



Effective Sb(V) immobilization from water by zero-valent iron with weak magnetic field



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ARTICLE INFO

Article history:

Received 18 January 2015

Received in revised form 23 July 2015

Accepted 25 July 2015

Available online 26 July 2015

Keywords:

Antimony

ZVI

Incorporation

Iron (hydr)oxides

XAFS

ABSTRACT

Weak magnetic field (WMF) was employed to enhance Sb(V) immobilization by zero-valent iron (ZVI) at pH_{ini} 4.0 in this study. The kinetics of Sb(V) removal by ZVI followed pseudo-first-order reaction law. Without WMF, the rate constants dropped substantially with increasing the initial Sb(V) concentration ([Sb(V)]_{ini}) from 5.0 to 40.0 mg/L. The application of a WMF increased the rate constants of Sb(V) sequestration by 5.56–7.71 times at [Sb(V)]_{ini} of 5.0–40.0 mg/L and enhanced the removal capacity of Sb(V) from 18.1 to 39.2 mg Sb(V)/g Fe. The co-existence of SO₄²⁻, NO₃⁻, Cl⁻, CO₃²⁻, SiO₃²⁻ and humic acid had minor influence on the removal efficiency of Sb(V) by ZVI when WMF was applied. The Fe K-edge XAFS, XRD and SEM results suggested that elevated [Sb(V)]_{ini} could inhibit the corrosion of ZVI without WMF while the application of WMF could alleviate the passivation of ZVI by Sb(V) and thus promote the removal of Sb(V) by corroded ZVI. The Sb K-edge XAFS spectra implied the incorporation of Sb(V) into the structure of iron (hydr)oxides. Consequently, no release of Sb(V) at pH 3.0, 6.0 or 9.0 from the Sb(V)-treated ZVI was observed in 30 days. Considering the large removal capacity of Sb(V) with low residual Sb(V) concentration, no release of Sb(V) after its incorporation into the structure of iron (hydr)oxides and slight influence of co-existing solutes, it was concluded that coupling ZVI with WMF was an effective Sb(V) immobilization technology.

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1. Introduction

Antimony is ubiquitously present in the environment as a result of mining, rock weathering, soil runoff, smelting activities, waste incineration, fossil fuel combustion, road traffic emissions, and spent ammunition [1–4]. High dissolved Sb concentrations in water ranging from 4.58 mg/L to 29.4 mg/L were reported in mining areas in China [5]. Antimony has been increasingly identified as a toxic heavy metal with implication in cancer development [6]. Thus, antimony and its compounds are considered to be pollutants of priority interest by the United States Environmental Protection Agency [7] and the European Union [8]. The World Health Organization sets safe drinking water levels for Sb at 20 µg/L [9]. In China, the maximum admissible Sb level in drinking water is 5 µg/L [10].

Sb(III) and Sb(V) are the most frequently observed species of antimony in the environment, and Sb(III) is ten times more poisonous than Sb(V) [6]. Sb(III) exists mainly as Sb(OH)₃ in anoxic condition while the dominant form of Sb(V) in aerobic

environment is Sb(OH)₆⁻ over most environmentally-relevant pH range [4,11–13]. Sb(OH)₆⁻ is an octahedron with a large ionic radius and low charge density, which differs much from that of As(V) and P(V) and hence its binding on solid surface is weaker than that of As(V) and P(V) [12]. In natural environment, Sb(OH)₃ can bind to adsorbents (hydroxides of Fe, Mn and Al as well as bentonite) [3,14–16] more strongly than the anionic Sb(OH)₆⁻ due to the neutral character of Sb(OH)₃ over a wide pH range and low solubility, making the latter more mobile in the neutral and alkaline environment [4,12,17]. Thus, Sb(V) was employed as the target contaminant in this study.

Several technologies have been investigated for removing Sb(V) from aqueous environment, including coagulation–precipitation [18,19], ion exchange [20], and adsorption [16,21–23]. Among these methods, adsorption is the most extensively investigated method to remove Sb(V). Although adsorption was proved to be efficient, cost-effective and simple to perform, previous studies indicated that the Sb(V) adsorption via most of adsorbents was very sensitive to environment factors, including environmental pH, ion strength, competitive anions, etc [14,24,25]. Thus, after Sb(V) was bound to the surface of adsorbents, the variation of environmental conditions might change the adsorption equilibrium

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and hence cause the desorption of adsorbed Sb(V) to environment again. Moreover, desorption of Sb from the adsorbent was observed due to the transformation of adsorbed Sb(III) to Sb(V) [14,26]. Therefore, simultaneous removal and immobilization of Sb(V) is preferred to avoid the secondary pollution. Mitsunobu et al. showed that Sb(V) could be incorporated in natural as well as in synthetic iron oxides [27]. Sb(V) incorporated into the structure of iron oxides would not be greatly influenced by variation of environmental factors and hence be more stabilized than those adsorbed on iron oxides in most aqueous environment [27]. Zero-valent iron (ZVI) has been extensively applied for the remediation/treatment of groundwater and wastewater contaminated with various contaminants. Under aerobic conditions, the oxidation of ZVI by O_2 yields Fe^{2+} , which will be subsequently oxidized by oxygen to Fe(III). The resulting Fe(III) readily hydrolyses and precipitates in this process, hence the contaminants can be entrapped in the structure of iron precipitates [28]. However, the immobilization of Sb(V) by ZVI has seldom been investigated. Our previous study showed that the application of a weak magnetic field (WMF) could promote ZVI corrosion, resulting in more rapid release of Fe^{2+} and greater sequestration of As(V), As(III), Se(IV), and Cu(II) [29–32]. Therefore, this study proposed to employ ZVI coupled with WMF to achieve the effective immobilization of Sb(V). The objectives of this study are to investigate the feasibility of employing WMF to enhance Sb(V) removal by ZVI and to explore the mechanisms of enhanced Sb(V) immobilization by ZVI with WMF.

2. Materials and methods

2.1. Materials

ZVI employed in this study was purchased from Sinopharm Chemical Reagent Co., Ltd (China), which had a mean diameter of 40 μm and BET surface area of 0.15 m^2/g . Chemical reagents used in this study, including $K_2H_2Sb_2O_7 \cdot 4H_2O$, NaOH, H_2SO_4 , HNO_3 , NaCl, Na_2SO_4 , $NaNO_3$, Na_2CO_3 , $Na_2SiO_3 \cdot 9H_2O$ and humic acid (HA) were of analytical grade purchased from Shanghai Qiangshun Chemical Reagent Company. The Sb(V) stock solution (1000 mg/L) used in our experiments was prepared from $K_2H_2Sb_2O_7 \cdot 4H_2O$. All solutions were prepared with Milli-Q water with these Chemical reagents.

2.2. Batch experiments and analytical methods

Batch experiments were carried out with the experimental setup employed in our previous study [29], as shown in Fig. S1. The maximum magnetic intensity was determined to be ~ 10 mT at the bottom of the reactor when a WMF was superimposed. Working solutions were freshly prepared by diluting the stock solution for each batch test and then the initial pH value was adjusted to 4.0 with NaOH and H_2SO_4 . No attempt was made to maintain a constant pH during the testing process. Batch experiments were initiated by adding 0.5 g ZVI to 0.5 L prepared working solution. The initial Sb(V) concentration ($[Sb(V)]_{ini}$) varied from 5.0 to 40.0 mg/L and from 5.0 to 80.0 mg/L, respectively, without and with WMF since the removal of Sb(V) dosed at 40.0 mg/L by ZVI without WMF was already inefficient. The influence of co-existing anions and HA on Sb(V) removal with WMF were investigated by fixing Sb(V) at 20.0 mg/L while two concentrations of co-existing anions and HA were chosen to be representative of the cases in surface and ground waters. Each experiment was carried out in duplicate.

The solution was mixed at 400 rpm with a mechanical stirrer to avoid the aggregation of ZVI induced by a WMF (the

same stirring intensity was used in tests without WMF). At given time intervals, approximately 5.0 mL of suspension was sampled and immediately filtered through a 0.22 μm membrane filter, and acidified with one drop of 65% HNO_3 for analysis. The concentrations of total Sb and Fe in the filtrate were determined with ICP-OES (The detection limits of ICP-OES for Sb and Fe were 30.0 and 2.0 $\mu g/L$, respectively). It should be specified that the speciation of Sb(V) and Sb(III) was determined with LC-ICP-MS but Sb(III) was not detected, which was reasonable since our experiments were performed open to the air.

After batch tests, the precipitates were collected on membrane filters (0.22 μm), washed with deionized water, freeze-dried under vacuum, and put into zipper bags before being subjected to analysis via X-ray Absorption Fine Structure spectroscopy (XAFS for Fe K-edge and Sb K-edge), SEM and XRD. The details of XAFS, SEM and XRD analyses were presented in Text S1 of Supporting Information.

To determine the stability of Sb(V)-treated ZVI, 20.0 mg/L of Sb(V) reacted with 1.0 g/L ZVI at pH_{ini} 4.0 for 10 days before the precipitates were collected, washed with deionized water and dispersed into three reactors. Each reactor contained 500 mL 0.01 M ClO_4^- and the initial pH was adjusted to 3.0, 6.0 and 9.0, respectively, with H_2SO_4 and NaOH. In the following 30 days, pH of the mixture in each reactor was maintained constant with dosing H_2SO_4 and NaOH manually. At given time intervals, samples were collected and filtrated for determining the amount of released Sb(V). All the experiments were conducted open to air and controlled at 25 $^{\circ}C$ by water bath.

3. Results and discussion

3.1. Influence of WMF on the kinetics and capacity of Sb(V) removal by ZVI

Fig. 1 shows the influence of WMF on Sb(V) removal by ZVI and the corresponding variations in total dissolved Fe and solution pH at $[Sb(V)]_{ini}$ of 5.0–40.0 mg/L. Obviously, the removal rates of Sb(V) by ZVI without the presence of WMF dropped with increasing the $[Sb(V)]_{ini}$, especially when the $[Sb(V)]_{ini}$ was elevated from 20.0 mg/L to 40.0 mg/L. Only $\sim 35\%$ of Sb(V) was removed by ZVI in 3 h without WMF when the $[Sb(V)]_{ini}$ was 40.0 mg/L and thus the removal of Sb(V) by ZVI without WMF was not examined at higher $[Sb(V)]_{ini}$. The application of WMF substantially enhanced Sb(V) removal by ZVI at various $[Sb(V)]_{ini}$. The kinetics of Sb(V) removal by ZVI with and without WMF could be well fitted with the pseudo first-order rate law, as illustrated by the solid lines present in the left column of Fig. 1. The obtained rate constants of Sb(V) removal by ZVI, as summarized in Table 1, decreased from 0.118 to 0.018 min^{-1} and from 0.014 to 0.003 min^{-1} , respectively, with and without WMF. The rate constants of Sb(V) removal by ZVI with WMF were 5.56–7.71 times greater than their counterparts without WMF.

Moreover, the pH experienced a greater increase in the presence of WMF compared to the case without WMF. The release of total soluble Fe in the process of Sb(V) removal by ZVI with or without WMF was observed increased to a maximum and then dropped gradually, except the case when the $[Sb(V)]_{ini}$ was 40.0 mg/L without WMF, which was ascribed to the relatively low pH value throughout the reaction period (4.0–5.6). The total soluble Fe was mostly consisted of Fe^{2+} according to our previous studies and thus the drop in the concentration of total soluble Fe was ascribed to the oxidation of Fe^{2+} by oxygen at elevated pH [30]. It is well known that ZVI corrosion under acidic conditions is characteristic of Fe^{2+} release and pH increase, as present in Eq. (1).

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