XANES evidence of arsenate removal from water with magnetic ferrite

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A B S T R A C T
ArSENic (As) in groundwater and surface water is a worldwide problem possessing a serious threat to public health. In this study, a magnetic ferrite, was synthesized and investigated for its As(V) removal efficiency. The adsorption of As(V) by magnetic ferrite exhibited an L-shaped nonlinear isotherm, suggesting limiting binding sites on the adsorbent surface. The As K-edge X-Ray Absorption Near-Edge Structure (XANES) revealed that the adsorbed As(V) on ferrite was not reduced to more toxic As(III) by Fe2+ in the ferrite structure. The maximum As adsorption capacity of ferrite was 14 mg/g at pH 3 and decreased with increasing pH due to enhanced electrostatic repulsion between As(V) and the adsorbent surface. Desorption of As(V) using six different acid and salt solutions showed that the desorption rate decreased in an order of H3PO4 > Na3PO4 > H2SO4 > Na2SO4 > HCl > HNO3. These results suggest that magnetic ferrite without surface modification is an effective adsorbent for removing As(V) from water, which was confirmed by the effective removal of As(V) from contaminated groundwater using this material. The used material can then be recovered using a magnet because of its paramagnetism; the adsorbed As(V) on the material can be recovered using H3PO4 or Na3PO4 solutions.

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1. Introduction

Arsenic (As) contamination is threatening water supplies in many countries (Mohan and Pittman, 2007), especially in Southern Asia (Charlet and Polya, 2006; Polizzotto et al., 2008). The anthropogenic sources of As include the waste and wastewater of various industries utilizing As and the materials used in agricultural production, such as herbicide and wood preservative (ATSDR, 2000; Mohan and Pittman, 2007). In addition to man-made pollutants, elevated levels of As in surface waters and groundwater also occur naturally in certain areas of the world as a result of leaching from As-bearing minerals (Charlet and Polya, 2006; Polizzotto et al., 2008). Arsenic is highly carcinogenic after long-term or high-dose exposure. The occurrence of As in water supplies can pose a deleterious impact on public health. Thus, developing techniques to remove As from contaminated water is an important task for healthy living.

The common treatment techniques for removing As from contaminated waters include membrane filtration (Heimann and Jakobsen, 2007; Iqbal et al., 2007; Fogarassy et al., 2009), precipitation (Jia et al., 2006; Janin et al., 2009; Xu et al., 2010), coagulation (Parga et al., 2005; Baskan and Pala, 2010; Ingallinella et al., 2011), and adsorption (Clifford, 1999; Opiso et al., 2009; Mamindy-Pajany et al., 2011). The adsorption method is considered more advantageous over others because of its removal efficiency, treatment cost, and ease in equipment handling. Because the oxyanions of As have relatively high affinity to Al and Fe oxides, there have been many studies proposing to use these oxide minerals to remove As in water (Mohan and Pittman, 2007). According to Edwards (Edwards, 1994), adsorption of arsenate and arsenite onto Fe and Al oxides ranged from 0.04 to 0.7 mols per mol of oxide, depending on the pH in the solutions and surface area of oxides. Meanwhile, to increase the adsorption capacity, nano-sized oxides are often used. The major drawback of using nano-materials in water treatment is its difficulty to remove the used materials through filtration, centrifugation and sedimentation.

In this study, the As(V) removal was investigated by using magnetic ferrite. Ferrite is a magnetic Fe oxide with a spinel structure containing both Fe2+ and Fe3+. The As(V) removal capacity of a ferrite was reported to be 1.575 mg/g (Parsons et al., 2009) and 3.70 mg/g (Chowdhury and Yanful, 2011). To achieve a better removal efficiency of As from waters, previous studies also focused on different preparations or surface modification of ferrite. However, the surface modification or coating processes in
preparing the materials imply an extra cost of applying them to treating As-containing water and wastewater. Thus, in this study, magnetic ferrite was synthesized without any modification and investigated for its As(V) adsorption capacity. The adsorption capacity of magnetic ferrite is expected to be better than its counterpart with a large crystal size due to its increasing surface area available for As adsorption. After treating As-containing water, this magnetic material can be recovered using an external magnetic field to avoid the difficulty in separating the material using traditional methods, such as centrifugation and filtration. Thus, the application of this magnetic material to treating As-containing water is expected to be more rapid and cost-effective. The objectives of this study were to investigate the effects of pH, contact time, and adsorbent dosage on the As(V) removal of magnetic ferrite and the possibility of regenerating the used material. The information provided by this study is essential for applying magnetic ferrite to further development of effective and safe methods for scavenging and recovering As(V) in water.

2. Material and methods

2.1. Synthesis of magnetic ferrite

Magnetic ferrite was synthesized using a hydrothermal method. 27.8 g of reagent grade FeSO₄·7H₂O was dissolved into 1000 mL water and the pH of the solution was subsequently adjusted to 8.0 by adding 0.1 M NaOH and 0.1 M HNO₃. Under continuous air purging (flow rate = 3 L/min), this synthesis process proceeded at 80 °C for 60 min while the pH of the solution was maintained constant at 8.0. The corresponding reaction is described as Eq. (1).

\[ 3\text{Fe}^{2+} + 6\text{OH}^- + 1/2\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4 + 3\text{H}_2\text{O} \]  

(1)

The synthesized product was collected using a magnetic separation method by taking advantage of its magnetism. The ferrite product was then washed with de-ionized water several times until the pH of the solution reached 7. The solid was then dried at 50 °C for 24 h in an oven and stored for further tests.

2.2. Characterization of ferrite

The synthesized ferrite sample was characterized using XRD (D8 Advance, Germany) with a graphite monochromatic copper radiation over the 2θ range of 20–80°. The BET surface area was determined using an ASAP 2010 analyzer (Micromeritics, USA) and N₂ adsorption at 77 K. The surface morphology and particle size were examined by scanning electron microscopy (JSM-6330J, Japan). The saturation magnetization of the synthesized ferrite was measured using a Superconducting Quantum Interference Device (SQUID, MPMS-XL7, Quantum Design, USA) at 27 °C.

The point of zero charge (pzc) determination was carried out according to the procedures described by Smiciklas et al. (2000). Briefly, aliquots of 0.1 M KNO₃ were prepared in a series of flasks and the pHs of the aliquots were adjusted to values ranging from 2 to 12 using 0.1 M KOH or HCl solution. The ferrite samples were then added into each of the flasks to have a solid-to-solution ratio of 1:200 (w/w). The suspensions were allowed to equilibrate for 24 h in a shaker thermostated at 27 ± 1 °C. Then, the suspensions were magnetically separated from the aqueous phase by using a magnet with 4000 Gauss and the pH values (pHₑ) of the residual solutions were measured using a pH meter (WalkLAB TI 9000, TRANS instruments, Singapore). For each sample, the values of the final pH (pHₑ) were plotted against the values of the corresponding initial pH (pHᵢ). The experimental pHₑ at the stable values was defined to be the PZC for the sample.

2.3. As(V) adsorption

As(V) adsorption experiments were conducted using the batch method. Ten mL of 10 mg/L As(V) solutions were added into 15 mL lid tubes containing 0.05 g magnetic ferrite. To investigate the effect of pH on the As(V) adsorption of ferrite, the pH of the As(V) solutions were controlled at 2.4 ± 0.1, 3.0 ± 0.1, 4.0 ± 0.1, 5.0 ± 0.1, 6.0 ± 0.1, 7.0 ± 0.1, 8.0 ± 0.1, 9.0 ± 0.1, 10.0 ± 0.1, 11.0 ± 0.1, 12.0 ± 0.1 by adding 0.1 M NaOH or 0.1 M HNO₃ solution. The lid tubes were then put on a rotary shaker with a rotating speed of 30 rpm and the temperature was maintained at 27 ± 1 °C. The solid and liquid phases were magnetically separated using a magnet with 4000 Gauss. The As concentrations in the supernatant were determined by ICP-MS (Element XR, Germany). The adsorbed amount of As(V) on the ferrite was determined using the differences between the initial and equilibrium As concentrations.

2.4. As K-edge XANES analysis

As K-edge X-ray Absorption Near-Edge Structure (XANES) analysis was conducted at the Beamline 17C in the National Synchrotron Radiation Research Center (NSRRC) in Hsin-Chu, Taiwan. Samples were fixed onto an aluminum holder sealed with Kapton tape. The As K-edge XANES spectra of the samples were obtained on fluorescent mode using a lytle detector with a 6-m germanium filter and a set of Soller slits. All spectra were calibrated to the edge of metallic As at 11,867.0 eV. The scans for each sample were averaged, followed by background removal and normalization. The XANES spectra of NaAsO₂ and Na₂H₃AsO₄ chemicals (J.T. Baker, Inc.) were also obtained to serve as the reference standards for the As(III) and As(V) oxidation states.

2.5. As(V) desorption

Desorption experiments were conducted using six different acid and salt solutions (HNO₃, HCl, H₂SO₄, Na₂SO₄, H₃PO₄, Na₃PO₄) with a concentration of 0.1 M. Magnetic ferrite was first reacted with 10 mg/L As(V) solution at pH 3. Subsequently, the ferrite samples were washed with de-ionized water several times to remove excessive salts and the acid or salt solution was added into the sample to initiate the desorption process. The suspensions were shaken for 30 min, and the ferrite solids were then separated from the solutions using a magnet with 4000 Gauss. The desorption efficiency was calculated from the amount of As released into the solutions.

3. Results and discussion

3.1. Characterization of adsorbent

Fig. 1a displays the SEM of the synthesized ferrite, showing that the primary particle size ranged from 30 to 90 nm. This result confirms that the synthesized ferrite is a nano-scaled adsorbent. The XRD pattern of this material showed the diffraction peaks at the d-spacings of 2.966, 2.530, 2.422, 2.098, 1.713, 1.615, 1.483, and 1.280 Å (Fig. 1b), which match well with those of magnetite (JCPDS file number 03-065-3107). No other crystalline phases were detected in the XRD pattern. The BET surface area, pore volume, and average pore diameter of the adsorbent were determined to be 40.3 m²/g, 0.07 cm³/g, and 15.41 Å respectively. The point of zero charge (PZC) of the synthesized ferrite was around 7.1 (Fig. S1), determined based on the procedure described in Smiciklas et al. (2000). This is consistent with the value measured by zeta sizer apparatus reported by Zhang et al. (2010). The saturation magnetization of synthesized nano-ferrite was determined to be 82.53 emu/g (Fig. S2). No remanence was detected in
the sample, confirming that this synthesized nano-ferrite was superparamagnetic.

3.2. Effect of pH on As(V) adsorption

The As(V) adsorption kinetics on ferrite at pHs ranging from 2.4 to 12 are shown in Fig. 2. The amount of removed As(V) initially increased rapidly with time. When the pH was lower than 7, the residual As(V) concentration reached a value close to zero or below detection limit in 240 min, indicating a fast and complete removal of As(V) at these pHs. An increase in pH resulted in a decrease in the As(V) adsorption rate and a substantial reduction occurred at pH > 10. At pH 11 and 12, the residual As concentrations were 4.76 and 7.74 mg/L respectively, even after 1440 min. Thus, the nano-ferrite was more effective in removing As(V) at lower pH.

The effect of pH on As(V) adsorption arose apparently from the charge properties of both As(V) and ferrite. The dissociation constants $pK_{a1}$, $pK_{a2}$ and $pK_{a3}$ of H$_3$AsO$_4$ are 2.1, 6.7 and 11.2 respectively. Depending on the pH value in solution, arsenate ions exist as different ionic species (i.e., H$_2$AsO$_4^-$, HAsO$_4^{2-}$, and AsO$_4^{3-}$) (Smedley and Kinniburgh, 2002). On the other hand, the surface of the adsorbent subjected to protonation/deprotonation, is depending on the solution pH. As indicated by the PZC of ferrite (i.e., 7.1), the net surface charge of ferrite at pH < 7.1 is positive, which is beneficial for adsorbing the anionic As(V) species (i.e., H$_2$AsO$_4^-$ and HAsO$_4^{2-}$ in the pH range of 2.1–7.1). This explains the high As uptake of the magnetic ferrite in acidic conditions. An increase in pH resulted in a buildup of negative charges on both adsorbent and adsorbate, leading to an enhanced electric repulsion between them. Consequently, the dramatic decreasing in As(V) adsorption was observed at high pH. Similar results were also found by Yean et al. (2005) and Zhang et al. (2010).

As indicated in Fig. 2, the adsorption equilibrium was established within 240 min under the selected conditions. The 240-min agitation time was therefore chosen when obtaining adsorption isotherms. Fig. 3 demonstrates the As(V) adsorption isotherms of magnetic ferrite at 27°C and at pH 3, 7 and 11. All the isotherms were L-shaped, suggesting the reaction is via surface adsorption with limited sites on the ferrite surface available for As(V). As more sites were occupied by As(V), the ferrite surface became increasingly difficult for As(V) adsorption. With these characteristics, the adsorption isotherms were analyzed by the Freundlich (1906) and Langmuir (1918) models. Detailed parameters of the adsorption isotherm models for As on magnetic ferrite were shown in Table 1 and the As(V) adsorption capacities were determined to be 14.35, 10.12 and 4.88 mg/g at pH 3, pH 7, and pH 11 respectively.

In Table S1, the As adsorption capacity of ferrite was compared with those of Fe$_3$O$_4$ and other adsorbents (Thirunavukkarasu et al., 2003; Sahiner et al., 2011; Zhang et al., 2010; Chowdhury and Yanful, 2010; Wu et al., 2011; Tu et al., 2012). Although the experimental conditions such as solution/adsorbent ratio used may vary.

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**Fig. 1.** (a) Scanning electron micrograph (SEM) and (b) X-ray diffraction pattern of synthesized ferrite.

**Fig. 2.** Effect of pH on As(V) adsorption of magnetic ferrite as a function of time at 27°C (Condition: Initial As(V) concentration = 10 mg/L, Fe$_3$O$_4$ = 0.05 g, volume = 10 mL, rotating speed = 30 rpm).

**Fig. 3.** As(V) adsorption isotherms of magnetic ferrite at pH 3, 7 and 11 and at 27°C (Condition: Fe$_3$O$_4$ = 0.05 g, volume = 10 mL, rotating speed = 30 rpm).
largely, the results indicate that ferrite is a very useful adsorbent for As(V) uptake from aqueous solution. After As(V) is adsorbed on the surface of ferrite, the Fe\(^{2+}\) sites in the ferrite structure may potentially reduce As(V) to As(III), which is more toxic and highly mobile in the environment (Smedley and Kinniburgh, 2002). Especially, the reduction of As(V) more likely occurs at lower pH because decreasing pH can result in an increase in the redox potential of the As(V)/As(III) couple. Thus, to investigate the possibility of this unfavorable As(V) reduction on the ferrite surface, the oxidation state of As adsorbed on magnetic ferrite at pH 3 was determined using As K-edge XANES (Fig. 4). The XANES of NaAsO\(_2\) and Na\(_2\)HAsO\(_4\) used as the standards of As(III) and As(V) respectively, were also shown for comparison. The XANES spectrum of As(III) had an absorption edge at 11,869.0 eV while that of As(V) was at 11,872.8 eV. For the ferrite sample containing 0.6, 2.0 and 2.8 mg/g As, the absorption edges all occurred near 11,873 eV. Because we saw no apparent down-shift of the edge in the XANES spectra for As(V) adsorbed on ferrite, we concluded that As(V) was the predominant oxidation state of As adsorbed on ferrite and no reduction of As(V) to As(III) occurred on the surface of ferrite.

3.3. Effect of adsorbent dosage on As(V) adsorption

Examination of Fig. 2 suggests that the adsorbent dosage (i.e., 5 g/L) was ample for removing 10 mg/L As(V) at pH < 7 because all As(V) concentrations in these pHs decreased to zero or detection limit (2.3 \(\mu\)g/L) after the 240-min reaction. In order to find the optimum adsorption dosage, the amount of nano-ferrite added to react with 10 mg/L As(V) solution was varied. As shown in Fig. 5,

<table>
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<th>pH</th>
<th>(K_F)</th>
<th>(n)</th>
<th>(R^2)</th>
<th>(K_L)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
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<td>8.190</td>
<td>0.9942</td>
<td>14.35</td>
<td>0.016</td>
</tr>
<tr>
<td>7</td>
<td>5.717</td>
<td>8.613</td>
<td>0.9505</td>
<td>10.12</td>
<td>0.044</td>
</tr>
<tr>
<td>11</td>
<td>1.288</td>
<td>3.670</td>
<td>0.9405</td>
<td>4.88</td>
<td>0.524</td>
</tr>
</tbody>
</table>

Note: \(K_F\) and \(n\) are Freundlich constants that are related to the adsorption capacity and adsorption intensity respectively. \(q_m\) is the maximum adsorption capacity (mg/g); \(K_L\) is the Langmuir constant.

Fig. 4. As K-edge XANES spectra of (a) As(III) and (b) As(V) standards, and As(V) adsorbed on magnetic ferrite with the adsorbed amounts of (c) 0.6, (d) 2.0 and (e) 2.8 mg/g.

Fig. 5. Effect of adsorbent dosage on the As(V) removal rates of magnetic ferrite at pH (a) 3, (b) 7 and (c) 11 and at 27 °C (Condition: volume — 10 mL, rotating speed — 30 rpm).
the increase in the adsorbent dosage had a positive effect on As(V) removal. For example, with the adsorbent dosage of 0.25 g/L, the residual As(V) concentration was 6.91 mg/L after reaching adsorption equilibrium at pH 3 (Fig. 5a). As the adsorbent dosage was increased to 0.5, 1 and 2 g/L, the residual As(V) concentrations after reaching adsorption equilibrium were 5.43, 3.61 and 1.42 mg/L respectively. A complete removal of As(V) was observed with the adsorbent dosage of 5 g/L (Fig. 5a). The extent of As(V) removal with the same adsorbent dosages generally decreased as the pH was increased (Fig. 5). At pH 7, a complete removal of As(V) could be achieved with the adsorbent dosage of 5 g/L (Fig. 5b). The removal rate significantly decreased as the pH was increased 11 (Fig. 5c) and, even with the highest adsorbent dosage, no complete removal of As(V) was achieved. As mentioned above, this negative effect of increasing solution pH is mainly due to the increasing repulsion between the As(V) and ferrite surface at higher pH.

3.4. As(V) desorption

To investigate the feasibility of regenerating used magnetic ferrite, desorption experimentation was carried out for the adsorbent after As(V) adsorption. Fig. 6a shows the effect of six kinds of acid or salt buffers on desorption efficiency of As(V) with a desorption time of 30 min. The recovery efficiencies of As(V) using different solutions were in the order of $\text{H}_3\text{PO}_4 > \text{Na}_3\text{PO}_4 > \text{H}_2\text{SO}_4 > \text{Na}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$, with the corresponding efficiencies of 83.52%, 63.26%, 52.80%, 43.34%, 1.56%, 0.61% respectively (Fig. 6). Meanwhile, with the same anion in the desorption solutions (e.g., $\text{H}_3\text{PO}_4$ vs. $\text{Na}_3\text{PO}_4$), the As(V) recovery was more effective in acidic (i.e., 83.52%) than in alkaline conditions (i.e., 63.26%). The same trend was also found in the case of $\text{H}_2\text{SO}_4$ and $\text{Na}_2\text{SO}_4$ (Fig. 6).

Because phosphate exhibited the best As(V) recovery rate among the anions under investigation, the effect of phosphate concentration on As(V) recovery was further investigated. As the concentration of $\text{H}_3\text{PO}_4$ or $\text{Na}_3\text{PO}_4$ solution was increased from 0.0125 M to 0.4 M, the amount of arsenic desorbed from ferrite increased (Fig. 6b). The As desorption could reach equilibrium within 30 min and the optimal As recovery rate in this system could reach 84% and 71% with 0.4 M $\text{H}_3\text{PO}_4$ and $\text{Na}_3\text{PO}_4$ solutions respectively. On the contrary, no As could be desorbed using $\text{Na}_3\text{PO}_4$ solution with a concentration $< 0.05$ M. This indicated that the strength of $\text{PO}_4^{3-}$ at low concentrations was not sufficient to desorb As(V) from the ferrite surface under alkaline conditions. After the desorption experiments, the nano-particles could be rapidly recovered from the solutions by a magnet because of their paramagnetism. This could facilitate the recovery of the magnetic nano-adsorbents.

3.5. Regeneration of $\text{Fe}_3\text{O}_4$

Four adsorption cycles were conducted to evaluate the reusability of the magnetic ferrite for the As(V) adsorption. In each cycle, the adsorbent was reused after $\text{H}_3\text{PO}_4$ treatment in the subsequent cycle. Fig. 7 demonstrates the As(V) adsorption efficiency during the four cycles assayed. The results revealed that As(V) removal efficiency could attain to 90.32% in all the four cycles. There was only slightly decreased after the first cycle then achieved a more stable state in the subsequent cycles. These results confirm that this adsorbent has high potential to be reused over many cycles at the given conditions.

3.6. As removal from As-contaminated groundwater

In order to investigate the feasibility of magnetic nano-adsorbents in real groundwater, six As contaminated groundwater sources were sampled and used to test the As removal performance of magnetic ferrite. Table S2 lists the chemical compositions of these six real samples. The As concentration ranged from 21.6 to 84.3 $\mu$g/L; these values were higher than the maximum...
Amount of adsorbent – 0.05 g Fe\textsubscript{3}O\textsubscript{4}. Volume – 10 mL. Temperature – 27 °C.

The adsorption pH were operated at neutral (pH 6.84–7.65) and acidic (pH 1.61–3.30) conditions to compare the As removal efficiency.

4 Concentration before adsorption.
5 Concentration after adsorption.
6 b.d.: below detection limit (for As: 2.3 μg/L; Fe: 5.6 μg/L).

4. Conclusion

Magnetic nano-ferrite synthesized by a hydrothermal method without surface modification appeared to be an effective adsorbent for As(V). The results show that this adsorbent has a great potential for treating As-containing groundwater and can be recovered using an external magnetic field. Because the PZC of nano-ferrite was 7.1, it exhibited a better As(V) removal rate at low pH. It is thus recommended that this nano-ferrite be used at low-to-neutral pH as an adsorbent for As(V). The removal of As(V) using this material from alkaline waters and wastewaters may be significantly enhanced via pre-acidification of the waters.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2013.02.006.

References


