Advantages of low pH and limited oxygenation in arsenite removal from water by zero-valent iron

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HIGHLIGHTS

▶ Limited aeration and acidic conditions are advantageous for arsenite removal by ZVI.
▶ Higher removal rate and lower ZVI demand, compared with anaerobic conditions.
▶ Higher reduction and lower sludge formation, compared with non-acidic conditions.
▶ Formation of Fe(II)-intermediate were associated with enhanced performance.

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ABSTRACT

The removal of toxic arsenic species from contaminated waters by zero-valent iron (ZVI) has drawn considerable attention in recent years. In this approach, arsenic ions are mainly removed by adsorption to the iron corrosion products. Reduction to zero-valent arsenic on the ZVI surface is possible in the absence of competing oxidants and can reduce arsenic mobility and sludge formation. However, associated removal rates are relatively low. In the current study, simultaneous high reduction and removal rates of arsenite (H_3AsO_3), the more toxic and mobile environmentally occurring arsenic species, was demonstrated by reacting it with ZVI under limited aeration and relatively low pH. 90% of the removed arsenic was attached to the ZVI particles and 60% of which was in the elemental state. Under the same non-acidic conditions, only 40–60% of the removed arsenic was attached to the ZVI with no change in arsenic oxidation state. Under anaerobic conditions, reduction occurred but total arsenic removal rate was significantly lower and ZVI demand was higher. The effective arsenite removal under acidic oxygen-limited conditions was explained by formation of Fe(II)-solid intermediate on the ZVI surface that provided high surface area and reducing power.

1. Introduction

Arsenic is a toxic element and its presence in natural and drinking water is restricted to very low levels [1]. The two soluble arsenic species commonly found in the environment are arsenite (As^{3+}-species) and arsenate (As^{5+}-species), with the former being more toxic and mobile [2,3]. Although several dissolved arsenic removal technologies such as membrane filtration, ion exchange and adsorption on activated carbon or on mineral surface are proven, cost effectiveness remains a major issue, especially in developing countries [4].

The use of elemental iron, also termed zero-valence iron (ZVI), to remove dissolved arsenic species is a promising approach due to its simplicity, low cost, efficiency and applicability in passive treatment (e.g., permeable reactive barriers) [2,5,6]. This method was shown to achieve complete arsenic removal [7] and has recently drawn considerable interest as reflected by a fairly large number of publications concerned with kinetic and mechanistic aspects [1–3,6–20]. This literature suggests that the main removal mechanism of both arsenite and arsenate is their adsorption onto the iron corrosion products surrounding the ZVI particle or onto the iron oxy-hydroxides released to the solution [1,19]. The adsorption is affected by pH, due to the weak-acid properties of the As ions [21] and by surface area [13]. The removal capacity may be enhanced by precipitation and co-precipitation of As-Fe compounds on solid surface [2,6,22], but these compounds may re-dissolve [22]. An additional removal mechanism is reduction of arsenic ions to elemental arsenic which is sequestered in the corrosion layer [8,17] or forms an intermetalic phase with Fe^0 [20]. This mechanism appears to occur in the absence of competing oxidants such as oxygen, where reduction of As(V) to As(III) and of As(III) to As(0) on the surface of ZVI was recorded [8,17,18]. Arsenic bound to ZVI media, probably in such manner, demonstrated low leaching rates [6,13]. Another advantage associated with anaerobic

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conditions is the absence of iron oxy-hydroxides that produce sludge and further treatment requirement. However, without the iron oxy-hydroxides and with the relatively low surface area of the ZVI particles, significantly lower arsenic removal rates compared with oxygenated conditions were recorded [8,21,23]. In the presence of oxidants such oxygen, ferric oxides, water, carbonate and reactive Fe(II)-Fe(III) corrosion intermediates, As removal was kinetically fast but As(III) was partially oxidized to As(V) [2,9,14,16,19,24,25]. The chemistry of the system, however, was recently shown to be more complex as nano-ZVI particles demonstrated the ability to simultaneously reduce and oxidize As(III) [17].

Using ZVI to remove selenate (SeO_4^{2-}) form water, we have recently shown that limited oxidation and acidic conditions resulted in surprisingly high removal rates together with low formation of sludge. This was explained by formation of green rust (GR) on the ZVI particles that provided high surface area and reducing power, allowing a large conversion rate of Se ions to the elemental state [26]. Although the effects of oxygen and pH on As removal using ZVI was previously investigated, these parameters were not maintained constant [21] and the removed As distribution was not characterized at different pH values [8,23].

The scope of the current work was to show that under acidic conditions and limited aeration, high arsenite removal rate *together* with high arsenite reduction and low iron oxy-hydroxides formation, is possible.

2. Experimental

2.1. Procedures

Four distinct sets of conditions were tested, namely pH 4.0 and 9.0, each under an anoxic (N_2) or mildly oxygenated (aerated) environment. Another test under aeration and pH 7 was also performed. Initial arsenite (analytical grade As_2O_3, Fisher Scientific Co.) concentration was 70 mg As L^{-1} to minimize interferences by impurities and side reactions, to evaluate the effect of As concentration on the removal rate and to enable comparison with published data.

The experimental set up was described in detail previously [26]. In short, the system comprised of a 2 L magnetically stirred container from which a 1.8 L solution was circulated at a rate of 1.8 L h^{-1} through a 30 mL glass column (30 cm long), partially filled by ZVI fillings (40 mesh, Fisher Scientific Co.) which were effectively mixed. Because of the short hydraulic residence time in the ZVI filled volume (<20 s), the system as a whole was considered to be closely analogous to a continuous stirred tank reactor (CSTR). N_2 bubbling or aeration (200 mL min^{-1}) started approximately 0.5 h prior to addition of 17.2 g ZVI fillings and pH was adjusted using 0.12 M HCl solution. The used aeration rate and Fe^0 mass followed a selenate removal study preformed under identical conditions. The system was operated at room temperature for 7 h after ZVI addition and a constant pH was maintained by 0.12 M HCl solution, a pH controller (Eutech 190 series) and a peristaltic pump. The HCl solution was stored in a 50 mL buret and its consumption was monitored intermittently, along with oxidation reduction potential (ORP, Accumet pH meter, model 10). 10 mL samples were drawn from the container using a syringe and filtered using a replaceable membrane (Whatman Nuclepore, 0.45 μm pore size) syringe filter. Determination of As and Fe concentrations in the suspended solids (SS) followed dissolution of the solids attached to the membrane, filter plates and O-ring using in 37% HCl solution. At the end of each trial, SS were extracted using centrifuge and dried at 40 °C for X-ray diffraction (XRD) and X-ray photoelectron spectrometry (XPS) analyses. The solids in the ZVI column were extracted at the end of each trial by filtration and kept without drying for several days

before XPS analysis of particles taken from the sample interior. A portion of each of these samples was dried at 40 °C for XRD analysis.

2.2. Analyses

Total dissolved Fe and As concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer, Optima 7300 DV). XRD (Philips PW 3710) analyses were conducted using Cu Kα radiation at 40 mA and 40 kV, at a scanning rate of 0.01 2θ s^{-1}. XPS was conducted using a Thermo Scientific Al Kα spectrometer (ThermoFisher, E. Grinstead, UK) and pass energy of 200 eV, followed by higher resolution (PE = 25 eV) at the As 3d region.

3. Results and discussion

Table 1 summarizes the operational conditions employed and the pH and ORP values measured in the mixed container and in the column outlet after 7 h of operation. The thermodynamically stable Fe and As species in solution and in the ZVI column were assessed according to the corresponding pH and ORP values and to Fe-H_2O [27] and As-H_2O [28] Pourbaix diagrams, as indicated in Table 1.

The concentration of dissolved As and Fe with time are depicted in Fig. 1. Fig. 1A shows, as expected, that the highest As removal rate was obtained under aeration. The somewhat higher rate at pH 4 and 7 compared with pH 9 was associated with lower concentration of SS in the latter (Fig. 2A), probably as result of uncontrolled lower aeration rate, and corresponding lower removal by adsorption. The possibility that the lower adsorption was a result of different arsenic speciation is not likely, because arsenic adsorption on the SS could not be correlated with pH (Fig. 2B). Fig. 1A also shows that As removal rates were greatly reduced at concentrations below 10 mg L^{-1}, very similar to selenate removal kinetics under identical conditions [26].

Fig. 1B shows that dissolved iron concentration was increasing only under pH 4, under both aerated and anoxic conditions. The dramatic (~10^4) oxidation rate increase of dissolved Fe(II) by O_2 between pH 6 and 8 [29] explains the accumulation of dissolved Fe(II) only at pH 4, as under pH 7 and 9, Fe(II) is rapidly oxidized and precipitates as ferric oxy-hydroxides (i.e., SS). This also explains the accumulation of SS only under non-acidic aerated conditions (Fig. 2A). Because ferric oxy-hydroxides, unlike Fe(II) solid species, precipitate readily at pH 4 [30], the accumulated dissolved iron under pH 4 was concluded to be predominantly divalent.

The iron concentration in the SS and the As to Fe mole ratio in them, are depicted in Fig. 2. The relatively high initial SS concentration was attributed to fine ZVI particles, washed off from the column. Fig. 2A shows a significant accumulation of SS only under aeration and non-acidic conditions, which was comparable in magnitude with the accumulated dissolved iron under acidic conditions (Fig. 1B). With the exception of pH 9.0 anaerobic conditions, where iron release was negligible, iron was released to solution in a similar rate under all conditions, suggesting that a similar amount of ZVI

Table 1
Operational conditions, pH, ORP and assessed stable species.

Gas	pH (out)[a]	ORP (out)[a] (mV)	Stable species[b]
Air	4.0 (5.9)	260 (65)	[Fe^{2+}], $H_2AsO_4^-$, (H_3AsO_3)
N_2	4.0 (5.7)	175 (−10)	[Fe^{2+}, H_3AsO_3]
Air	9.0 (9.1)	70 (−10)	[Fe_2O_3, $HAsO_4^{2-}$]
N_2	9.0 (9.2)	−400 (−290)	[H_3AsO_3, As, Fe_2O_3, Fe_3O_4]
Air	7.0 (7.3)	−115 (−180)	[Fe_2O_3, H_3AsO_3]

[a] Steady-state values measured in the stirred container (out = at ZVI column outlet at t = 7 h)
[b] Thermodynamically stable species in solution (ZVI column) [both].