Removal of arsenite from water by synthetic siderite: Behaviors and mechanisms

Huaming Guo\textsuperscript{a,∗}, Yuan Li\textsuperscript{a}, Kai Zhao\textsuperscript{a}, Yan Ren\textsuperscript{a}, Chao Wei\textsuperscript{b}

\textsuperscript{a} School of Water Resources and Environment, China University of Geosciences, Xueyuan Road 29, Haidian District, Beijing 100083, PR China
\textsuperscript{b} Chemical Metrology and Analytical Science Division, National Institute of Metrology, Beijing 100013, PR China

A R T I C L E   I N F O

Article history:
Received 9 September 2010
Received in revised form 28 October 2010
Accepted 16 December 2010
Available online 23 December 2010

Keywords:
Arsenic
As(III)
Kinetic
Thermodynamic
XANES

A B S T R A C T

Synthetic siderite has been used as adsorbent for As(III) removal in this study. Effects of contact time, temperature, pH, co-existing anions on As(III) adsorption were intensively investigated. Adsorption mechanisms were also studied using the X-ray absorption technique. Results show that the maximum adsorption capacity is up to 9.98 mg g\textsuperscript{−1} at 25 °C at a siderite dosage of 2 g L\textsuperscript{−1}. Adsorption kinetics agrees with the Lagergren pseudo-second order model. Arsenic(III) adsorption can be better described by Langmuir isotherm model for As(III) adsorption at 55 °C, indicating that the coverage of the adsorption sites is in the form of monolayer, although Freundlich isotherm yields a better fit to the experimental data at 25, 35 and 45 °C. Thermodynamic study indicates that As(III) adsorption on the synthetic siderite is spontaneous and endothermic in nature. The adsorption capacity is enhanced with the increase in reaction temperature. The adsorption is independent on solution pH between 3.0 and 9.6. The presence of NO\textsubscript{3}{−}, SO\textsubscript{4}{2−}, PO\textsubscript{4}{3−} or SiO\textsubscript{3}{2−} with element concentrations less than 20 mg L\textsuperscript{−1} does not have adverse effect on As(III) adsorption. XANES spectra indicate that As mainly occurs as As(V) in the As adsorbed-materials, and the fraction of oxidized As(III) increases with the decrease in As(III) concentration. The formation of Fe hydroxide minerals (such as lepidocrocite and goethite) followed by As(III) oxidation and adsorption is shown to be the main mechanism of As(III) removal by the synthetic siderite.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Arsenic contamination in natural water is a worldwide problem and has become an important issue. Chronic As poisoning due to long term exposure to As-contaminated drinking water has been one of the worst human health hazards in Bangladesh, India, USA, Japan, Argentina, and some regions in China including Xinjiang, Inner Mongolia, Guizhou and Shanxi [1–4]. The chronic effects commonly include skin diseases (including black foot, pigmentation, and dermal hyperkeratosis), lung cancer, kidney cancer, and many other diseases [5,6]. Recent studies show that As in drinking water is more harmful to human health than expected. Many countries, including China, USA, Western Europe and Japan, have considered As in drinking water as environmental priority pollutant and made strict guidelines for As concentration in waste disposals and drinking water. The maximum contaminant level (MCL) of As in drinking water has been revised by European Commission in 1998. According to the new directive, all drinking water supply systems within European Union would have to comply with the new limit by 2003, which has reduced As limitation in drinking water from 50 μg L\textsuperscript{−1} to 10 μg L\textsuperscript{−1} [7]. The U.S. EPA has decided to move forward in implementing the same standard for drinking water [8]. This standard has been recommended by WHO [9]. The new standard for drinking water quality has been executed in China, which adopts 10 μg L\textsuperscript{−1} for As in drinking water (GB5749-2006) [10]. Therefore, it is an emerging issue to improve novel treatment technologies and to develop new materials for As removal from As-contaminated drinking water. Iron(III)/Fe(II) substances have been widely evaluated to remove As from aqueous solution due to their high specific surface area [11–21].

Arsenic exists in natural water predominantly as inorganic arsenite (As(III)) and arsenate (As(V)) [22]. The former is more toxic. The predominant species is As(V) under oxidizing conditions, which is mainly presented as oxyanion forms (H\textsubscript{2}AsO\textsubscript{4}{−}, H\textsubscript{3}AsO\textsubscript{4}{2−}) at neutral pH [22,23]. Most treatment technologies, such as adsorption and precipitation, are effective in removing As(V) from waters because of positive charge on the surface of the adsorbents. On the other hand, under mildly reducing conditions such as in groundwaters, As(III) is the thermodynamically stable form, which is presented as non-ionic form of arsenic acid (H\textsubscript{2}AsO\textsubscript{3}{−}) at neutral pH [23]. Thus, As(III) is more difficult to be removed from water by means of adsorption and coprecipitation due to the lack of electrostatic attraction [11,24]. Whereas, As-enriched groundwater is generally dominated by As(III), up to 96% [23,25]. Therefore, the removal of As(III) from drinking water has received much atten-
tion from both scientific communities and government agencies [26,27].

Arsenic(III) forms bidentate binuclear corner-sharing sorption complexes, monodentate mononuclear corner-sharing complexes, and bidentate mononuclear edge-sharing complexes on iron minerals. It shows that binuclear corner-sharing complexes are important for As(III)-sorbed ferric (oxyhydr)oxides, regardless of the substrate and the surface coverage [52]. Arsenic(III) forms inner sphere bidentate surface complexes on both goethite and lepidocrocite [14,53,54], while it forms a weak outer-sphere complex on siderite in anaerobic condition [18]. Although As(III) adsorption on Fe oxides forms both inner- and outer-sphere complexes, their relatively importance depends on experimental conditions [55].

Natural siderite and natural hematite have showed effective in removing As(III) from aqueous solution [12,28,29]. Although they are cost-effective, the kinetic rates for As(III) adsorption are relatively low [12,28]. In comparison with natural siderite, synthetic siderite (FeCO₃) has much higher As(V) adsorption capacity and greater adsorption rate due to the great number of active sites on the surface [30]. The adsorption capacity for As(V) reached 10.73 mg g⁻¹ at 25 °C, which is much higher than natural siderite (0.516 mg g⁻¹) [30]. The equilibrium time for As(V) adsorption on synthetic siderite is about 3 h [30], much shorter than that on the natural siderite (24–72 h) [12,28]. Nevertheless, there is no information on As(III) adsorption on synthetic siderite. It is necessary to test kinetics and thermodynamics of As(III) adsorption on synthetic siderite.

In this study, synthetic siderite has been synthesized and used as adsorbent for As(III) removal. Effects of contact time, temperature, pH, co-existing anions on As(III) adsorption are intensively studied with initial As(III) concentration of 1.0 mg L⁻¹. Adsorption isotherm studies were conducted by varying initial As(III) concentrations (2.0–40.0 mg L⁻¹) at initial solution pH 7.0, contact time of 10, 20, 30, 60, 90, 120, 180, 300, 480 min at 25 °C and 45 °C. Adsorption isotherm studies were conducted by varying initial As(III) concentrations (2.0–40.0 mg L⁻¹) at initial solution pH 7.0, at different temperatures (i.e., 25, 35, 45, and 55 °C). Effects of co-existing anions (NO₃⁻, SO₄²⁻, PO₄³⁻ and SiO₃²⁻) was studied with initial As(III) concentration of 1.0 mg L⁻¹. Batch tests were performed using As(III) solutions containing 0.5, 1, 2, 5, 10 and 20 mg L⁻¹ of P as PO₄³⁻, N as NO₃⁻, S as SO₄²⁻ or Si as SiO₃²⁻, separately. Effect of background electrolyte concentration was tested using As(III) solution with sodium chloride concentrations between 1 and 100 mmol L⁻¹. Effects of contact time and PO₄³⁻ on adsorption were duplicate conducted. The results of duplicate batches are quite similar. The difference between them is less than 2%. Therefore, other batches have not been investigated duplicate.

2. Materials and methods

2.1. Materials

Ferrous sulfate (FeSO₄·7H₂O) and ammonium hydrocarbonate (NH₄HCO₃) were used as raw materials to produce ferrous carbonate crystal (synthetic siderite) [31]. The reaction can be presented as Eq. (1).

\[
{\text{Fe}}^{2+} + 2\text{HCO}_3^- \rightarrow \text{FeCO}_3 \downarrow + \text{H}_2\text{O} + \text{CO}_2 \uparrow \tag{1}
\]

The precipitate was filtered, rinsed with distilled water, air dried for 24 h and ground to powder (200 mesh). The product, namely synthetic siderite, was kept in a dessicator. The mineral purity and specific surface area were verified by SEM and XRD [30]. The mineral specific surface area was determined by N₂-BET procedure guarantees decontamination of glassware for working with As [30].

2.2. Batch experiments

Adsorption process was conducted in a shaking water bath with a temperature controller. The shaker speed was controlled at 150 rpm. Batch tests were performed in 100 mL polyethylene bottles (height: 9.0 cm; diameter: 4.0 cm; cap diameter: 3.0 cm) containing 0.100 g of adsorbents and 50 mL of As(III) solution with a certain level.

Effect of solution pH was studied with initial As(III) concentration of 1.0 mg L⁻¹ and contact time of 180 min. Initial solution pH was adjusted by using 0.05 mol L⁻¹ HCl and 0.01 mol L⁻¹ NaOH. Effect of contact time on adsorption of As(III) was investigated with initial As(III) concentration of 10.0 mg L⁻¹, initial solution pH of 7.0, contact time of 10, 20, 30, 60, 90, 120, 180, 300, 480 min at 25 °C and 45 °C. Adsorption isotherm studies were conducted by varying initial As(III) concentrations (2.0–40.0 mg L⁻¹) at initial solution pH 7.0, at different temperatures (i.e., 25, 35, 45, and 55 °C). Adsorption isotherm studies were conducted by varying initial As(III) concentrations (2.0–40.0 mg L⁻¹) at initial solution pH 7.0, at different temperatures (i.e., 25, 35, 45, and 55 °C). Adsorption isotherm studies were conducted by varying initial As(III) concentrations (2.0–40.0 mg L⁻¹) at initial solution pH 7.0, at different temperatures (i.e., 25, 35, 45, and 55 °C). Adsorption isotherm studies were conducted by varying initial As(III) concentrations (2.0–40.0 mg L⁻¹) at initial solution pH 7.0, at different temperatures (i.e., 25, 35, 45, and 55 °C).

2.3. Data analysis

The pseudo-first order Lagergren equation is widely used to investigate adsorption kinetics, while the pseudo-second order equation would allow evaluating effective adsorption capacity, initial adsorption rate and the rate constant of the kinetic model using kinetic data [33]. In order to investigate the mechanism of adsorption, constants of adsorption are determined using the pseudo-first order equation and the pseudo-second order equation, which are shown in Eqs. (2) and (3), respectively:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1 \cdot t}{2.303} \tag{2}
\]

\[
\frac{t}{q_t} = \frac{1}{K_2 \cdot q_m^2} + \frac{t}{q_2} \tag{3}
\]

where \(q (\text{mg g}^{-1})\) is the amount of As(III) adsorbed at contact time \(t\); \(q_e (\text{mg g}^{-1})\) is the amount of As(III) adsorbed at equilibrium; \(q_2 (\text{mg g}^{-1})\) is the equilibrium adsorption capacity of theoretical value in the pseudo-second order model; \(K_1 (\text{min}^{-1})\) is the rate constant of the pseudo-first order model; \(K_2 (\text{g mg}^{-1} \text{min}^{-1})\) is the rate constant of the pseudo-second order model.

The data obtained from the isotherm studies was used to analyze the adsorption isotherms in order to estimate the constants, adsorption density and adsorption maxima. The experimental results were fitted to both the Langmuir and Freundlich isotherms, which are shown in Eqs. (4) and (5), respectively [35,36].

\[
\frac{C_e}{q_e} = \frac{1}{(b \cdot q_m)} + \frac{C_e}{q_m} \tag{4}
\]

\[
\log q_e = \log K + n \cdot \log C_e \tag{5}
\]

where \(K_e (\text{mg L}^{-1})\) is the equilibrium As concentration; \(q_e (\text{mg g}^{-1})\) is the amount of As adsorbed at equilibrium; \(q_m (\text{mg g}^{-1})\) and \(b\)
(L mg m⁻¹) are the Langmuir constants related to the saturated monolayer adsorption capacity and the binding energy of the adsorption system, respectively. K and n are empirical constants of Freundlich isotherms, indicating the adsorption capacity and adsorption intensity, respectively.

2.4. Analytical methods

After adsorption, the aqueous samples were centrifuged for 5 min at 4500 rpm, and then filtered through a 0.45 μm cellulose acetate filter in order to remove small colloids. The supernatant was acidified to pH < 2 with 1:1 HNO₃, and analyzed for dissolved Fe and total As using ICP-MS (7500C, Agilent). Unless specified otherwise, the concentration of the As species was expressed as the element (As).

The mineral composition of the adsorbents was determined by X-ray diffraction analysis (XRD), using a URD-6 powder diffractometer (Cu Kα radiation, graphite monochromator, 2θ range 2.6–70°, step 0.01°, counting time 5 s per step). Morphological analysis of the pristine and used adsorbent was performed by field emission scanning electron microscopy (FE-SEM) using Zeiss SUPRA 55 microscope (at 15 kV) with energy-dispersive X-ray analyses.

The X-ray absorption data were recorded at room temperature at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. Beamline was equipped with a double-crystal Si(111) monochromator. Spectra were collected both in transmission mode using ion chambers and in the fluorescent mode with silicon drift fluorescence detector, from –150 to 800 eV relative to the As K-edge of 11,867 eV. During the measurement, the synchrotron was operated at energy of 3.5 GeV and a current between 150 and 210 mA. Data processing was performed using the program ATHENA. All fits to the EXAFS data were performed using the program ARTEMIS.

3. Results and discussion

3.1. Effect of solution pH

There is a significant increase in adsorption capacity with the increase in pH between 2 and 3 (Fig. 1). At pH > 3, the adsorption capacity generally keeps constant. The results evidently show that the synthetic siderite efficiently adsorbed As(III) in a wide pH range. The natural siderite also exhibited the stable adsorption capacity for As(III) at solution pHs between 3.0 and 10.0 [28]. The effect of solution pH would be related to formation of Fe hydroxide minerals, since Fe hydroxide minerals mainly attribute to As removal (which will be discussed later).

Except for the batch at pH 2.0, equilibrium solutions have a neutral pH around 6.8 (data not shown), which means that adsorbent has capability in maintaining a neutral solution pH and keeps the adsorption system at near neutral pH during the experiments. It also showed that As(V) adsorption remained relatively constant at pHs 3.0–10.0 [30]. The independence of As(III) adsorption on solution pH could be explained by the amphoteric nature of Fe oxides/oxyhydroxides [30].

Arsenic(III) adsorption on synthetic siderite is closely related to electro-static attraction as well as physico-chemical reactions. As an important form of Fe oxides/oxyhydroxides, hydrous ferric oxides (HFO) have many surface hydroxyl groups. At pH around 6.8, HFO have positive charge, and therefore electrostatic and Lewis acid–base (LAB) interactions immobilize arsenic on the surface of the adsorbent. Since equilibrium pH is around 6.8 when the initial pHs range between 3.0 and 9.6, those interactions would be less affected by initial solution pH. However, the adsorbent is partially dissolved at initial solution pH 2.0, which substantially reduce adsorption sites. Although equilibrium pH is much less than 6.8 and the adsorbent is positively charged, adsorption is low due to the presence of a low amount of adsorbent.

3.2. Effect of contact time

It is clearly seen from Fig. 2 that adsorption of As(III) on the synthetic siderite increases significantly with an increase in contact time for both reaction temperatures. The adsorption rate is quite high in the first 30 min, and gradually decreases as the adsorption process continues (up to 180 min). The high adsorption rate attributes to the great amount of adsorption sites and the large adsorption sites on the surface of the adsorbents [13,32].

Actually, the adsorption achieves equilibrium in 120 min at 45 °C, when 97.5% of As(III) is removed. However, at 25 °C, the adsorption equilibrium is reached at contact time of 180 min, at which about 85.6% of As(III) is adsorbed. A reaction time of 180 min is chosen for further studies. The equilibrium time for As(III) adsorption on the synthetic siderite is much shorter than that on the natural siderite at 25 °C (72 h) [12], indicating that the adsorption rate of As(III) on the material is much higher than that on the natural siderite.

Three general stages normally occur for As adsorption onto solid particles. Firstly, As is transported to the external surface of the adsorbent from bulk solution across the boundary layer (external mass transfer); then As is adsorbed onto particle surfaces; and
finally the adsorbed As is exchanged with the structural elements of adsorbent particles or diffused in the internal surfaces of porous materials (intraparticle diffusion) [33]. At the early stage of kinetic tests, first two steps would be predominated, which always happens very fast. However, major processes would be the intraparticle diffusion at the late stage, being considered to be slow.

The kinetic models adequately fit the data obtained in the batch experiments. Results are shown in Fig. 3. Model parameters, including kinetic constants, equilibrium adsorption capacities and correlation coefficients, are presented in Table 1. It shows that the adsorption kinetics at two different temperatures can be better described in terms of the pseudo-second order rate model than the first order rate model.

Guo et al. has also got the pseudo-second order rate parameters for As(V) adsorption on the synthetic siderite [30], which are included in Table 1. As shown in Table 1, the values of $K_2$ for As(III) and As(V) at 25 °C are 0.0105 and 0.0202 g mg$^{-1}$ min$^{-1}$, while at 45 °C 0.0602 and 0.4958 g mg$^{-1}$ min$^{-1}$, respectively. The $K_2$ value increases with the increase in reaction temperature for both As(III) and As(V), which indicates that the overall adsorption rate is faster at high temperatures than at low temperatures. Furthermore, a comparison of the $K_2$ values indicates that the adsorption rate of As(V) is faster than that of As(III) at the same reaction temperature.

Adsorption of monodentate nonionized As(III) happens only through a Lewis acid–base (ligand exchange) reaction, and is favorably adsorbed onto the non-ionized surface functional group at neutral pH [14,34]. On the contrary, adsorption of As(V), such as H$_2$AsO$_4^−$, HAsO$_4^{2−}$, is known to take place via Coulombic as well as Lewis acid–base interactions (ligand exchange reactions) and to form monodentate and bidentate inner sphere complexes. That is the possible reason for the higher adsorption rate of As(V) on the synthetic siderite.

### 3.3. Adsorption Isotherms

Adsorption isotherm describes a relationship between the amount of chemical adsorbed on adsorbent and the concentration of adsorbate in solution at adsorption equilibrium at a constant temperature. Langmuir and Freundlich isotherms are plotted in Fig. 4. The values of the Langmuir parameters $b$ and $q_m$ are evaluated from the linear plot of $C_e/q_e$ vs. $C_e$, while those of the Freundlich constants from the linear plot of log $q_e$ vs. log $C_e$. These parameters are presented in Table 2.

Results show that correlation coefficients ($r^2$) for both the isotherms range between 0.955 and 0.998, representing an excellent fit of observed data. Generally, Freundlich isotherm better describes the adsorption than Langmuir at 25, 35 and 45 °C, while Langmuir isotherm yields a better fit to the experimental data at 55 °C.

Because Freundlich isotherm model can be applied to multilayer sorption as well as nonideal sorption on heterogeneous surfaces [12], it could be speculated from our data that the multilayer adsorption would be involved in the As(III) adsorption on the synthetic siderite at temperatures between 25 and 45 °C.

Langmuir isotherm indicates that the reaction is a reversible phenomenon and the coverage is monolayer [37]. The fact indicates that As(III) was adsorbed in the form of monolayer coverage on the surface of the adsorbent at 55 °C. It has been reported that the adsorption of As(III) on hematite [38], As(III) and As(V) on activated alumina [39], and goethite [40], follows Langmuir isotherm (Table 2).

In this study, As(III) adsorption capacity of the synthetic siderite at 25 °C, estimated from Langmuir isotherm, is 9.98 mg g$^{-1}$. It has been reported that the values of $q_m$, the Langmuir constant related to saturated monolayer adsorption capacity for natural hematite [12], hematite [38], iron oxide coated sand [16], iron oxide coated cement [17] are 0.104, 0.18, 0.028, and 0.69 mg g$^{-1}$, respectively (Table 2). Importantly, in comparison with the natural siderite (1.04 mg g$^{-1}$) [28], the synthetic siderite has a much higher adsorption capacity for As(III) removal at 25 °C (9.98 mg g$^{-1}$).

The $n$ value of Freundlich isotherm is related to the strength of adsorption. The calculated $n$ lies in the range between 0.39 and 0.66, denoting favorable adsorption of As(III) onto the synthetic siderite.

### Table 1

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>As(III)</th>
<th>Lagrgren's first order</th>
<th>Lagrgren's pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r^2$</td>
<td>$K_1$</td>
<td>$r^2$</td>
</tr>
<tr>
<td>25</td>
<td>0.9868</td>
<td>0.0138</td>
<td>0.0979</td>
</tr>
<tr>
<td>45</td>
<td>0.9843</td>
<td>0.0237</td>
<td>0.0999</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.0602</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.125</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>As(V)$^a$</th>
<th>Lagrgren's pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r^2$</td>
<td>$K_2$</td>
</tr>
<tr>
<td>25</td>
<td>0.9974</td>
<td>0.0202</td>
</tr>
<tr>
<td></td>
<td>1.0000</td>
<td>4.221</td>
</tr>
</tbody>
</table>

$^a$ Guo et al. [30].

![Fig. 3. Plot of Lagergren's first order rate (a) and pseudo-second order rate (b) for As(III) adsorption on synthetic siderite (initial As(III) concentration = 10.0 mg L$^{-1}$, adsorbent dosage = 2 g L$^{-1}$, initial pH = 7.0).](image)
Isotherm parameters for As(III) adsorption on synthetic siderite and other Fe compounds at different temperatures.

<table>
<thead>
<tr>
<th>(°C)</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r^2$</td>
<td>$q_m$ (mg g$^{-1}$)</td>
</tr>
<tr>
<td>25</td>
<td>0.955</td>
<td>9.98</td>
</tr>
<tr>
<td>35</td>
<td>0.979</td>
<td>10.01</td>
</tr>
<tr>
<td>45</td>
<td>0.982</td>
<td>14.51</td>
</tr>
<tr>
<td>55</td>
<td>0.997</td>
<td>24.88</td>
</tr>
<tr>
<td>20</td>
<td>0.982</td>
<td>1.04</td>
</tr>
<tr>
<td>27</td>
<td>0.980</td>
<td>0.028</td>
</tr>
<tr>
<td>27</td>
<td>0.999</td>
<td>0.069</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>0.18</td>
</tr>
<tr>
<td>25</td>
<td></td>
<td>1.05</td>
</tr>
<tr>
<td>25</td>
<td>0.998</td>
<td>0.38</td>
</tr>
</tbody>
</table>

The greater the value of $n$, the stronger the adsorption bond is. Table 2 also shows that the $n$ value generally increases with the increase in reaction temperature. It suggests that high temperature would strengthen the adsorption bond between As and the adsorbent.

3.4. Thermodynamic characteristics

A good fit of the data with Langmuir isotherm ($r^2 > 0.955$) were obtained, although Freundlich isotherm mostly yields a better fit to the experimental data than Langmuir isotherm. Because Langmuir isotherm permits to investigate thermodynamic characteristics of the adsorption process, Langmuir parameters are used to analyze adsorption thermodynamics.

Thermodynamic parameters, including standard free energy ($\Delta G^0$), standard enthalpy ($\Delta H^0$) and standard entropy ($\Delta S^0$), can be calculated using the following equations (Eqs. (6)-(8)) [37,41].

\[
\Delta G^0 = RT \ln \left( \frac{1}{b} \right) \tag{6}
\]

\[
\ln b = \ln b_0 - \frac{\Delta H^0}{RT} \tag{7}
\]

\[
\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{8}
\]

where $b$ is Langmuir constant related to the energy of adsorption, $b_0$ is a constant, $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), and $T$ is the absolute temperature in Kelvin (K).

The energy parameters $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ were calculated and are given in Table 3. The negative $\Delta G^0$ values were obtained for the adsorption process ($-35.54$ to $-24.57$ kJ mol$^{-1}$), confirming the feasibility of the process and the spontaneous nature of As(III) adsorption on the synthetic siderite. The decrease in $\Delta G^0$ with the rise in temperature shows an increase in feasibility of adsorption at higher temperatures [42]. The value of $\Delta H^0$ for As(III) adsorption is 81.7 kJ mol$^{-1}$, being much higher than that for As(V) adsorption on the synthetic siderite [30]. The positive value of $\Delta H^0$ indicates that the adsorption reaction is endothermic in nature. The positive values of $\Delta S^0$ reflect the affinity of the synthetic siderite for As(III) and suggest some structural changes during the interaction between As(III) and the synthetic siderite [43]. Ho and Ofomaja [33] have suggested that the positive value of $\Delta S^0$ should show increasing randomness at the solid–liquid interface during adsorption of Pb(II) on palm kernel fibre.

3.5. Effects of co-existing anions and background

The results of effects of competing anions (such as NO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$ or SiO$_3^{2-}$) are shown in Table 4. For all the batches, As adsorption ranges between 460 and 490 µg g$^{-1}$, showing that the presence of competing anions has no significant effect on the removal of As(III); NO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$ or SiO$_3^{2-}$ (with element concentration less than 20 mg/L) does not significantly compete with...
As(III) for adsorption sites of the synthetic siderite. It would imply that the adsorption of As(III) onto the synthetic siderite is mainly specific adsorption. Other investigation has showed that SiO$_3^{2-}$ significantly reduces the total quantity of As(III) adsorbed because of the competition of adsorption sites on the surface of goethite [15]. However, Roberts et al. showed that the presence of 30 mg L$^{-1}$ Si (as SiO$_3^{2-}$) leads to a moderate decrease of As(III) removal with Fe(III) addition, while it does not affect removal with Fe(II) addition [44]. They found P (as PO$_4^{3-}$) as the main factor limiting removal of As(V) and As(III).

Most high As groundwater had P concentrations ranging from <0.1 to 4.14 mg L$^{-1}$ and Si concentrations from 3.3 to 16.9 mg L$^{-1}$ in China [25,45,46], which are lower than concentrations of P and Si investigated in the study. Furthermore, As-enriched groundwater is generally dominated by As(III), up to 96% of total As [25]. It indicates that the co-existing anions would have no significant constraint on As removal in case that the adsorbent is applied to remove As from high As groundwater.

In contrast, the presence of competing anions has adverse effect on As(V) removal by the synthetic siderite, with Si and P being the major limiting factors [30]. It was observed that an increase in Si from 0.5 to 10 mg L$^{-1}$ led to a decrease in removal efficiency from 98.44 to 93.75%, which amounts to a 5% decrease in As(V) adsorption [30].

Background electrolyte concentration (1–100 mmol L$^{-1}$ NaCl) does not affect the adsorption of As(III). The adsorption was kept around 490 μg g$^{-1}$ from As(III) solution with 1–100 mmol L$^{-1}$ NaCl of the background electrolyte (data not shown). The same phenomena were found when the material was used to adsorb As(V) from aqueous solution [30]. It suggests that the synthetic siderite should be effective for As removal from high As groundwater with high total dissolved solid (~5850 mg L$^{-1}$), which has been widely found in China [25].

### 3.6. Mechanisms of As removal

The FESEM images of pristine and used materials are shown in Fig. 5. For the pristine material, there is a relatively rough and loosen surface with small cracks (Fig. 5a). It is noted that many spherical particles (~100 nm diameter) are presented on the surface of the pristine adsorbent, which are expected to be siderite crystals. The used synthetic siderite (Fig. 5b and c) is found to be covered by crystalline substances, being generally different from the pristine material in surface morphology. The scaly particles are presented on the surface of the adsorbent having adsorbed As(III) at 25 °C (Fig. 5b), which are believed to be lepidocrocite. In comparison, the adsorbent having adsorbed As(III) at 45 °C is covered with needle-like substances (Fig. 5c), which are believed to be goethite. It indicates that transformation of mineral phase from siderite into lepidocrocite and goethite has taken place during As(III) adsorption, as shown in chemical formulae (Eqs. (9) and (10)).

\[
\text{FeCO}_3 + \text{H}_2\text{O} \leftrightarrow \text{Fe}^{2+} + \text{HCO}_3^{-} + \text{OH}^- \tag{9}
\]

\[
2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \leftrightarrow 2\text{FeOOH} + 4\text{H}^+ \tag{10}
\]

The mineral transformation is consistent with thermodynamic results. It has been found that siderite has mostly been changed into goethite and lepidocrocite after the synthetic siderite was used for As(V) removal [30]. These Fe-hydroxide minerals have a high affinity for As, contributing to the high As(III) adsorption capacity. Bonding of As(III) with lepidocrocite or goethite is shown.

![Fig. 5. SEM images (a–c) and energy-disperse spectra (d, e) of the adsorbent before and after As(III) adsorption (a and d: the pristine material; b: the adsorbent having adsorbed As(III) at 25 °C; c: and e: the adsorbent having adsorbed As(III) at 45 °C).](image-url)
as Eq. (11).

$$2 \equiv \text{FeOOH} + H_3\text{AsO}_3 \leftrightarrow (\equiv \text{FeO})_2\text{HAsO}_3 + 2H_2O$$

(11)

≡FeOOH represents one reactive surface hydroxyl group bound to the mineral surface. In this reaction, arsenite oxyanion replaces two singly coordinated surface OH groups to form binuclear bridging complexes. The formation of goethite at 45° C batches shows that the elevation of temperature is propitious to the stability of Fe hydroxide minerals [47]. Energy-disperse spectra of the adsorbent before and after As(III) adsorption (Fig. 5d and e) shows that there is a significant increase in As content on the surface of the materials after adsorption.

Arsenic K-edge XANES spectroscopy was used to determine the redox state of As after adsorption. The XANES spectra exhibit a well-resolved edge structure with an adsorption maximum at 11874.0 eV and 11877.6 eV, corresponding to As(V) and As(III), respectively (Fig. 6). XANES spectra indicate that As occurs as both As(V) and As(III) in the As adsorbed-materials in the batches with contact time of 180 min at initial solution pH 7.0 at 25 °C and initial As concentrations of 5.0, 10.0, 20.0 and 40.0 mg/L. The As(V) is the major species for all the materials, which accounts for more than 70% of total As. After completion of As adsorption, the coexistence of As(V) and As(III) was also found on the Fe⁶⁺ surface [48].

Fig. 6 also indicates that the fraction of oxidized As(III) increases with the decrease in As(III) concentration. Ona-Nguema et al. also observed that the oxidation of As(III) in As-sorbed magnetite samples increased when decreasing the As(III) concentration in the magnetite-As(III) solution batches with O₂-renewed/limited conditions [49]. It suggests that the siderite substrate is involved in the oxidation reaction. Since our experiments were carried out in oxic conditions, molecular oxygen is supposed to be involved in the oxidation reaction.

Although it was found that As(III) forms a weak outer-sphere complex on siderite in anaerobic condition [18], the adsorption mechanisms seem to be different in our experimental investigations (the aerobic condition). Since lepidocrocite and goethite are present in the As-adsorbed materials, these newly formed minerals are expected to play an important role in removing As from solution. Spectroscopic evidence suggests that As(V) predominantly forms inner-sphere bidentate surface complexes with goethite [50] and lepidocrocite [51]. Arsenic(III) forms dominantly bidentate binuclear corner-sharing sorption complexes on goethite and lepidocrocite with a minor amount of monodentate mononuclear cornersharing complexes [52]. Farquhar et al. showed that both As(III) and As(V) formed inner sphere bidentate surface complexes on both goethite and lepidocrocite [53]. An FTIR spectroscopic study supported inner-sphere complexation of both As(V) and As(III) on goethite [54]. However, Sverjensky and Fukushi suggested that As(III) adsorption on Fe oxides forms both inner- and outer-sphere complexes and their relatively importance depends on experimental conditions [55].

4. Conclusions

This study has investigated the behaviors and mechanisms of As(III) removal by synthetic siderite. The following conclusions could be drawn:

1. The adsorption kinetics can be better explained by the pseudo-second order rate model than the first order rate model. Arsenic(III) adsorption kinetics is dependent on reaction temperature. At higher temperature, As(III) shows higher removal rates.

2. Although Langmuir isotherm better describes As(III) adsorption on the synthetic siderite at relatively high temperature (55 °C), Freundlich isotherm yields a better fit to the experimental data at low temperatures (25–45 °C). The maximum adsorption capacity at 25 °C is around 9.98 mg g⁻¹.

3. The thermodynamic study confirms the feasibility of the process and the spontaneous nature of As(III) adsorption. Arsenic adsorption increases with an increase in reaction temperature, indicating that the adsorption reaction is endothermic in nature. It indicates the affinity of the synthetic siderite for As(III) and some structural changes during the interaction between As(III) and the synthetic siderite.

4. The As(III) removal is independent on solution pH between 3.0 and 9.6, which is of great advantage in practical application. The presence of SO₄²⁻, NO₃⁻, PO₄³⁻ and SiO₃²⁻ has no significant effect on the adsorption of As(III) on the adsorbent, indicating that they do not compete with As(III) for adsorption sites on the surface of the adsorbent.

5. Arsenic mainly occurs as As(V) in the As-adsorbed materials, the fraction of which increases with the decrease in As(III) concentration. The formation of Fe hydroxide minerals confirms that oxidation and adsorption of As(III) is the main mechanism of As(III) removal by the synthetic siderite. According to the current price of synthetic siderite (about $300/t) and adsorption capacity of 4.0 mg/g, the cost for treatment of 500 µg/L As water would be around $0.04/t. The presented results have confirmed the potential of synthetic siderite as an efficient adsorbent for As removal from aqueous solution.

Acknowledgements

Funding for this study has been provided by the Natural Science Foundation of China (No. 40872160), the Program for New Century Excellent Talents in University (No. NCET-07-0770), the Cultivation Fund of the Key Scientific and Technical Innovation Project, Ministry of Education of China (No. 708012), and the National Key-technologies R&D Program (No. 2006BAJ08004) of the 11th 5-Year Plan of the People's Republic of China. The authors would like to thank beamline BL14W1 (Shanghai Synchrotron Radiation Facility) for providing the beam time.

References


