



Reduction of As(V) to As(III) by commercial ZVI or As(0) with acid-treated ZVI

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ABSTRACT

Zero-valent iron (ZVI) consists of an elemental iron core surrounded by a shell of corrosion products, especially magnetite. ZVI is used for *in situ* removal or immobilization of a variety of contaminants but the mechanisms for removal of arsenic remain controversial and the mobility of arsenic after reaction with ZVI is uncertain. These issues were addressed by separately studying reactions of As(V) with magnetite, commercial ZVI, and acid-treated ZVI. Strictly anoxic conditions were used. Adsorption of As(V) on magnetite was fast with pH dependence similar to previous reports using oxic conditions. As(V) was not reduced by magnetite and Fe(II) although the reaction is thermodynamically spontaneous. As(V) reactions with ZVI were also fast and no lag phase was observed which was contrary to previous reports. Commercial ZVI reduced As(V) to As(III) only when As(V) was adsorbed, i.e., for pH < 7. As(III) was not released to solution. Acid-treated ZVI reduced As(V) to As(0), shown using wet chemical analyses and XANES/EXAFS. Comparisons were drawn between reactivity of acid-treated ZVI and nano-ZVI; if true then acid-treated ZVI could provide similar reactive benefits at lower cost.

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1. Introduction:

High arsenic concentrations in groundwater have been reported throughout the world, notably in Bangladesh and Taiwan [1]. Arsenic in aquatic environments usually exists in inorganic forms as arsenate (As(V)) and arsenite (As(III)). As(III) is usually more mobile and toxic than As(V) although As(III) can also become immobilized in the presence of sulfide. Elevated arsenic concentrations in groundwater can occur due to reductive dissolution of ferric oxide sorbents and consequent reduction and mobilization of As(III), desorption of As(V) under alkaline pH conditions especially in the presence of phosphate or other competing adsorbates, or oxidation of sulfidic materials [1,2].

Zero-valent iron (ZVI) has been used to remove organic and inorganic contaminants including chlorinated solvents, nitrate, uranyl ion, chromate, lead, and arsenic [3,4]. ZVI can be incorporated into permeable reactive barriers or nano-ZVI (nZVI) can be injected into contaminated soils [5]. ZVI is also found in some point-of-use potable water treatment systems [6]. ZVI is usually reported to have a core-shell structure. The shell contains oxidized iron that is mostly magnetite and often with maghemite ($\gamma\text{-Fe}_2\text{O}_3$) or lepidocrocite ($\gamma\text{-FeOOH}$) [3,7–10].

ZVI immobilizes arsenic by adsorption of As(V) or As(III) onto iron corrosion products in the shell surrounding the elemental iron core and this is sometimes accompanied by reduction of As(V) to As(III) [11–14]. Detailed mechanisms have been reported for removal of many contaminants by ZVI. Fe(0), dissolved Fe(II), solid-bound Fe(II), and H_2 have been proposed as elementary reductants [3,9,15]. However there is still controversy about the mechanisms for removal of arsenic especially regarding redox reactions. The rate and extent of As(V) reduction by ZVI may depend on the experimental conditions. In different studies, 25% of initial As(V) was reduced to As(III) by nano-ZVI at neutral pH after 90 days [13,16], As(V) was partially reduced to As(III) by commercial ZVI at slightly basic pH after 60 days [17], and there was no As(V) reduction using iron wires [18]. It was also reported that As(III) was reduced to As(0) with acid-treated iron filings [19].

Magnetite is often observed to be a dominant component in the corroded ZVI shell. In an effort to identify mechanisms by which ZVI immobilized contaminants, Lago and co-workers [20,21] used mechanical grinding to produce a magnetite/ZVI reactant that reduced methylene blue, H_2O_2 , and Cr(VI). Other iron oxides ($\alpha\text{-Fe}_2\text{O}_3$, FeOOH, or $\gamma\text{-Fe}_2\text{O}_3$) mixed with ZVI were much less reactive. It was suggested that the semi-conductor behavior of magnetite was important for effective reduction of contaminants. The reactivity of magnetite may depend on whether the ZVI has been in contact with air. In this context White and Peterson [22] showed that magnetite reduced Cr(VI) at a much faster rate under anoxic conditions than under oxic conditions. It has also been shown that

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“stoichiometric magnetite” that is produced and maintained under strictly anoxic conditions has a Fe(II)/Fe(III) ratio close to 0.5 and is a stronger reducing agent than “non-stoichiometric magnetite” that has been produced or stored in the presence of O₂ resulting in a Fe(II)/Fe(III) ratio <0.5 [23]. Magnetite is a strong adsorbent for arsenate [24–26]. Magnetite in the presence of Fe(II) is theoretically capable of reducing arsenate to arsenite (discussed later in this paper) but to our knowledge there are no reports of As(V) reduction using magnetite. There are several previous studies dealing with the reduction of arsenate by ZVI but these were all conducted under oxic conditions that can result in the production of “non-stoichiometric magnetite”.

The objectives of this study were to identify the reaction mechanisms and reaction products when As(V) is remediated using ZVI. Experiments were conducted using three solid phases: (1) stoichiometric magnetite, (2) commercial ZVI, and (3) ZVI that had been acid-treated to disrupt the adherent layer of magnetite. Experiments were run under rigorously anoxic conditions [27]. The rate and extent of reactions were followed by analyzing for As(V) and As(III) in both dissolved and solid phases. The nature of the reduced arsenic species was also investigated using X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS).

2. Materials and methods

2.1. Materials and chemicals

Commercial ZVI (Alfa-Aesar, 99.2% Fe and ~0.3 mm diameter) was used as received and also after acid pre-treatment. Acid-treated ZVI was prepared by adding 50 mL 1 M HCl to 50 g commercial ZVI to dissolve the oxidized film [28]. The slurry was aerated for 2 h, washed 3 times with DI water, dried overnight at 80 °C, and stored in the anaerobic chamber. Commercial ZVI materials were also stored in the anaerobic chamber. Magnetite was prepared in the anaerobic chamber by mixing equal volumes of 4.0 mM FeCl₃ (1.08 g/L as FeCl₃·6H₂O) and 2.0 mM FeCl₂ (0.40 g/L as FeCl₂·4H₂O) and pH adjustment to 11 [24]. Settled precipitates were washed with deoxygenated water three times. XRD analysis showed that the sample was magnetite. No other solid phases were identified. Samples were completely dissolved in concentrated HCl and then analyzed for Fe(II) and Fe(III). The Fe(II)/Fe(III) molar ratio was 0.47, thus the magnetite was stoichiometric Fe₃O₄. All stock solutions were prepared in deoxygenated Milli-Q water in an anaerobic chamber (Coy Laboratory Products, Inc., 5% H₂ in N₂ with Pd catalyst). Deoxygenated water was prepared by bubbling 99.9% nitrogen gas while heating to 70–80 °C for at least five hours before transfer and storage in the anaerobic chamber.

2.2. Wet chemistry

All experiments were conducted in reactors that were connected to an O₂-trap (in the anaerobic chamber) to maintain <7.5 × 10⁻⁹ atm of O₂ [27,29] unless specified.

As(V) and the sum of As(V) + As(III) (after oxidation with 0.2 mM potassium iodate at pH 1) were determined by molybdenum blue colorimetric analysis [30]. Adsorbed arsenic was extracted with 5 M NaOH in the anaerobic chamber for 24 h. Separate experiments demonstrated that >98% of adsorbed As(V) or As(III) was recovered without change in oxidation state. The detection limit of As(V) by molybdenum blue analysis was ~1 μM.

Total Fe(II) plus Fe(III) was measured by adding 100 mM ascorbic acid to 1 g ZVI at pH 3 for 48 h, reducing iron oxides to Fe(II) [31], which was measured with ferrozine [32].

As(V)/magnetite experiments with fixed pH were performed in 250 mL bottles. After adding 100 mL of 0.65 mM As as Fe₃O₄ (0.15 g/L) the bottles were connected to the O₂-trap in the anaerobic chamber and were continuously shaken (VWR Model 3750 500 rpm). After 8 h, As(V) stock solution was injected to achieve 100 μM. Suspension samples (1.5 mL) were extracted by syringe and needle through the cap for subsequent measurement of dissolved and adsorbed As(V)/As(III) concentrations.

As(V)/magnetite experiments with variable pH were conducted in five polypropylene vials (30 mL). Twenty millilitre 0.65 mM magnetite suspension and As(V) stock solution to obtain 50 μM were added to each vial. The pH was adjusted with concentrated NaOH or HCl. The vials were placed in a dark box on a shaker in the anaerobic chamber for 48 h. Suspension samples were taken at intervals for determination of dissolved and adsorbed As(V) and As(III).

Reactions of As(V) and commercial or acid-treated ZVI were conducted in 30 mL polypropylene vials, with sequential additions of 2.0 g ZVI (100 g/L), 20 mL deoxygenated DI water, As(V) stock solution, and pH adjustment. Samples were handled as in the As(V)/magnetite experiments. Dissolved arsenic was determined after centrifugation (Eppendorf MiniSpin Microcentrifuge) of 1 mL samples. Adsorbed As(V) and As(III) were measured after NaOH extraction.

2.3. Characterization of solids

Magnetite was filtered using 0.2 μm Teflon membranes and the filter and deposits were dried in the anaerobic chamber at room temperature. Commercial and acid-treated ZVI were characterized without further treatment. XRD patterns were measured with a PANalytical Theta-2-Theta Powder Diffractometer using Cu Kα radiation at 60 kV and a PIXcel solid detector. SEM was performed using a FEI Quanta 200 scanning electron microscope. A WITec CRM200 confocal Raman spectroscopy configured with 514 nm laser excitation was used to record the Raman spectra. The laser power was kept below 0.5 mW to avoid sample degradation [33]. The laser was focused into a round spot with ~0.5 μm in diameter with a resolution of 1 cm⁻¹.

Samples for XANES and EXAFS analysis were prepared by reacting commercial ZVI (pH 8.5 ± 0.5) and acid-treated ZVI (pH 7) with 100 μM As(V) for 5 days. The samples were rinsed and dried, with all operations in the anaerobic chamber. Na₂HAsO₄·7H₂O and NaAsO₂ powders were used as As(V) and As(III) standards. Arsenic K-edge (11.868 keV) EXAFS spectra were collected on the bending magnet beamline (9-BM) at the advanced photon source (APS), Argonne National Laboratory using Si (1 1 1) monochromator crystals. Harmonics were rejected by use of an Rh-coated flat mirror in the experimental station. Energy was calibrated using a Ga foil by setting its K-edge energy to 10,367 eV. The beam was focused to a 1 mm diameter spot size using an Rh-coated toroidal mirror. The XAFS spectra were collected in fluorescence mode using a SII Vortex 4-element Silicon Drift Detector. An aluminum filter was placed before the fluorescence detector to suppress Fe fluorescence. Ten scans were collected and averaged.

XANES and EXAFS spectra were processed using Iffefit software (Athena and Artemis) [34]. A straight line to the pre-edge and a spline function to the post-edge region were used for background removal. XANES spectra were normalized to unity edge height. Fitting EXAFS data to retrieve structural information was performed using Artemis [34]. Data processing and fitted parameters are described elsewhere [35]. The As EXAFS oscillations $\chi(k)$ were weighted by k^2 and windowed between 2.5 < k < 10 Å⁻¹ using a Hanning window with $dk = 1.0$ Å⁻¹. The fits were to both real and imaginary parts of $\tilde{\chi}(R)$ in the region of 1.0 < R < 2.0 Å. The amplitude-reduction factor S_0^2 was determined by fitting two standards Na₂HAsO₄·7H₂O and NaAsO₂ [36,37]. Fitting included only

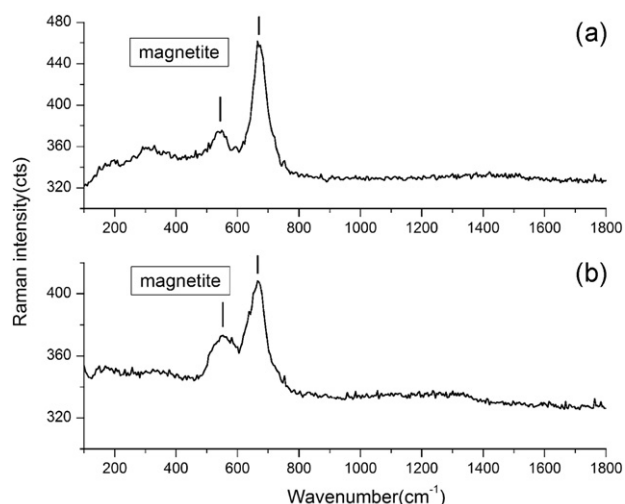


Fig. 1. Raman spectra of commercial ZVI and acid-treated ZVI: (a) commercial ZVI; (b) acid-treated ZVI.

one As–O path based on bond distance (R), coordination number (N), and the Debye–Waller factor (σ^2).

3. Results and discussion

3.1. Characteristics of commercial ZVI and acid-treated ZVI

Iron oxides (from ascorbic acid dissolution) constituted <0.2% (w/w) of commercial ZVI and >10% of acid-treated ZVI. Fig. 1 shows that magnetite was the only iron oxide phase detected by Raman spectroscopy (542 cm^{-1} and 671 cm^{-1}). Fig. 2 shows XRD results, confirming magnetite in acid-treated ZVI. Magnetite was not iden-

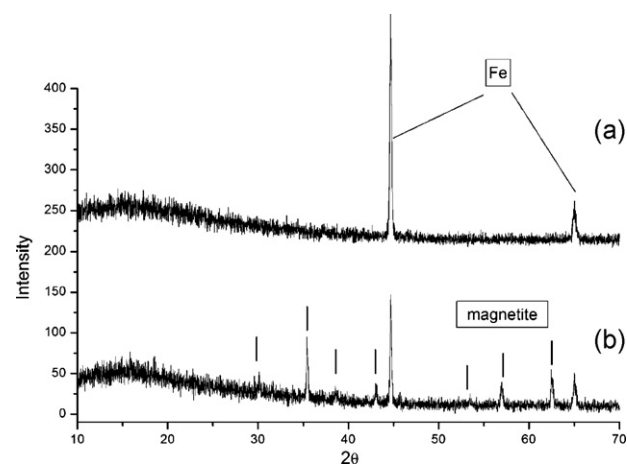


Fig. 2. X-ray diffraction spectra of (a) commercial ZVI and (b) acid-treated ZVI.

tified in the XRD pattern for commercial ZVI because it was below the detection limit ($\sim 3\%$ by weight) [7,38]. Others have reported that commercial ZVI has an oxide surface film [3,7,38,39] with an inner magnetite layer and an outer $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) layer [9]. SEM images in Fig. 3 show that commercial ZVI (a and b) had a smooth surface and acid-treated ZVI (c and d) had a more porous surface that was covered with $\sim 0.5\text{ }\mu\text{m}$ particles.

3.2. Adsorption of As(V) on magnetite

The first experiments were conducted with stoichiometric magnetite. Fig. 4a shows that removal of As(V) at pH 6.5 was fast, with half-time ($t_{1/2}$) for adsorption <1 h. The adsorption capacity was $\sim 0.08\text{ As(V)/Fe}_3\text{O}_4$ (mol/mol), similar to adsorption of As(V) onto magnetite under oxic conditions [24]. Desorption with 5M

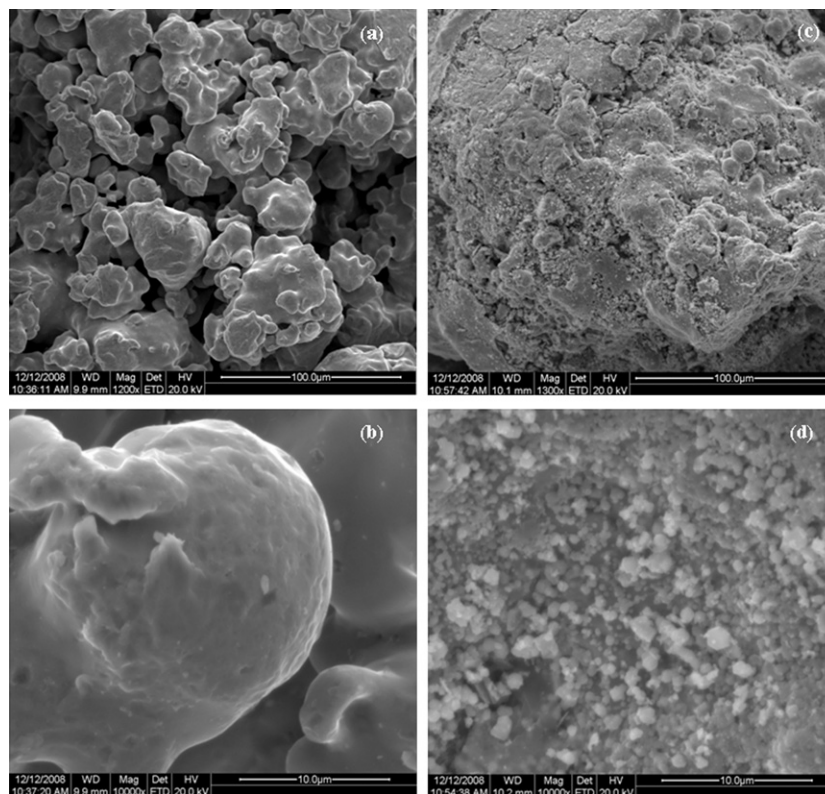


Fig. 3. SEM images of commercial ZVI and acid-treated ZVI at two magnifications: (a and b) commercial ZVI; (c and d) acid-treated ZVI.

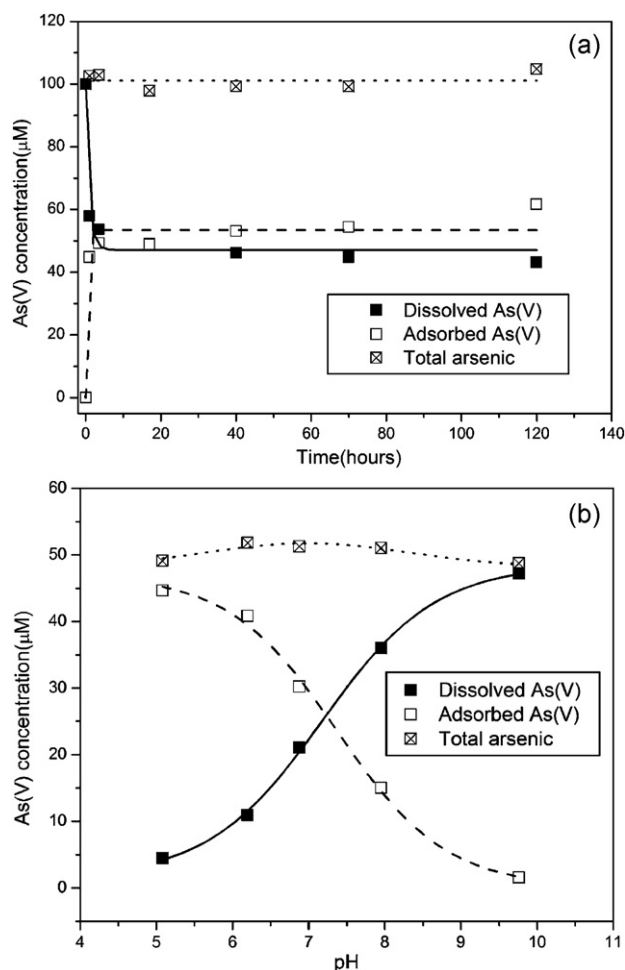


Fig. 4. As(V) adsorption on stoichiometric magnetite in an anoxic environment: (a) As(V) removal versus time at pH 6.5; (b) pH dependence of As(V) removal (As(V) = 50 μM, Fe₃O₄ = 0.65 mM, 25 days).

NaOH recovered ~100% recovery of arsenic from magnetite, all in the +5 valence. Fig. 4b shows the pH dependence of As(V) adsorption on magnetite. Adsorption of As(V) decreased at pH above the $pH_{zpc} = 6.6$ of pristine magnetite [40]. The pK_{a1} and pK_{a2} of H₃AsO₄ are 2.2 and 7.0. The anions H₂AsO₄⁻ and HAsO₄²⁻ are major dissolved species over the entire pH range for Fig. 4b. An electrostatic model was used by Dixit and Hering [41] to explain the adsorption of As(V)/As(III) on hydrous ferric oxides (HFO) and goethite. Surface species ≡FeH₂AsO₄, ≡FeHAsO₄⁻ and ≡FeAsO₄²⁻ (in the order of increasing pH) were proposed as the surface complexes formed from As(V) adsorption on HFO and goethite. The formation constants of the surface species have this order: $k(\equiv\text{FeH}_2\text{AsO}_4) > k(\equiv\text{FeHAsO}_4^-) > k(\equiv\text{FeAsO}_4^{2-})$, which is consistent with decreased As(V) adsorption with increasing pH. As(V) adsorption on magnetite formed similar inner-sphere complexes as on HFO and goethite [42] and similar adsorption fonts have been reported [24–26,42]. As(V) adsorption on magnetite under anoxic conditions in this study showed similar pH dependence as previously reported for oxic conditions.

All of the dissolved and adsorbed arsenic in the magnetite experiments was recovered as As(V), even when the experiment was conducted in the presence of excess dissolved Fe(II). Information about the arsenic oxidation state is shown in Fig. S1. Although we used stoichiometric magnetite (a stronger reducing agent than non-stoichiometric magnetite [22,23]), a rigorous anoxic

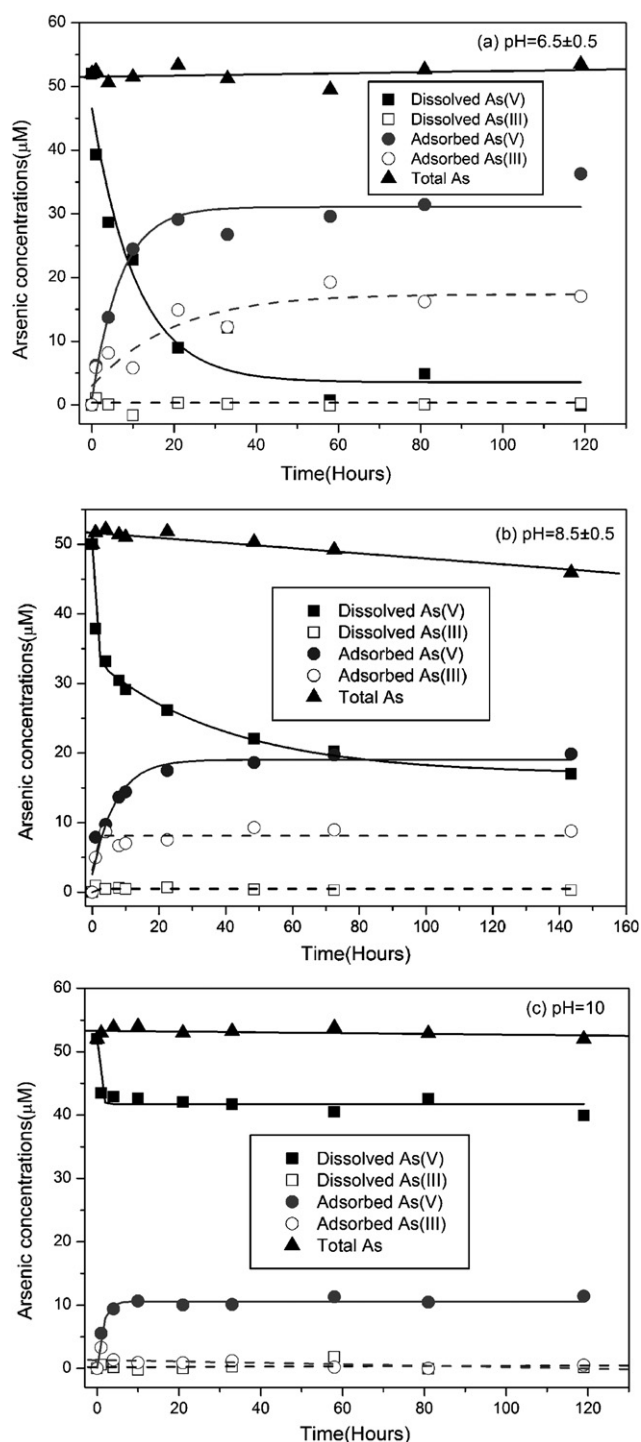


Fig. 5. As(V) adsorption and reduction to As(III) using commercial ZVI (2.0 g/0.02 L) in an anoxic environment: (a) pH = 6.5 ± 0.5; (b) pH = 8.5 ± 0.5; (c) pH = 10.

environment, and a stoichiometric excess of dissolved Fe(II), magnetite did not reduce As(V) at pH 5–10.

3.3. Reactions of As(V) with commercial ZVI

The results of experiments with As(V) and commercial ZVI at pH 6.5 ± 0.5, 8.5 ± 0.5 and 10 are shown in Fig. 5 in which concentrations of dissolved and adsorbed As(V) and As(III) are plotted against time. There was partial reduction of As(V) to As(III) at the two lower pH ranges and some loss of As(V) + As(III) at pH 8.5 ± 0.5.

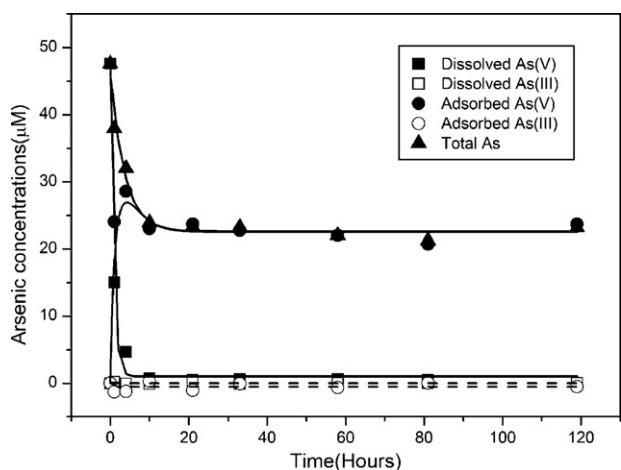


Fig. 6. As(V) adsorption and reduction to As(0) using acid-treated ZVI (2 g in 0.02 L) in an anoxic environment at pH 7. No As(III) was produced.

The $t_{1/2}$ for adsorption and for reduction to As(III) were <10 h at pH 6.5 ± 0.5 and at pH 8.5 ± 0.5 . Adsorption was very fast at pH 10 ($t_{1/2} < 1$ h) even though the extent of adsorption was less than for lower pH values. None of the As(III) was released back into solution, suggesting that the reduction occurred within the bulk magnetite or at the Fe(0)/magnetite interface.

Previous investigators reported slow reduction of As(V) with a 60–90 days lag time, which was probably due to less rigorous exclusion of O_2 in their experimental systems [13,17]. Dissolved oxygen (DO) could be an important factor that changes the reduction kinetics. It has been reported that As(III) could be oxidized to As(V) on iron oxides in the presence of O_2 through a Fenton-like reaction mechanism [43]. In order to study the effect of dissolved oxygen on As(V) reduction by commercial ZVI, additional experiments were conducted in which the closed reactors were removed from the anaerobic chamber after 5 days and placed on a shaker. As(III) was completely re-oxidized to As(V) within a few hours at pH 6.5, 8.5 and 10 by O_2 that diffused through the tightly attached screw caps. The results indicated that As(III) oxidation even with low DO was an important back-reaction that inhibits early observation of As(V) reduction by ZVI. The long incubation time observed by previous researchers was likely the time required for complete removal of DO due to direct or indirect reaction with ZVI. Care was taken in the current study to eliminate any O_2 in the reaction vials and consequently fast As(V) reduction kinetics were observed.

3.4. Reactions of As(V) with acid-treated ZVI

Fig. 6 shows the removal of As(V) using acid-treated ZVI at pH 7. Adsorption was very fast ($t_{1/2} < 1$ h) and there was no measurable dissolved arsenic after ~ 5 h. The concentration of As(V) decreased with time even though the colorimetric procedures demonstrated that there was no accumulation of As(III). These results led to the hypothesis that As(V) was reduced to As(0), which is a thermodynamically spontaneous reaction as shown in Fig. 7.

Reduction of As(V) to As(0) in the presence of acid-treated ZVI was confirmed by XANES. Fig. 8 shows the XANES spectra of the As(V) reaction products using commercial ZVI or acid-treated ZVI. The As(V) white line (first most intense absorption peak) was at 11,872.8 eV and the As(III) white line was at 11,869.5 eV. Both As(V)/ZVI samples had a white line at 11,872 eV, confirming the presence of As(V) species. Reaction between As(V) and commercial ZVI produced an As(III) shoulder at 11,870 eV. Although the XANES results are not quantitative, the spectrum was consistent

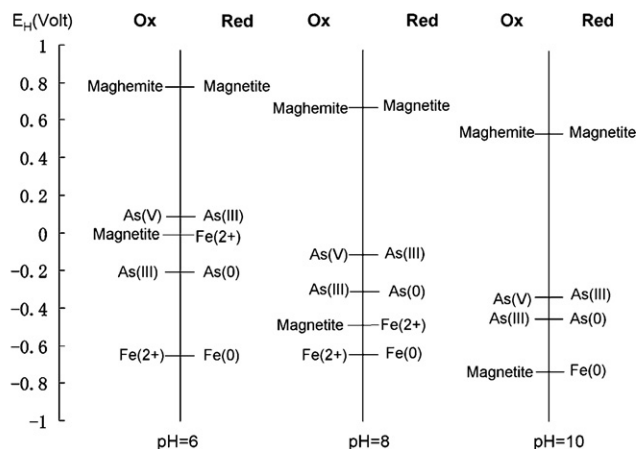


Fig. 7. pe -pH redox ladder of arsenic-ZVI system. Thermodynamic data were taken from V-miniteq (v2.51): $Fe^{2+} = 1$ mM, $As = 0.1$ mM. The redox ladder indicates Fe(0) can reduce As(V) or As(III) to As(0), and Fe(II) is not a dominant species for any pe conditions at pH 10.

with the previously observed 20% conversion of As(V) to As(III) at pH 8.5 ± 0.5 (see Fig. 5b).

The XANES spectrum for the reaction products of As(V) with acid-treated ZVI contained a shoulder near 11,865 eV. The binding energy for As(0) K electrons is 11,866.7 eV [44]. This result was consistent with reduction of As(V) to As(0) by acid-treated ZVI. To further evaluate this hypothesis, the first shell of the radial structure function (RSF) from Fourier-transformed EXAFS data was fitted with a theoretical model. Experimental data (solid line) and fitting results (dotted line) are compared in Fig. S2. The amplitude value was set to 0.91 based on the results from the As(V) standard. The data were not phase corrected. The fitting showed that there were 2.3 ± 0.5 oxygen atoms at the As–O first-shell inter-atomic distance of 1.69 Å. The corresponding Debye–Waller parameter (σ^2) is 0.0003 \AA^{-2} . Since the As–O coordination number is four for As(V), three for As(III), and zero for As(0) [45], the experimental result of 2.3 oxygen atoms is consistent with a mixture of As(V) and As(0). Thus the EXAFS data, the wet chemical analyses, and the XANES results all support the hypothesis that As(0) was produced due to reaction between As(V) and acid-treated ZVI.

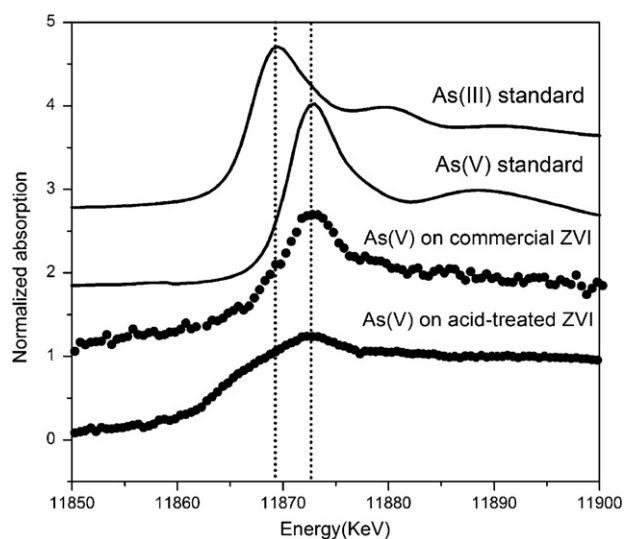


Fig. 8. XANES spectra at near-K α adsorption edge of As(V) (Na_2HAsO_4), As(III) ($NaAsO_2$), As(V)+commercial ZVI at pH 8.5 ± 0.5 , As(V)+acid-treated ZVI at pH 7.

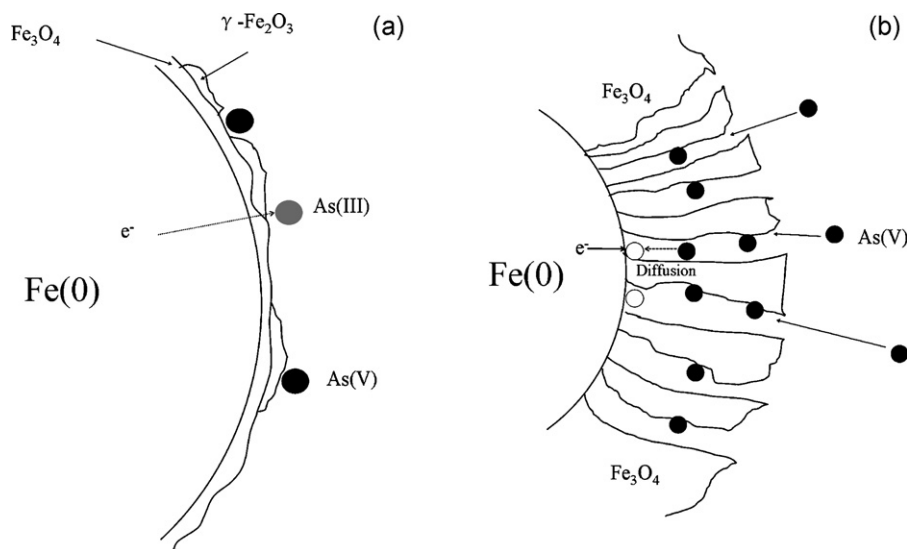


Fig. 9. Schematic mechanisms of As(V) adsorption/reduction on (a) commercial ZVI, and (b) acid-treated ZVI.

3.5. Mechanisms

The experimental findings demonstrated the following differences among magnetite, commercial ZVI, and acid-treated ZVI: (1) stoichiometric magnetite adsorbed As(V) but did not reduce As(V) even with a stoichiometric excess of dissolved Fe(II) although magnetite/Fe(II) is theoretically capable of reducing As(V) to As(III) at pH 6 and to As(0) at pH 8 and 10 as shown in Fig. 7; (2) commercial ZVI adsorbed As(V) and reduced As(V) to As(III) rapidly and without a lag phase although Fig. 7 shows that Fe(0) can reduce As(V) to As(0); and, (3) acid-treated ZVI adsorbed As(V) and partially reduced As(V) to As(0).

The physical structures of commercial ZVI and acid-treated ZVI and proposed mechanisms for As(V) removal are illustrated in Fig. 9. Commercial ZVI is covered with a continuous adherent film of magnetite which inhibits direct contact of As(V) with the Fe(0) core. Reducing species such as e^- , Fe^{2+} , H_2 , or H^\bullet [3] are produced by corrosion of the core and migrate through the magnetite shell to react with As(V). Magnetite is a semiconductor with conductivity 10^6 higher than other iron oxides [46] and it is possible that there is a potential gradient through the magnetite shell [20,21,47]. Using commercial ZVI, As(V) was partially reduced to As(III) at pH 6.5, reduced to As(III) and perhaps partially to As(0) at pH 8.5. As(V) was not reduced by commercial ZVI at pH 10 because the reaction is not thermodynamically spontaneous at that pH.

Acid-treatment of ZVI disrupted the adherent magnetite film, producing a massive and porous oxidized iron shell that could have allowed transport of As(V) to the Fe(0) core where the redox potential was low enough to produce As(0), as shown in Fig. 9. These observations were consistent with a study [48] in which nZVI reduced Ag(I), Cu(II), and Hg(II) to the zero valence but Zn(II) and Cd(II) were adsorbed without being reduced. The first group of metals have higher redox potentials and the second group have lower redox potentials than $Fe(II) \rightarrow Fe(0)$. The reaction products were consistent with predictions based on direct reaction of the metal cations with the ZVI core.

Acid-treated and nZVI have relatively massive and flocculated shells due to rapid precipitation [13] resulting in a porous oxidized shell. The oxidized shell on commercial ZVI is formed during slow corrosion in the presence of air and this produces a thin adherent passivation layer that could inhibit direct contact of contaminants with Fe(0). Both nZVI and acid-treated ZVI used in these studies are produced and stored under anoxic conditions and this could further

inhibit formation of a thin adherent passivation layer. Perhaps acid-treated ZVI can be produced *in situ* by introducing commercial ZVI followed by an acid flush. The acid-flushing procedure might be analogous to renovation of sampling or other wells during which acids and other agents are used to reductively dissolve oxidized precipitates. This treatment could result in inexpensive, rapid, no-lag removal of arsenic and other contaminants from contaminated soils and ground waters.

Reduction to As(0) could have significant effects on mobility and toxicity of arsenic in ground water environments. As(V) and As(III) can be released from solids due to change in pH or addition of competing adsorbates [41,49]. Pump and treat remediation efforts can require years to decades for remediation due to rebound effects. To the contrary As(0) does not dissolve and is relatively inert against O_2 or even O_3 [50]. Partly for these reasons As(0) is less toxic than As(III) or As(V). These properties could make As(0) an attractive reaction product when remediating contaminated water or soil.

4. Conclusions

We conducted experiments using strictly anoxic conditions and found that both adsorption and reduction of As(V) were fast, with no lag phase, when reacted with either commercial ZVI or acid-treated ZVI. Previous studies have reported a significant lag phase before commencement of the reduction of As(V) by ZVI.

These experiments showed that the Fe(0) core of ZVI is necessary for reduction of As(V), even though magnetite/Fe(II) is theoretically capable of reducing As(V). Further, although commercial ZVI only reduced As(V) to As(III) (with the possibility of slow reduction of As(V) to As(0) at slightly alkaline conditions), disruption of the adherent magnetite shell by acid-treatment resulted in reduction of As(V) to As(0). Thus the physical nature of ZVI can have profound effects on reactivity and acid-treatment of ZVI should be considered for field applications.

Reduction to As(0) could result in reduced toxicity and increased stability after remediation of arsenic-contaminated soil and water. In addition As(V) removal capacity on acid-treated ZVI was ~ 10 times higher than commercial ZVI of similar size, probably due to both reduction to As(0) and also increased adsorption due to the thicker iron oxide shell.

We have drawn comparisons between the reactivity of acid-treated ZVI and nZVI, which was previously observed to reduce some metal cations to their zero valence [48]. Production of nZVI

also results in the formation of a relatively massive flocculated shell of iron oxides, similar to the shell formed on acid-treated ZVI. Thus it is possible that reduction to As(0) could also occur with nZVI. If acid-treated ZVI has similar reactivity to nZVI and can be produced *in situ* by acidification of commercial ZVI, then it will be possible to produce a material with reactivity of nZVI but at a much lower cost.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.09.029.

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