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Influence of weak magnetic field and tartrate on the oxidation and sequestration of Sb(III) by zerovalent iron: Batch and semi-continuous flow study

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Graphical abstract

Highlights

- Oxidation of Sb(III)-tartrate and Sb(III) in the Fe⁰-H₂O-O₂ system was studied.
- WMF greatly enhanced Sb(III)-tartrate and Sb(III) removal by ZVI.
- WMF also increased the removal capacity of Sb(III)-tartrate and Sb(III) by ZVI.
- Tartrate significantly retarded Sb(III) removal by ZVI.
- The mechanisms of the inhibiting effect of tartrate were clarified.

ABSTRACT

The influence of weak magnetic field (WMF) and tartrate on the oxidation and sequestration of Sb(III) by zerovalent iron (ZVI) was investigated with batch and semi-continuous reactors. The species analysis of antinomy in an aqueous solution and solid precipitates implied that both Sb(III) adsorption preceding its conversion to Sb(V) in solid phase and Sb(III) oxidation to Sb(V) preceding its adsorption in aqueous phase occurred in the process of Sb(III) sequestration by ZVI. The application of WMF greatly increased the rate constants of Sb_{tot} (total Sb) and Sb(III) disappearance during Sb(III)-tartrate and uncomplexed-Sb(III) sequestration by ZVI. The enhancing effect of WMF was primarily due to the accelerated ZVI corrosion in the presence of WMF, as evidenced by the influence of WMF on the change of solution and solid properties with reaction. However, tartrate greatly retarded Sb removal by ZVI. It was because tartrate inhibited ZVI corrosion, competed with Sb(III) and Sb(V) for the active surface sites, increased the negative surface charge of the generated iron (hydr)oxides due to its adsorption, and formed soluble complexes

with Fe(III). The positive effect of WMF on Sb(III)-tartrate and uncomplexed-Sb(III) removal by ZVI was also verified with a magnetic semi-continuous reactor.

Keywords: Adsorption, antimonite, antimonate, antimony, ZVI.

1. Introduction

Metalloid antimony (Sb) is the ninth mined metal and is widely used in the manufacture of many industrial products [1, 2]. The mining and consumption of antimony increase continuously. The estimated output from antimony mining in 2012 was 1.3 times the output in 2007, and the world production of antimony in 2013 was 1.63×10^5 tons [3, 4]. About 88% of commercial antimony in the world is produced in China, and large quantities of antimony have been released to the environment from mining antimony and processes of smelting, resulting in significant soil and water contamination [5-11]. Antimony concentrations up to 4.6-29.4 mg/L in mine drains and 7.3-163.0 µg/L in natural waters have been detected in the world's largest antimony mine, Xikuangshan in Hunan province, China [12, 13].

Antimony and its compounds have acute toxicity [14]. Chronic symptoms can be induced by prolonged exposure to Sb [15]. Thus, antimony has been identified to be a toxic and potentially carcinogenic element [16-19], and arisen many concerns all over the world. Sb(III) and Sb(V) are the most frequently observed species of antimony in the environment [1], and Sb(III) is ten times more toxic than Sb(V) [19, 20]. In the pH range of 2.0-10.0, Sb(III) exists mostly as Sb(OH)₃ [21]. Meanwhile, Sb(III) tends to coordinate strongly with carboxylic acid and phenolic moieties [22-25]. Complexing

with organic ligands greatly reduces the solubility and mobility of Sb(III) in water and elevates the environmental risks of antimony contamination [26-28]. Therefore, there are two methods to prepare synthetic wastewater containing Sb(III) in the literature because of the poor solubility of Sb₂O₃. The first method is to dissolve Sb₂O₃ in concentrated acid (uncomplexed-Sb(III)) and use it as stock solution, and the other method is to dissolve K(SbO)C₄H₄O₆·0.5H₂O (Sb(III)-tartrate) directly in deionized water. Nevertheless, none of the previous studies has compared the difference in the removal behaviors of Sb(III) prepared with these two methods.

Several technologies have been employed to sequester Sb(III) from water, including coagulation [29-31], precipitation [32], electro-deposition [33, 34], solvent extraction [35, 36], ion exchange [37, 38], reverse osmosis [39], membrane filtration [40], adsorption [41-48], and biosorption [49]. However, all these technologies have some limitations. For instance, coagulation and adsorption generally have low removal capacity for Sb(III) and adsorbent is difficult to be regenerated [29-31, 41-48]. Some other technologies, e.g., reverse osmosis, are costly or time-consuming [39]. Therefore, it is critical to develop a more effective method for removing Sb(III) from water.

Sustained formation of fresh iron (hydr)oxides resulting from the corrosion of zerovalent iron (ZVI) is a promising approach for removing contaminants via adsorption or precipitation/co-precipitation. However, the low intrinsic reactivity of ZVI due to its inherent passive layer may limit its ability to remove contaminants [50]. In recent years, it has been reported that applying weak magnetic field (WMF) is an

efficient, low-cost, environmentally friendly, and promising technique to enhance the performance of ZVI for sequestering various contaminants because it can accelerate ZVI corrosion. Several studies have proved that the ZVI/WMF technique could efficiently remove Se(IV)/Se(VI) [51, 52], As(III)/As(V) [53], Cr(VI) [54], Cu(II) [55], and Cu^{II}-EDTA [56]. Xu et al. [57] showed that the application of WMF also enhanced the removal of Sb(III)-tartrate by ZVI, but neither did they mention the oxidation-reduction behavior of Sb(III) in this process nor notice the influence of tartrate on Sb(III)'s removal behavior. Furthermore, most published data on the ZVI/WMF technique were obtained from batch tests. To promote the application of the ZVI/WMF technique, it is necessary to examine the influence of WMF on ZVI's contaminant removal ability in continuous or semi-continuous experiments.

Therefore, the main objectives of this study were to (1) investigate the influence of WMF and tartrate on Sb(III) sequestration by ZVI as a function of initial pH (pH_{ini}) and Sb(III) concentrations; (2) examine the influence of WMF on the redox transformations of Sb(III) in both aqueous and solid phases to clarify the mechanisms of Sb(III) removal by ZVI; (3) explore the feasibility of applying WMF to improve Sb(III) removal by ZVI in a semi-continuous mode using a designed semi-continuous flow magnetic reactor.

2. Materials and methods

2.1 Materials

All chemicals were of analytical grade and all solutions were prepared with deionized (DI) water from a Milli-Q system. ZVI used in this study was purchased

from Sinopharm Chemical Reagent Co., Ltd., with a d₅₀, which stands for the average particle diameter by mass in particle size distribution measurements, of 40.5 μ m and BET surface area of 0.15 m²/g. All other chemical reagents were supplied by Shanghai Qiangshun Chemical Reagent Co., Ltd. Stock solutions of 1000 mg/L Sb(V), Sb(III)-tartrate, and uncomplexed-Sb(III) were prepared by dissolving K₂H₂Sb₂O₇·4H₂O, K(SbO)C₄H₄O₆·0.5H₂O in DI water, and Sb₂O₃ in 2.0 mol/L HCl, respectively. It should be noted that Sb(III) in all figures of this paper represents uncomplexed-Sb(III) for simplification.

2.2 Batch and semi-continuous experiments

Batch experiments were carried out with the setup used in our previous study [52]. In brief, a static and inhomogeneous WMF was generated by two pieces of neodymium-iron-boron permanent magnets beneath the reactor, with the maximum magnetic intensity of ~15 mT. A typical batch test was initiated by adding 0.5 g of ZVI into a 500 mL wide-mouth bottle containing a working solution of Sb(III)-tartrate or uncomplexed-Sb(III) or Sb(V). The initial concentrations of Sb were set at different values: 10, 20, 25, 30, or 40 mg/L for Sb(III)-tartrate; 10, 40, or 60 mg/L for uncomplexed-Sb(III); 10 or 40 mg/L for Sb(V). The working solution with 1.0 mM Na₂SO₄ as background electrolyte was freshly prepared by diluting the corresponding stock solution for each batch test. The volume of the working solution in the batch experiments was 500 mL. The pH_{ini} of the working solution was adjusted with H₂SO₄ or NaOH to certain values prior to ZVI dosing, and no attempts were made to maintain a constant pH during the experiment. The solution was mixed at 400 rpm

with a propeller agitator (D2004W, Shanghai Sile Instrument Co. Ltd.). Control experiments were performed with the same procedure of the typical batch test but without ZVI dosing to examine the oxidation of Sb(III) by oxygen in the air. At fixed periods (5, 10, and 30 min, 1, 1.5, 2, 3, 4, and 6 h), approximately 5 mL of the suspension was withdrawn and passed through a 0.22 μ m membrane filter, and was acidified for analysis. The reacted ZVI particles after the batch tests were collected by vacuum filtration with 0.22 μ m membrane filters, washed with DI water, freeze-dried in vacuum, and then preserved in a glove box for subsequent solid characterization. All batch tests were performed open to the air and at 25 ± 1 °C in a water bath. Each test was performed in duplicate, and error bars in the figures show the standard deviations of test results. A semi-continuous flow magnetic reactor was designed, as presented in Figure S1, to determine the influence of WMF on antimony removal by ZVI in a semi-continuous flow mode at room temperature (20 ± 1 °C) and the details are present in Text S1.

2.3 Analytical methods

The concentrations of aqueous total Sb (Sb_{tot}) and total Fe (Fe_{tot}) were determined with ICP-MS (Agilent ICP-MS 7700), whereas the speciation of Sb(III) and Sb(V) in aqueous phase was determined with HPLC-ICP-MS (Agilent HPLC 1200-ICPMS 7700) using a published method [58, 59]. The methods of analyzing other parameters and the details of characterizing the solid phase are summarized in Text S2.

3. Results and discussion

3.1 Influence of WMF on oxidation and removal of uncomplexed-Sb(III) and Sb(III)-tartrate by ZVI

The control experiment showed that less than 1% of the Sb(III) in the uncomplexed-Sb(III) and Sb(III)-tartrate solutions was transformed to Sb(V) (exposure to the air without dosing ZVI) at pH 5.0-9.0 in 10 hours (Figure S2), confirming that the oxidation of Sb(III) by O₂ is very slow [60, 61]. However, it has been reported that the corrosion of ZVI by oxygen produces strong oxidants capable of oxidizing various organic and inorganic compounds. Under acidic conditions, two electrons are transferred from Fe⁰ surfaces to oxygen (reaction (1)) to produce hydrogen peroxide (H₂O₂). The interaction of H₂O₂ with Fe²⁺ generates hydroxyl radicals (•OH), in accordance to the reaction (2) at a low pH, or Fe(IV) at a pH above 5.0, via reaction (3) [62-64].

$$\mathrm{Fe}^{0} + \mathrm{O}_{2} + 2\mathrm{H}^{+} \rightarrow \mathrm{Fe}^{2+} + \mathrm{H}_{2}\mathrm{O}_{2} \tag{1}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$$
(2)

$$Fe^{2+} + H_2O_2 \rightarrow Fe(IV) + H_2O$$
(3)

Additionally, it was reported that Sb(III) was oxidized more readily than As(III), and Sb(V) was at a stable oxidation state that existed over a wide range of Eh in mineral-water systems [8]. The literature showed that Sb(III) could be readily oxidized by H_2O_2 in aqueous solutions [60, 65], and the oxidation of Sb(III) in both solid and aqueous phases can be catalyzed on the surfaces of minerals, especially iron (hydr)oxides [42, 66].

Therefore, the disappearance of Sb_{tot} and Sb(III), as well as the evolution of Sb(V), during the treatment of uncomplexed-Sb(III) and Sb(III)-tartrate with ZVI (with or without WMF at pH_{ini} 5.0, 7.0 and 9.0) were investigated, as depicted in Figure 1. There are several palpable features in the data sets of Figure 1. Firstly, the removal of uncomplexed-Sb(III) or Sb(III)-tartrate by ZVI in the absence of WMF generally consists of two periods. At the beginning of the reaction, a decrease in Sb(III) concentration is accompanied by an accumulation of Sb(V) in aqueous phase, while the concentration of Sbtot declines. The concentration of Sbtot decreases at a greater rate in the second period than in the first, and is accompanied by a drop in Sb(V) concentration. This indicates that the removal of uncomplexed-Sb(III) or Sb(III)-tartrate by ZVI is limited by the transformation of uncomplexed-Sb(III) or Sb(III)-tartrate to Sb(V). The two-period phenomenon was not observed in the change of Sb_{tot} with time during the removal of uncomplexed-Sb(III) by ZVI at pH_{ini} 5.0 in the absence of WMF, which should be ascribed to the rapid transformation of uncomplexed-Sb(III) to Sb(V) in this case. Secondly, the application of WMF greatly improved the removal rates of the uncomplexed-Sb(III) and Sb(III)-tartrate by ZVI at various values of pH_{ini}. Moreover, the two-period phenomenon only appeared in the time evolution of Sbtot when Sb(III)-tartrate was treated by ZVI at pHini 7.0 and 9.0 in the presence of WMF. This should be due to the accelerated ZVI corrosion (discussed in detail in Section 3.4) and the accelerated oxidation of the uncomplexed-Sb(III) or Sb(III)-tartrate to Sb(V) in the presence of WMF. Thirdly, increasing pH_{ini} resulted in a drop in the rates of uncomplexed-Sb(III) and Sb(III)-tartrate removal by ZVI,

regardless of the application of WMF, which should be ascribed to the reduced ZVI corrosion at higher pH_{ini} .

To quantify the effect of WMF on the removal of uncomplexed-Sb(III) and Sb(III)-tartrate by ZVI, the disappearance kinetics of Sb(III) and Sb_{tot} shown in Figure 1 was simulated with a pseudo first-order rate law. It should be noted that only the removal kinetics of Sb_{tot} in the first period was modeled when the two-period phenomenon had been observed. The rate constant of Sb_{tot} sequestration represents the removal rate of total Sb during uncomplexed-Sb(III) or Sb(III)-tartrate removal by ZVI, and the rate constant of Sb(III) disappearance represents the decrease rate of Sb(III) concentration in the solution, which manifests the oxidation and removal rate of Sb(III). The rate constants are summarized in Figure 2. The rate constants of Sb(III) and Sb_{tot} disappearance decreased progressively with the increase in pH_{ini}, regardless of the presence of WMF. The application of WMF increased the disappearance rate constants of Sb_{tot} and Sb(III) over the pH_{ini} range of 5.0-9.0 by 4.0-5.7 times and 2.2-4.8 times, respectively, for the removal of uncomplexed-Sb(III) by ZVI. However, WMF induced less significant improvement in Sb(III)-tartrate sequestration by ZVI. The rate constants of Sb_{tot} removal and that of Sb(III) disappearance during Sb(III)-tartrate sequestration by ZVI were enhanced by 1.3-4.1 and 1.7-4.1 folds, respectively, due to the application of WMF.

Since the removal capacity of ZVI for Sb(III)-tartrate directly determined the amount of ZVI consumed for Sb(III)-tartrate treatment, the influence of WMF on the ZVI capacity for Sb(III)-tartrate removal was investigated at different initial

Sb(III)-tartrate concentrations. The experiments on the kinetics of Sb(III)-tartrate sequestration by ZVI as a function of initial Sb(III)-tartrate concentration, as illustrated in Figure S3, revealed that 48 hours was enough to reach equilibrium. Therefore, the influence of WMF on the removal capacity of Sb(III)-tartrate by ZVI after 60 hours of reaction was determined and shown in Figure 3. The maximum removal capacity of Sb(III)-tartrate by ZVI without WMF was determined to be 14.6 mg Sbtot/g ZVI, which was achieved at an initial Sb(III)-tartrate concentration of 20.0 mg/L. The increase in Sb(III)-tartrate concentration resulted in a drop in the amount of Sb removed without WMF. However, the amount of Sb_{tot} removed by ZVI in the presence of WMF increased from 20.0 to 21.8 mg Sbtot/g ZVI when the initial Sb(III)-tartrate concentration increased from 20.0 to 25.0 mg/L and then decreased to 13.2 mg Sb_{tot}/g ZVI with further increasing the Sb concentration to 40.0 mg/L. Consequently, the application of WMF not only accelerated Sb(III)-tartrate removal by ZVI but also induced a 48.6% increase (21.8 mg Sbtot/g ZVI vs. 14.6 mg Sbtot/g ZVI) in the removal capacity of Sb(III)-tartrate by ZVI.

3.2 Influence of WMF on antimony speciation in the Sb(III)-treated ZVI corrosion products

Figure 4 shows the Sb *K*-edge X-ray absorption near edge structure (XANES) spectra of the ZVI samples treated by Sb(III)-tartrate for different durations at pH_{ini} 5.0 and their liner combination fitting (LCF) results. It was found that the Sb in solid phase was predominantly present as Sb(V), regardless of the presence of WMF. The fraction of Sb(III) in the Sb(III)-tartrate-treated ZVI samples without WMF

progressively decreased from 32.7% at 1 h to 14.9% at 4 h and Sb(III) disappeared in the samples with a further increase in reaction time. The application of WMF decreased the fraction of Sb(III) in the Sb(III)-tartrate-treated precipitates collected at 1-4 h, which was caused by the enhanced oxidation of Sb(III) to Sb(V) in the presence of WMF. Combining the results of Sb(III)'s removal behavior and Sb speciation in aqueous and solid phases, it was concluded that both Sb(III) adsorption prior to its conversion to Sb(V) in solid phase and Sb(V) adsorption following Sb(III) oxidation to Sb(V) in aqueous phase occurred in the process of Sb(III) sequestration by ZVI. Therefore, the oxidation of Sb(III) occurred not only in aqueous phase but also in solid phases. Moreover, the transformation of Sb(III) to Sb(V) in both aqueous and solid phases was improved by applying WMF.

3.3 Influence of WMF on ZVI corrosion during antimony removal by ZVI

As mentioned above, the enhanced Sb(III) removal was believed to be related to the WMF-induced improvement in ZVI corrosion. Indeed, as depicted in Figures S4 and S5, compared to the scenario in the absence of WMF, the solution pH, the concentration of Fe²⁺, ORP, and DO varied more dramatically during the removal process of the uncomplexed-Sb(III) or Sb(III)-tartrate by ZVI upon the application of WMF. This confirmed the fact that WMF could accelerate ZVI corrosion. Furthermore, a comparison of the XRD patterns of the Sb(III)-tartrate-treated ZVI samples collected at different reaction durations (Figure S6) or at different initial Sb(III)-tartrate concentrations (Figure 5) also indicated that the application of WMF

accelerated the transformation of metallic Fe⁰ to iron (hydr)oxides (lepidocrocite herein). The reacted ZVI samples collected at 2 h and 6 h in the presence of WMF had a flake- or scale-like structure (Figure S7), which agrees with the structure of lepidocrocite [67]. It should be noted that fewer, weaker XRD peaks of nonmetallic Fe species were observed in the corresponding precipitates as the Sb(III)-tartrate concentration was increased (Figure 5), which implied that Sb(III)-tartrate at high concentration retarded ZVI corrosion. Therefore, the increase in Sb(III)-tartrate concentration resulted in a significant drop in the amount of Sb removed without WMF, and the enhancing effect of WMF on the removal capacity of Sb(III)-tartrate by ZVI should be mainly ascribed to the fact that the passivating effect of Sb(III)-tartrate on ZVI corrosion was alleviated by WMF.

To further verify the influence of WMF on ZVI corrosion at various Sb(III)-tartrate concentrations, XAFS analysis was performed. The Fe *K*-edge XANES spectra and Fe k^3 -weighted EXAFS spectra of reference materials and those of Sb(III)-tartrate-treated ZVI samples at different concentrations of Sb(III)-tartrate were illustrated in Figure S8. At a fixed concentration of Sb(III)-tartrate, the XANES line patterns of the Sb(III)-tartrate-treated ZVI samples with WMF were found to be more similar to those of iron oxides than those without WMF. This indicated that the application of WMF promoted the ZVI corrosion. On the other hand, with the increase in the initial Sb(III)-tartrate concentration, the XANES and EXAFS spectra of the Sb(III)-tartrate-treated ZVI samples became more analogous to those of pristine ZVI, regardless of the presence of WMF. This phenomenon was consistent with the XRD

results and all of them indicated that ZVI corrosion was inhibited by Sb(III)-tartrate at high concentrations. To identify the composition of the products of ZVI corrosion, LCF analysis was carried out based on the Fe k^3 -weighted EXAFS spectra (Figure S8b) and the corresponding results are summarized in Figure S9. According to the fitting results, lepidocrocite, magnetite, and maghemite were determined to be the major corrosion products. Moreover, in the absence of WMF, as the concentration of Sb(III)-tartrate increased from 20.0 mg/L to 30.0 mg/L, the residual metallic Fe^0 in the reacted samples increased from 59.4% to 98.2%, resulting from the inhibitory effect of the Sb(III)-tartrate on ZVI corrosion. While in the presence of WMF, less metallic Fe⁰ (37.4-90.1%) was detected in the reacted ZVI samples. It should be noted that the samples obtained at 40.0 mg/L Sb(III)-tartrate could not be identified by LCF due to the limited number of XAFS references, and the data mainly composed of strong signals from metallic Fe⁰. Sb(V) at high concentration was also reported to inhibit ZVI corrosion [68]. However, as demonstrated in Figure S9, the consumed Fe^0 at 40.0 mg/L Sb(V) within 30 h was 81.0-94.8%, which was much higher than that with 20.0 mg/L Sb(III)-tartrate (40.6-63.6%). This phenomenon suggested that, compared to Sb(V), Sb(III)-tartrate could inhibit ZVI corrosion to a greater extent and this inhibitory effect may be related to the presence of tartrate ions.

3.4 Influence of tartrate on Sb(III) removal by ZVI and the mechanisms

As shown in Figure 2a, the k_{obs} values of uncomplexed-Sb(III) removal by ZVI with and without WMF were 1.61-8.19 and 1.53-7.06 times greater than those of

Sb(III)-tartrate removal by ZVI with and without WMF, respectively. Furthermore, the amount of uncomplexed-Sb(III) removed by ZVI at an initial uncomplexed-Sb(III) concentration of 40.0 mg/L was as high as 37.8 mg Sb_{tot}/g ZVI, while a further increase in uncomplexed-Sb(III) concentration to 60.0 mg/L resulted in a sharp drop in the amount of removed uncomplexed-Sb(III) without WMF, as illustrated in Figure 3. The presence of tartrate significantly decreased the removal of Sb(III) without WMF when the initial Sb(III) concentration was 40.0 mg/L. With the presence of WMF, the amounts of uncomplexed-Sb(III) removed by ZVI were 40.0 and 44.2 mg Sb_{tot}/g ZVI, respectively, when the initial uncomplexed-Sb(III) concentrations were 40.0 and 60.0 mg/L (Figure 3). Thus, the uncomplexed-Sb(III) removal by ZVI with WMF was much more favored compared to the case of Sb(III)-tartrate.

To further explore the influence of tartrate, more experiments were carried out and the results were demonstrated in Figure 6. Clearly, when the initial concentration of Sb(III) was 40.0 mg/L, 94.5% (no WMF) or 100.0% Sb(III) (with WMF) could be wiped off from the uncomplexed-Sb(III) solution in 36 hours, while only 32.4% (no WMF) and 42.5% (with WMF) Sb(III) could be removed from Sb(III)-tartrate solution in 60 hours (Figure 6a). Although there were no reported data on the complexation of Sb(V) with tartrate, the presence of tartrate also considerably inhibited Sb(V) sequestration by ZVI, as demonstrated in Figure 6b. More than 99% of the Sb(V) could be sequestrated by ZVI in 10 hour (without WMF) or 4 hour (with WMF) if no tartrate ions were present, whereas only ~32.4% (no WMF) and ~42.5% (with WMF) of the Sb(V) could be removed after 60 hours when tartrate was added to

the solution (Figure 6b).

The above results confirmed that tartrate anions could restrain the removal of Sb(III) and Sb(V) by ZVI, which has seldom been discussed before. The inhibiting effect of tartrate on the Sb(III) and Sb(V) removal by ZVI should be mainly due to the following reasons. Firstly, as revealed in Figure 5, the presence of tartrate greatly retarded ZVI corrosion, regardless of Sb species and the application of WMF. The generated iron (hydr)oxides arising from ZVI corrosion could offer active surface sites for sequestering Sb(III) and thus the inhibited ZVI corrosion would result in a drop in Sb(III) removal. Secondly, tartrate may compete with Sb(III) and Sb(V) for the active surface sites. To investigate the adsorption of tartrate, TOC of the solution was determined in this study and the results are shown in Figure S10. As expected, within 10 h, 51.2% and 25.1% of the TOC was removed during Sb(III)-tartrate removal by ZVI/WMF and ZVI alone, respectively, which should be mainly attributed to tartrate adsorption onto freshly generated iron (hydr)oxides and then co-precipitation. Thirdly, the incorporation of tartrate with the generated iron (hydr)oxides made the surface more negatively charged, which could suppress Sb(V) adsorption due to electric repulsion. As shown in Figure S11, the zeta potentials of ZVI suspension became much more negative when tartrate ions were present in the system. As mentioned in Section 3.2, a conversion of Sb(III) to Sb(V) occurred during the process of either uncomplexed-Sb(III) or Sb(III)-tartrate removal by ZVI. Sb(V) always exists as $Sb(OH)_{6}^{-}$ over the environmentally-relevant pH range [21]. Therefore, the decrease in zeta potential would inhibit the adsorption of $Sb(OH)_6^-$ on the

corroded ZVI surface. Fourthly, the complexation of Fe^{3+} with tartrate ions promoted the dissolution of Fe^{3+} and inhibited the formation of newly generated iron (hydr)oxides in solid phase. Figure S12 shows that 5.7-36.5 mg/L Fe³⁺ was present in the tartrate solution after 12 hours, whereas almost no Fe³⁺ was detected in the tartrate-free solution. It was reported that Fe³⁺ and tartrate ions tend to form dimers with a stability constant of $10^{11.87}$ [69]. Therefore, the increase in soluble Fe³⁺ concentration induced by the presence of tartrate should be ascribed to the formation of soluble Fe³⁺-tartrate complexes.

In general, the process of Sb(III)-tartrate sequestration by ZVI involved many steps: the transformation of Sb(III)-tartrate to Sb(V) and tartrate, the adsorption on or incorporation of Sb(V) and tartrate in the newly formed iron (hydr)oxides, the complexation of Fe³⁺ with tartrate, the direct adsorption on or incorporation of Sb(III)-tartrate in the newly formed iron (hydr)oxides and the interfacial oxidation of Sb(III)-tartrate that followed. The major reactions that occurred in the process of Sb(III)-tartrate removal by ZVI are illustrated schematically in Figure 7.

3.5 Application of WMF to enhance uncomplexed-Sb(III) and Sb(III)-tartrate removal by ZVI in the semi-continuous flow reactor

To explore the possibility of improving Sb(III) removal in practical applications by applying WMF, the influence of WMF on the removal of uncomplexed-Sb(III) and Sb(III)-tartrate in a semi-continuous flow experiment was examined as functions of initial pH and flow rate. The application of WMF could enhance Sb_{tot} removal, lower the concentration of Sb_{tot} in the effluent, and prolong the breakthrough time under

four different reaction conditions (Figure 8). At pH_{ini} 7.1 and 5.0, the concentrations of Sb_{tot} decreased to ≤ 0.05 mg/L and remained stable until ~ 40.0 L Sb(III)-tartrate bearing water was treated in the magnetic reactor (Figure 8a, b). However, without WMF, the concentration of Sb_{tot} dropped to 0.15-0.40 mg/L and rose progressively to the original value after 14.0-20.0 L of the water was treated (Figure 8a, b). When the flow rate increased from 6.67 mL/min to 13.33 mL/min (Figure 8c), the removal of Sb(III)-tartrate by ZVI in both the magnetic and non-magnetic reactors became less efficient, while the Sb_{tot} concentration in the effluent of the magnetic reactor was always lower than in the non-magnetic reactor before breakthrough. When Sb(III) in the influent was changed from Sb(III)-tartrate to uncomplexed-Sb(III) (Figure 8d), the performance of the semi-continuous flow reactor was improved. The concentration of Sb_{tot} in the effluent kept steady at <0.05 mg/L when the volume of treated water increased from 0.8 to 62.4 L in the magnetic reactor. The Sb_{tot} concentration in the effluent of the non-magnetic reactor was in the range of 0.10-0.20 mg/L when the volume of treated water varied from 0.8 to 38.4 L.

4. Conclusion

This study demonstrated that the sequestration of Sb(III)-tartrate or uncomplexed-Sb(III) by ZVI could be enhanced by WMF at pH_{ini} 5.0-9.0. The application of WMF increased the rate constants of Sb_{tot} and Sb(III) disappearance over the pH_{ini} range of 5.0-9.0 by 4.0-5.7 times and 2.2-4.8 times, respectively, for uncomplexed-Sb(III) removal by ZVI. The rate constants of Sb_{tot} removal and that of

Sb(III) disappearance during Sb(III)-tartrate sequestration by ZVI were enhanced by factors of 1.3-4.1 and 1.7-4.1, respectively, due to the superimposition of WMF. The WMF-induced enhancement in Sb(III) oxidation and sequestration was resulted from the accelerated corrosion of ZVI, which was verified by the variations in solution pH, concentration of Fe²⁺, ORP, DO, and by the characterization of the reacted ZVI precipitates through XAFS, XRD, SEM analyses.

The presence of tartrate greatly inhibited the removal of Sb(III) by ZVI at various pH_{ini} levels and different initial Sb(III) concentrations. The inhibitive effect of tartrate should mainly be due to the following reasons: reduced ZVI corrosion in the presence of tartrate, its competition with Sb(III) and Sb(V) for the active surface sites, the more negative surface charge of the generated iron (hydr)oxides, and the formation of soluble Fe(III)-tartrate complexes. Applying WMF can alleviate the tartrate-induced suppression of antimony removal by ZVI to some extent.

The semi-continuous magnetic reactor performed much better for the removal of Sb(III)-tartrate and uncomplexed-Sb(III) by ZVI than its non-magnetic counterpart, indicating the possibility of employing WMF to enhance Sb(III) removal by ZVI in practical applications.

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Appendix A. Supplementary data

Supplementary data associated with this article is available free of charge and can be

found in the online version (at website).

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Figure 1. Depletion of Sb_{tot} and Sb(III) as well as evolution of Sb(V) in the process of uncomplexed-Sb(III) removal without or with WMF (a-f) and Sb(III)-tartrate removal without or with WMF (g-l) by ZVI at various pH_{ini} values. Reaction conditions: ZVI = 1.0 g/L, [Sb(III)]₀ = 10.0 mg/L. The solid lines are the results of simulating the data with pseudo-first-order rate law.



Figure 2. Pseudo-first-order rate constants (k_{obs}) of (a) Sb_{tot} sequestration and (b) Sb(III) disappearance in the process of uncomplexed-Sb(III) and Sb(III)-tartrate removal by ZVI at various pH_{ini}s. Reaction conditions: [Sb(III)]₀ = 10 mg/L, ZVI = 1.0 g/L.



Figure 3. Influence of WMF on the amount of Sb_{tot} removed in the process of uncomplexed-Sb(III) and Sb(III)-tartrate removal by ZVI at different initial substrate concentrations at pH_{ini} 5.0. Reaction conditions: ZVI = 1.0 g/L, reaction time = 60 h.



Figure 4. Time evolution of Sb *K*-edge XANES spectra and linear combination fits of the Sb(III)-tartrate-treated ZVI (a) without WMF and (b) with WMF at pH_{ini} 5.0. Reaction conditions: ZVI = 1.0 g/L, [Sb(III)-tartrate]₀ = 10 mg/L. Experimental XANES data are shown as thick black solid lines and red dashed lines represent the linear combination fits.



Figure 5. X-ray diffraction scans of ZVI precipitates reacted with different substrates and substrates of different concentrations at pH_{ini} 5.0. Reaction conditions: ZVI = 1.0 g/L, reaction time = 60 h.



Figure 6. Influence of tartrate and WMF on Sb removal by ZVI: (a) $[Sb(III)]_0 = 40 \text{ mg/L}$; (b) $[Sb(V)]_0 = 40 \text{ mg/L}$, $[C_4H_4O_6^{2-}]_0 = 0.33 \text{ mM}$. Reaction conditions: ZVI = 1.0 g/L, pH_{ini} 5.0.



Figure 7. Illustration of the major reactions occurring in the ZVI-H₂O-O₂ system and mechanisms of Sb(III)/Sb(III)-tartrate oxidation and sequestration.



Figure 8. Influence of WMF on the change of total antimony concentration in the process of Sb(III) and Sb(III)-tartrate removal by ZVI in the semi-continuous flow experiment. Reaction conditions: ZVI = 10 g, V = 1.6 L, $[Sb(III)]_0 = 1.0 \text{ mg/L}$. (a) v = 6.67 mL/min, pH_{ini} 7.1 (not adjusted); (b) v = 6.67 mL/min, pH_{ini} 5.0; (c) v = 13.33 mL/min, pH_{ini} 5.0; (d) v = 6.67 mL/min, pH_{ini} 5.0.