD patterns obtained using Cu Kx filtered radiation (45 kV, 30 mA, 2θ range 5–50°, 2θ steps 0.04° and a scanning speed of 2° (X-pert PRO NPD) were compared to the JCPDS in order to identify the crystal structures. SEM studies were performed by FE-SEM (FESEM, Hitachi, SU-70) couple with energy dispersive X-ray spectroscopy (EDX). The determination of point of zero charge (pHpzc) was performed using the solid addition method [20,21]: the values for ΔpH (pHfinal – pHinitial) were plotted against those for pHinitial. The surface area and porosity were determined from the nitrogen adsorption/desorption isotherms obtained on a BELSORP-mini II using the BET equation for estimation of the overall surface area. The BJH equation was used to estimate the surface area in the mesoporous region and the pore size distribution. Changes in surface topography were observed via AFM using an advanced scanning probe microscope (SPM) (PSIA XE-100).

2.4. General procedure

Batch experiments for As(III) and As(V) adsorption were performed using the three different alginate beads. Separate stock solutions (1000 mg L⁻¹) of As(III) and As(V) were prepared using distilled water. Either the As(III) or As(V) solution and an adsorbent (ABs, GABs, or AABs) were placed in a 50 mL conical tube and shaken in a shaking incubator (150 rpm) at 25 °C. The beads were separated by centrifugation. All aliquots were collected and filtered through 0.22 μm polyvinylidene fluoride syringe filters prior to arsenic analysis. The total concentration of dissolved arsenic in the solutions was determined via inductively coupled plasma optical emission spectroscopy (ICP-OES 730, Varian Inc., USA) and inductively coupled plasma mass spectrometer (ELAN DRC-e, PerkinElmer, USA). All of the solutions were adjusted by using 0.1 N HNO₃ and 1 N NaOH. The solution pH was determined using a Thermo Ross pH meter, which was calibrated daily using three buffers: pH 4.0, 7.0, and 10.0. Each batch experiment was duplicated in order to confirm the reproducibility, and the results are reported as the average values.

2.5. Effect of pH

The effect of pH on As(III) and As(V) sorption onto ABs, GABs, AABs was studied. For the pH-edge experiment, adsorption of As(III) and As(V) was evaluated at pH values ranging from 3 to 11, and the initial concentrations of As(III) and As(V) were both 10 mg L⁻¹. 0.1 g of an adsorbent (ABs, GABs, or AABs) was suspended in 20 mL
of solution in a 50 mL conical tube. The reaction temperature and shaking method were the same as the general procedure.

2.6. Adsorption kinetics

The kinetics experiments were conducted using a 10 mg L\(^{-1}\) initial concentration for each of the As(III) and As(V) solutions at 25°C. Here, 20 mL of solution was taken with 0.1 g of an adsorbent (ABs, GABs, or AABs) into a 50 mL conical tube. Initial pH of each solution was adjusted to 5.0 ± 0.1 and samples were withdrawn at various time intervals within the range from 0 to 168 h. The shaking method was the same as the general procedure.

2.7. Adsorption isotherms

Adsorption isotherm studies were completed by varying the initial concentration of both As(III) and As(V) ranging from 1 to 600 mg L\(^{-1}\) and were conducted by batch mode at pH 5.0 ± 0.1 and 25°C. Here, 20 mL of solution was taken with 0.1 g of an adsorbent (ABs, GABs, or AABs) into a 50 mL conical tube and this mixture was shaken at 150 rpm for 96 h. The shaking method was the same as the general procedure. The adsorbed amount (mg g\(^{-1}\)) at equilibrium \(q_e\) and at any time \(t\) \(q_t\) was calculated as

\[
q_e \quad \text{or} \quad q_t = \frac{[C_0 - C_e \quad \text{or} \quad C_t]}{M} \times V
\]

where \(C_0\), \(C_e\), and \(C_t\) are solute concentration (mg L\(^{-1}\)) at initial, equilibrium, and any time, \(t\), respectively. \(M\) is the mass of the adsorbent (g), and \(V\) is the volume of the solution (L).

2.8. As K-edge XANES analysis

As K-edge XANES analyses were conducted at the Beamline 8C (Nano XAFS) in the Pohang Accelerator Laboratory in Pohang, Korea. Samples were fixed to an aluminum holder and sealed with Kapton tape. The As K-edge XANES spectra of the samples were obtained in fluorescent mode using a 7-elements Ge-array detector (Canberra detector). The scans for each sample were averaged then subjected to background removal and normalization using the program package SixPACK [22]. The XANES spectra of NaAsO\(_2\) and Na\(_2\)HAsO\(_4\) \(\cdot\) 7H\(_2\)O (Sigma-Aldrich) were used as references.

3. Results and discussion

3.1. Characterization of the AMDS

XRF analysis indicated that Fe\(_2\)O\(_3\) (77.2%), CaO (11.1%), SiO\(_2\) (4.8%), Al\(_2\)O\(_3\) (2.5%), and MnO (1.0%) were the major constituents of the AMDS, reflecting high amounts of iron oxide together with the low Ca, Si, Al, and Mn contents (Table 1). The XRD pattern of the AMDS displayed a goethite (\(\alpha\)-FeOOH) peak (Fig. 1(b)) similar to that of commercial goethite (\(\alpha\)-FeOOH) (Fig. 1(a)), as well as a calcite (CaCO\(_3\)) peak. The Fe-rich AMD used in the present study to prepare the AMDS was passed through an active treatment system that involved neutralization with limestone (CaCO\(_3\)). Thus, goethite, which is a significant portion of the AMDS, may have been generated during the active treatment process. However, the XRD pattern of AMDS reported by Ko et al. [3] exhibited an amorphous material peak shape with small goethite peaks similar to that of granular ferric oxide. Based on these previous results, it is possible that amorphous ferric hydroxide was also present in the AMDS prepared in the current study.
Goethite generation during the active treatment of AMD may follow a mechanism similar to that for the preparation of synthetic goethite using ferrous ions [6]. Thus, oxidation of pyrite (Fe₂S₄) could result in the release of ferrous ions (Eq. (2)) [23], which could then form ferrous carbonate and ferrous hydroxide (Eqs. (3) and (4)) [6]. The ferrous hydroxide could then be oxidized to Green Rust Carbonate (Eq. (5)) [6], which in turn could be oxidized to iron oxyhydroxide (α-FeOOH) (Eq. (6)) [6]. It is also possible that mineral transformation from schwertmannite to goethite occurred (Eq. (7)) [23]. Schwertmannite can be produced via the precipitation of oxidized metal species such as hydroxysulfates. The reactions for goethite generation can be written as follows:

**Pyrite oxidation** [23]:

\[
\text{FeS}_2 + 3.5 \text{O}_2 + 3\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ 
\]

**Limestone (CaCO₃) injection** [6]:

\[
\text{FeCO}_3 + \text{OH}^- \rightarrow \text{FeOH}^{3+} + \text{CO}_3^{2-} 
\]

**Fe(OH)₂ oxidation** [6]:

\[
\text{Fe(OH)}_2 + \text{Fe}^{2+} + \text{CO}_3^{2-} + 0.5\text{O}_2 + 3\text{H}_2\text{O} 
\]

**Green rust carbonate** [6]:

\[
5\text{Fe(OH)}_2 + \text{Fe}^{2+} + \text{CO}_3^{2-} + 0.5\text{O}_2 + 3\text{H}_2\text{O} 
\]

**Goethite generation** [6]:

\[
\text{[Fe}_2\text{Fe}_5\text{O}_6(\text{OH})_{12}]\text{[CO}_3\cdot\text{2H}_2\text{O}] \rightarrow 6\text{Fe}^{2+} + 3\text{H}_2\text{O} + 2\text{CO}_3^{2-} + \text{H}_2\text{O} 
\]

**Mineral transformation (Schwertmannite-goethite)** [23]:

\[
\text{Fe}_8\text{O}_8(\text{OH})_{12}(\text{SO}_4)_{1.25} + 2.5\text{H}_2\text{O} 
\]

\[
\text{O} \rightarrow 8\text{Fe}^{3+} + 2.5\text{H}^+ + 1.25\text{SO}_4^{2-} 
\]

### 3.2. Characterization of AABs and GABs

In the XRD patterns of the AABs (Fig. 1(d)) and GABs (Fig. 1(c)), peaks for goethite (α-FeOOH) were mainly observed. The nitrogen adsorption-desorption isotherms and BJH plots for the AABs, GABs, and AABs are shown in Fig. 2. The BET surface area of the AABs, GABs, and AABs were 2.011, 0.404, and 4.619 m² g⁻¹, respectively. Based on BJH theory, the pore volume and pore diameter were estimated to be 0.005 cm³ g⁻¹ and 185.28 nm for the AABs, 0.006 cm³ g⁻¹ and 139.99 nm for the GABs, and 0.011 cm³ g⁻¹ and 185.28 nm for the AABs, respectively. These results indicated that the AABs had a larger surface area and larger pore volume than the GABs. In addition, all of the beads were macroporous materials (type II in the IUPAC classification) [24]. Moreover, SEM analysis of the AABs showed that small precipitates, i.e., AMDs particles, were spread over the surface of the alginate beads. Characteristic three dimensional surface topography images of the AABs and GABs are presented in Fig. A.1 (Supporting information). The pure alginate beads exhibited clear and wave-like surface topographies (Fig. A.1(a), Supporting information). Upon AMDs injection, however, a significant change in the surface topography occurred (Fig. A.1(b), Supporting information). Specifically, larger distinguished domains were observed, and thus the roughness of the AAB surfaces increased.

<table>
<thead>
<tr>
<th>Material</th>
<th>Extractants</th>
<th>Extracted Fe (mg L⁻¹) Extracted Mn (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMDS</td>
<td>Distilled water (pH 5)</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Ammonium oxalate solution</td>
<td>913.3 ± 90.6</td>
</tr>
<tr>
<td>Goethite</td>
<td>Distilled water (pH 5)</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Ammonium oxalate solution</td>
<td>61.4 ± 1.3</td>
</tr>
</tbody>
</table>

### 3.3. Effect of pH

Fig. 3 shows the effect of pH on the removal of As(III) and As(V) by the AABs, GABs, and AABs. Pure alginate beads, which originate from brown seaweeds, have a high affinity toward divalent cations [25]. The alginate molecules have a carboxyl group, and therefore, the surfaces of the alginate beads are negatively charged. For this reason, the adsorption level for As(III) and As(V) using the AABs were <10% at pH values ranging from 2 to 10. On the other hand, with the AABs, greater than 90% of the As(III) and As(V) were removed from the solutions at pH values ranging from 2 to 10. The maximum removal efficiency of As(III) was 95.3% at pH 4, while the minimum value was 85.2% at pH 2. Moreover, the maximum removal efficiency of As(V) was 99.4% at pH 2, and the minimum value was 84.8% at pH 11. These results are in good agreement with those of Ko et al. [3]. They reported that the adsorption level for As(III) and As(V) by AAMDS in solution in the pH range from 3 to 9 were above 95.0%, and the maximum removal efficiencies for As(III) and As(V) were 98.8% and 99.0% at pH 7, respectively. Ko et al. also reported that the large surface area of the AMDS was strongly influenced by the amorphous phase of the iron involved in As adsorption.

It should also be noted that in the present study, the adsorption level for As(III) and As(V) onto the AABs were not only greater than those for the AABs but also for the GABs. Thus, it is possible that amorphous ferric hydroxide influenced the adsorption level for As(III) and As(V). Amorphous Fe(OH)OH has the highest adsorption capability due to the large surface area [26]. According to the present XRD analysis, goethite was present in the AMDS. However, it was not likely that all of the iron oxide in the AMDS existed as goethite, and amorphous ferric hydroxide was expected to be present as well. To confirm the existence of such an amorphous phase, the extraction of amorphous ferric hydroxide was performed [27]. Notably, iron ions were not detected when either the AMDS or goethite were extracted using distilled water at pH 5. However, when the AMDS and goethite were extracted using 0.2 M ammonium oxalate solution, the concentration of extracted iron was 440.48 ± 4.73 and 0.86 ± 0.02 mg L⁻¹, respectively (Table 2). This result indicated that the amount of amorphous ferric hydroxide present in the AMDS were greater than that in the goethite.

The pH values for the mixed solutions (pHmix) were found to be 5.91, 7.89, and 5.03 for the AABs, GABs, and AABs, respectively. Interestingly, adsorption of As(III) and As(V) using the AABs and GABs was not affected by the pHmix in the present study. This phenomenon can be explained if specific bonding reactions on the surfaces of the AABs and GABs were more dominant than electrostatic interactions. Jain et al. [28] reported that adsorption occurs when ligands of arsenic species are exchanged for functional groups on the iron oxide/hydroxide surface. Separately, Sherman and Randall [29] found that the mechanism for As(V) adsorption onto goethite, lepidocrocite, hematite, and ferrihydrite proceeds via the formation of bidentate, inner-sphere surface complexes.

### 3.4. Kinetics study

Adsortion kinetics are typically studied at the solid/solution interface and expressed by the solute removal rate as a function of time. In the present study, the batch data were applied to the
Fig. 2. Adsorption/desorption isotherm of AB (a), GAB (c) and AAB (e), and BJH plot of AB (b), GAB (d), and AAB (f) (inserted images were from SEM analysis).
adsorption kinetics analyses, and pseudo-first order and pseudo-second order adsorption kinetics models were used [30–33]. The pseudo-first order kinetics rate equation (Eq. (8)) can be expressed as follows:

$$\log(q_e - q_t) = \log q_e \frac{k_1 t}{2.303}$$  \hspace{1cm} (8)

where \(q_e\) and \(q_t\) are the quantity of adsorbed arsenic ions (mg g\(^{-1}\)) at equilibrium and time \(t\), \(k_1\) is the adsorption rate constant for pseudo-first order kinetics, and \(t\) is the time required for adsorption.

On the other hand, the pseudo-second order kinetics rate equation (Eq. (9)) can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (9)

where \(k_2\) is the rate constant for pseudo-second order kinetics.

The kinetics parameters for the adsorption of As(III) and As(V) onto the three types of beads were estimated via linear or non-linear analysis of the data (Fig. 4) using Eqs. (8) and (9), and the results are summarized in Table 3. The \(q_{e\text{cal}}\) (mg g\(^{-1}\)) values for the AABs were larger than those for both the ABs and GABs, indicating that the AABs exhibited a slightly higher removal capacity for both As(III) and As(V) than the others two beads. The kinetics parameters also indicate that the reaction kinetics for As(III) and As(V) sorption by the beads can be explained more accurately using the pseudo-second order kinetics model. The calculated values for \(q_{e\text{cal}}\) (mg g\(^{-1}\)) using the pseudo-second order kinetics model were closer to the experimental values for \(q_{e\text{exp}}\) (mg g\(^{-1}\)) than those calculated using the pseudo-first order kinetics model.
The $q_{\text{cal}}$ (mg g$^{-1}$) values and correlation coefficient ($R^2$) obtained using the pseudo-second order kinetics model were in good agreement with the results obtained for the present reaction. The pseudo-second order rate constants $k_2$ for the AABs and GABs were $5.7 \times 10^{-4}$ g mg$^{-1}$ min$^{-1}$ and $3.2 \times 10^{-4}$ g mg$^{-1}$ min$^{-1}$, respectively. These results suggested that As(III) and As(V) adsorption followed pseudo-second order kinetics and As(III) and As(V) were adsorbed onto the AABs and GABs via chemical interactions [34].

### 3.5. Adsorption isotherms

The adsorption data were further analyzed using two isotherm models, e.g., the Langmuir and Freundlich models [35,36]. The Langmuir isotherm model may be expressed in its non-linear (Eq. (10)) and linear (Eq. (11)) forms as follows:

$$q_e = \frac{q_m K_l C_e}{1 + K_l C_e} \text{ (non-linear form)}$$  \hspace{1cm} (10)

$$\frac{C_e}{q_e} = \frac{1}{K_l q_m} = \frac{C_e}{q_m} \text{ (linear form)}$$  \hspace{1cm} (11)

where $q_e$ is the quantity adsorbed at equilibrium concentration $C_e$, $q_m$ is the Langmuir constant symbolizing the maximum monolayer adsorption capacity, and $K_l$ is the Langmuir constant.

The Freundlich model assumes adsorption on heterogeneous surface sites and was also used to explain the adsorption isotherms. The non-linear (Eq. (12)) and linear (Eq. (13)) forms of the Freundlich equation are given as follows:

$$q_e = K_f C_e^1/n \text{ (non-linear form)}$$  \hspace{1cm} (12)

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \text{ (linear form)}$$  \hspace{1cm} (13)

where $q_e$ is the quantity of solute adsorbed per unit weight of adsorbent, $C_e$ is the equilibrium concentration of the solute in the bulk solution, $K_f$ is a constant that indicates the relative adsorption capacity of the adsorbent, and $n$ is a constant that indicates the intensity of the adsorption. Table 4 lists the values for the Langmuir ($q_m$ and $K_l$) and Freundlich ($K_f$ and $n$) constants and the correlation coefficients for As(III) and As (V) adsorption onto the three types of beads. The maximum adsorption capacities for the ABs, GABs, and AABs for As(III) and As(V) using the Langmuir model were 2.85 and 4.28, 4.97 and 10.92, and 21.79 mg g$^{-1}$, respectively.

High $K_l$ values indicate a relatively high As bonding strength by iron oxide. Lafferty and Loepert [37] reported that the $K_l$ parameter can be used for evaluation of the comparative adsorption behavior between treatments but has little or no significance as a theoretical chemical binding constant. In the present study, the calculated $K_l$ values for the Langmuir function decreased in the order AABs > GABs > ABs. These results therefore, suggested that the As bonding strength decreased in the following order: AABs > GABs > ABs, and that in all cases the chemical bonding constant was stronger for AMDS than goethite.

In addition, the dimensionless constant separation factor ($R_l$) can be defined using (Eq. (14)):

$$R_l = \frac{1}{1 + b C_0}$$  \hspace{1cm} (14)

where $b$ (L mg$^{-1}$) is the Langmuir constant ($K_l$) and $C_0$ (mg L$^{-1}$) is the initial concentration of the As(III) or As(V). When $R_l > 1$, an adsorption process is unfavorable, while if $0 < R_l < 1$, the process is favorable. If adsorption is linear, $R_l$ is 1, and if it is irreversible, $R_l$ is 0. The calculated $R_l$ values for As(III) and As(V) onto the AABs and GABs fell in the range $0 < R_l < 1$, indicating favorable adsorption.

### 3.6. XANES analyses

When As(III) was adsorbed on the surfaces of the AABs, it was possible that the manganese oxides contained in the AMDS oxidized the As(III) to As(V) (see Tables 1 and 2). Therefore, to investigate the possibility of As(III) oxidation on the AAB surfaces, the oxidation state of As adsorbed on the AABs at pH 5 was determined using As K-edge XANES analysis (Fig. 6). The XANES spectra of NaAsO$_2$ and Na$_2$HAsO$_4$ were used as references for As(III) and As(V), respectively, and are shown for comparison. The XANES spectrum of As(III) exhibited an adsorption edge energy at 11,870.0 eV, while...
that of As(V) was observed at 11,873.7 eV (Fig. 6(a) and (b)). These results coincided with the adsorption edge energies for As(III) and As(V) on NP FeS[38]. For As(III) adsorption onto the AABs at pH 5, the two absorption edges occurred near 11,870.0 eV for As(III) and 11,873.7 eV for As(V) (Fig. 6(c)). The absorption edges of As(III) and As(V) onto GAB occurred near 11,871.0 and 11,873.7 eV, respectively (Fig. 6(e) and (f)). These results indicated that As(III) and As(V) coexisted on the AAB surfaces, and oxidation of As(III) to As(V) occurred on the surfaces of AABs. This phenomenon enhanced the adsorption capacity of the AABs for As(III), and was supported by the adsorption isotherm for As (III) onto the AABs (see Fig. 5(a)). Thus, the maximum adsorption capacity (q_m) for As(III) onto the AABs (i.e., 18.25 mg g⁻¹) was nearly as great as that for As(V) onto the AABs (i.e., 21.79 mg g⁻¹) (see Table 4). Gupta et al. [39] reported that the sorption of As(III) by manganese associated hydrous iron (III) oxide (MNHFO) took place with surface oxidation to As(V). A possible mechanism for the sorption reaction of As(III) onto the AABs can therefore be described by the following equations (Eqs. (15)–(19)) [39]:

\[
S_{\text{Fe-Mn(MnO}_2\text{)}} + \text{As(III)} \rightarrow S_{\text{Fe-Mn(MnO}_2\text{)}} + \text{As(V)} + \text{OH}^- \quad (16)
\]

\[
S_{\text{Fe-Mn(MnOOH)}} + \text{As(III)} \rightarrow S_{\text{Fe-Mn(MnOOH)}} + \text{As(V)} + 3\text{OH}^- \quad (18)
\]

\[
S_{\text{Fe-Mn}} + \text{As(V)} \rightarrow S_{\text{Fe-Mn}} + \text{As(V)} \quad (19)
\]

4. Conclusions

Three different alginate beads (e.g., ABs, GABs, and AABs) were used for adsorption of As(III) and As(V). The synthesized beads were characterized using XRD, SEM, BET, and PZC analyses, and basic performance data, including their pH edges, adsorption kinetics, and adsorption isotherms, were collected. The AABs exhibited higher adsorption capacities for As (III) and As(V) compared with those of the GABs, because the AABs contain both goethite and amorphous ferric hydroxide. In addition, the AMDS used as the adsorbent material for the AABs contains a small amount of manganese that oxidizes As(III) to As(V) on the surfaces of the AABs at pH 5 as observed via XANES analysis. Consequently, AABs, which are prepared from reclaimed waste materials, may possibly be employed as an efficient adsorbent for the removal of As from contaminated water.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2015.03.026.

References


