

Effect of Weak Magnetic Field on Arsenate and Arsenite Removal from Water by Zerovalent Iron: An XAFS Investigation

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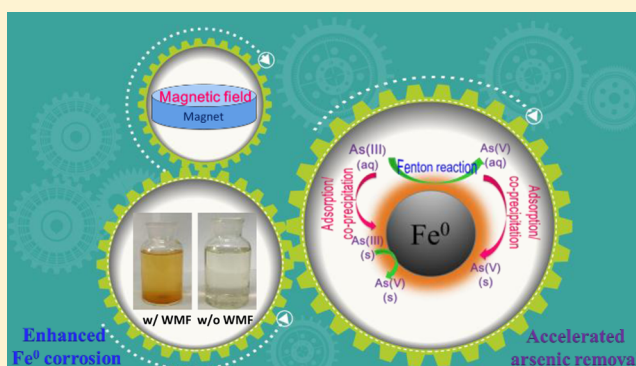
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S Supporting Information

ABSTRACT: In this study, a weak magnetic field (WMF), superimposed with a permanent magnet, was utilized to improve ZVI corrosion and thereby enhance As(V)/As(III) removal by ZVI at pH_{ini} 3.0–9.0. The experiment with real arsenic-bearing groundwater revealed that WMF could greatly improve arsenic removal by ZVI even in the presence of various cations and anions. The WMF-induced improvement in As(V)/As(III) removal by ZVI should be primarily associated with accelerated ZVI corrosion, as evidenced by the pH variation, Fe²⁺ release, and the formation of corrosion products as characterized with X-ray absorption fine structure spectroscopy. The arsenic species analysis in solution/solid phases at pH_{ini} 3.0 revealed that As(III) oxidation to As(V) in aqueous phase preceded its subsequent sequestration by the newly formed iron (hydr)oxides. However, both As(V) adsorption following As(III) oxidation to As(V) in solution and As(III) adsorption preceding its conversion to As(V) in solid phase were observed at pH_{ini} 5.0–9.0. The application of WMF accelerated the transformation of As(III) to As(V) in both aqueous and solid phases at pH_{ini} 5.0–9.0 and enhanced the oxidation of As(III) to As(V) in solution at pH_{ini} 3.0.

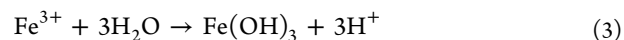
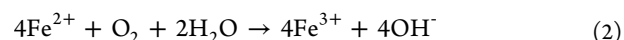
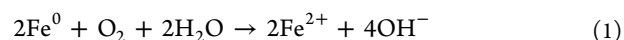


INTRODUCTION

Arsenic-contaminated water is a significant, worldwide problem that poses a great health threat to millions of people.¹ Naturally occurring arsenic that exceeds the guideline value of WHO (10 µg/L) in well water supplies has always been reported as a serious health risk in Bangladesh,² China,³ and elsewhere.⁴ Arsenic is present in aquatic environments largely in inorganic arsenate As(V) and arsenite As(III). Because As(III) is more toxic,⁵ more soluble, and more mobile than As(V),⁶ it is typically first oxidized to As(V); then the As(V) is removed using adsorption, precipitation, or ion exchange processes.⁷

Application of zerovalent iron (ZVI) has been proved to be an environmentally friendly approach for both As(III) and As(V) removal from water due to its low cost, simplicity in handling, and scalability.^{8–10} Moreover, ZVI can simultaneously remove As(V) and As(III) without oxidation pretreatment so that no additional chemicals are required to achieve complete arsenic removal.¹¹ It is generally accepted that the mechanisms of As(III) and As(V) removal by ZVI is based on adsorption and coprecipitation, coupled with the continuous generation of iron (oxyhydr)oxides resulting from the Fe⁰ corrosion

reaction.^{12–14} Reactions 1–3 represent the most relevant processes that may be involved in the formation of iron species associated with As uptake. Under oxic conditions, Fe⁰ is oxidized to Fe²⁺ by oxygen accompanied by an increase in solution pH, as shown in reaction 1,¹⁵ and the generated Fe²⁺ can be further oxidized to Fe³⁺, following reaction 2. Fe³⁺ will hydrolyze immediately and generate Fe(OH)₃, following reaction 3.



One can thus infer that efficient arsenic removal largely depends on the ZVI corrosion rate and the subsequent

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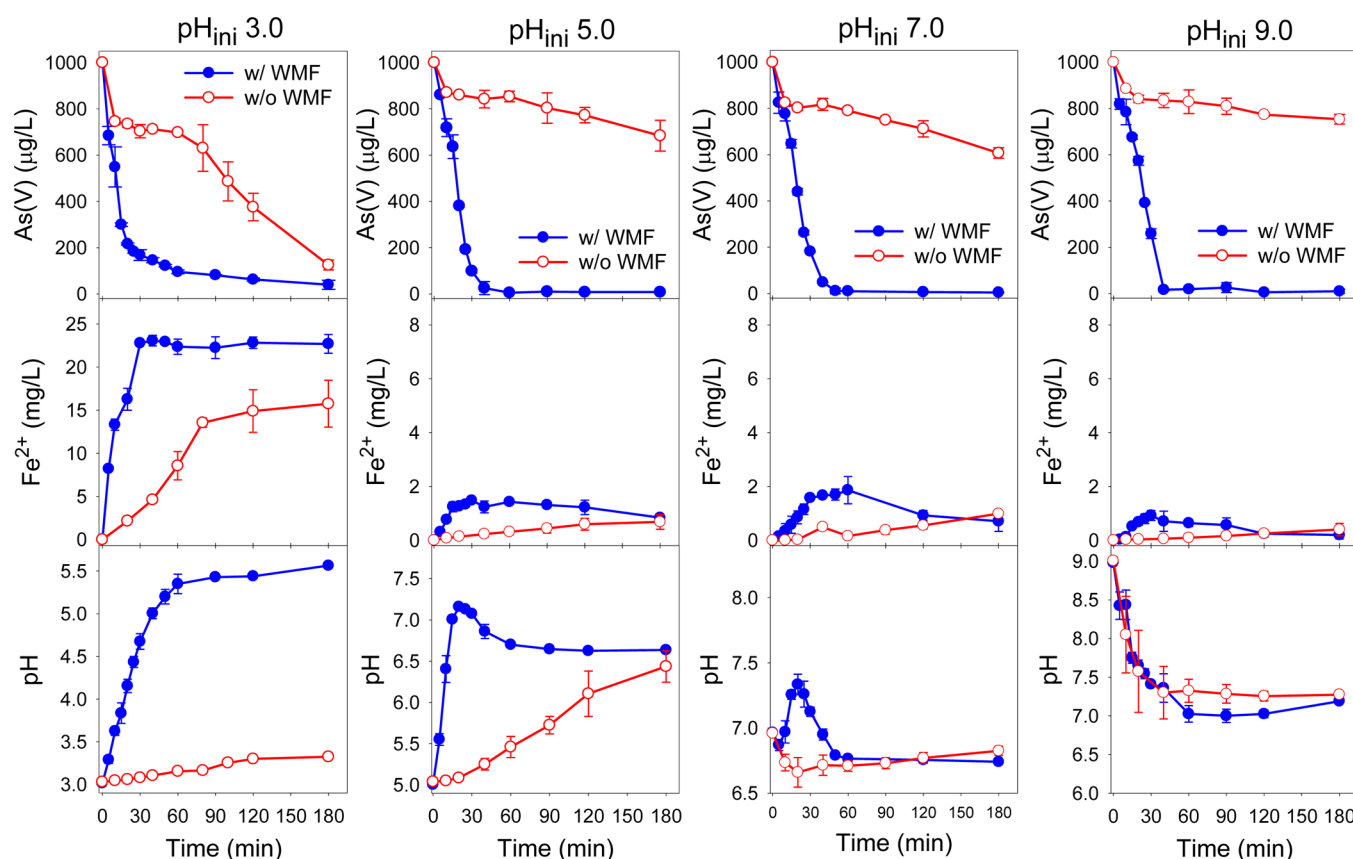
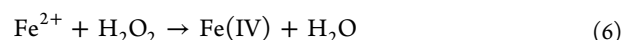
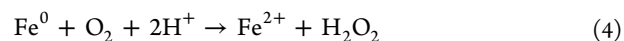


Figure 1. Influence of WMF on As(V) removal by ZVI and the corresponding variations in dissolved Fe^{2+} and solution pH at various initial pH values (ZVI = 0.10 g/L, initial As(V) = 1000 $\mu\text{g/L}$, $T = 25^\circ\text{C}$).

formation rate of Fe(III) (oxyhydr)oxides.¹⁶ In these three reactions, reaction 3 is very fast and unlikely to be the limiting step for arsenic sequestration. The oxidation rate of Fe^{2+} by oxygen drops exponentially with decreasing pH,¹⁷ indicating that reaction 2 may become the limiting step for arsenic removal under very acidic conditions. Under most conditions, conventional ZVI technology has low arsenic removal efficiency because of its slow corrosion rate (reaction 1).¹⁸

In our previous study, it was found that the application of a weak magnetic field (WMF) could promote ZVI corrosion over a wide pH range, resulting in more rapid release of Fe^{2+} and greater sequestration of Se(IV).¹⁹ ZVI is magnetized in a superimposed WMF and generates an induced magnetic field (MF). It has been reported that the Lorentz force acting on the charged ions can increase the mass transport²⁰ and the magnetic field gradient force can result in the transportation of paramagnetic Fe^{2+} along the higher field gradient at the ZVI particle surface,²¹ which may thus induce accelerated corrosion of the ZVI. Considering that arsenic removal by ZVI is generally limited by its corrosion rate, enhanced As(V) and As(III) uptake by ZVI may be achieved through the introduction of a WMF. However, this hypothesis has not been validated.

The corrosion of ZVI by oxygen also produces strong oxidants capable of oxidizing various organic and inorganic compounds. Under acidic conditions, Fe^0 surfaces transfer two electrons to oxygen (reaction 4) to produce hydrogen peroxide (H_2O_2). The interaction of H_2O_2 with Fe^{2+} will generate hydroxyl radical ($\cdot\text{OH}$), following reaction 5 at a low pH, or Fe(IV) at a pH above 5.0, via reaction 6.^{22–24}



Several spectroscopic investigations of arsenic speciation after reaction with ZVI have shown the partial oxidation of As(III) to As(V).^{9,14,25} However, it is unclear whether the redox transformation of arsenic species could be affected by WMF. In addition, with respect to the As(III) removal mechanism by ZVI, there is still a dispute on whether the As(III) oxidation occurs in solution or on the surface of iron oxides.^{26,27} To address this issue, simultaneous analysis of the arsenic species in solution and solid phases versus reaction time will be helpful, and the application of WMF may provide new insight into this issue.

Accordingly, the main objectives of this study were to (1) investigate the feasibility of enhancing As(V) and As(III) removal by ZVI with WMF at various pH values; (2) examine As(III) redox transformations in both aqueous and solid phases to clarify the mechanisms of As(III) removal by ZVI; (3) explore the mechanisms of WMF-induced improvement in As(V) and As(III) removal by ZVI; (4) evaluate the effect of WMF on arsenic removal from a real groundwater sample.

MATERIALS AND METHODS

Materials. All solutions were prepared with Milli-Q water and all chemicals employed in this study were of analytical grade. The ZVI used in this study was purchased from the Shanghai Jinshan Reduced Iron Powder Factory (China), which

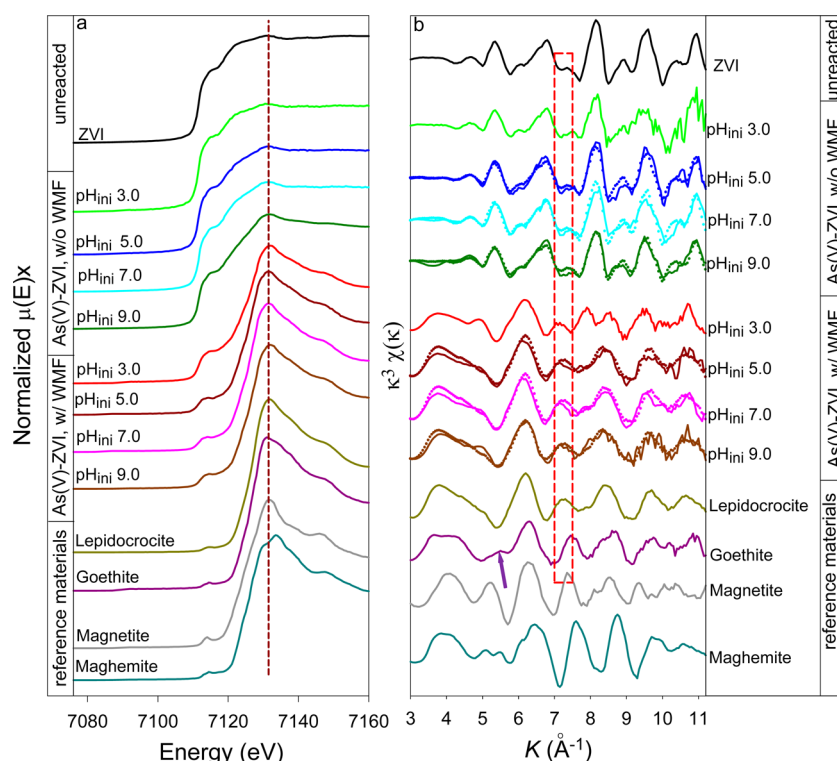


Figure 2. Fe *K*-edge XANES spectra (a) and k^3 -weighted EXAFS spectra (b) of As(V)-treated ZVI corrosion products and reference materials (ZVI = 0.10 g/L, initial As(V) = 1000 $\mu\text{g/L}$, reaction time: 180 min, $T = 25^\circ\text{C}$). Experimental data is shown as thick solid lines. The dashed lines and the arrow ($k \sim 5.7 \text{ \AA}^{-1}$) in (b) represent the linear combination fits and the line shape feature of goethite, respectively.

had a mean diameter of 40 μm and a BET surface area of 0.76 m^2/g .

Batch Experiments and Analytical Methods. The static, nonuniform magnetic field was supplied by a permanent magnet with a diameter of 20 mm and a thickness of 1 mm under the reactor. The maximum magnetic intensity was determined to be $\sim 15 \text{ mT}$ at the bottom of the reactor. Stock solutions of 1000 mg/L As(V) and As(III) were prepared from $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$ and NaAsO_2 , respectively. Working solutions (1000 $\mu\text{g/L}$ As(V) or As(III) in 0.003 M CaSO_4) were freshly prepared for each batch test. The initial pH values were adjusted with NaOH and H_2SO_4 , and no attempt was made to maintain a constant pH during the process. Batch tests were started by adding 0.05 g ZVI in 500 mL solution, and the solution was mixed at 400 rpm with a mechanical stirrer which avoided the aggregation of ZVI induced by a WMF (the same stirring intensity was used in tests without WMF). The experimental reactor was open to the air, unless otherwise specified. At given time intervals, approximately 5 mL of suspension was sampled, filtered through a 0.22 μm membrane filter, and acidified for analysis. Each experiment was carried out in duplicate. Concentrations of aqueous As were determined by ICP-MS, whereas speciation of As(III) and As(V) in solution was determined by HPLC-ICP-MS using a published method.²⁸ The Fe^{2+} concentration was determined by the 1,10-phenanthroline colorimetric method using an UV-visible spectrophotometer at 510 nm.²⁹

After specific 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 Fe *K*-edge and As *K*-edge X-ray absorption fine structure (XAFS) analysis. The details of XAFS analysis are presented in Text S1 of Supporting Information (SI).

A groundwater sample, collected from an arsenic-contaminated place in Shanxi (China), was used to determine the influence of WMF on arsenic removal from groundwater (see parameters in SI Table S1). The experiments were performed in a series of 25 mL glass vials. To initiate the reaction, different amounts of ZVI were dosed into the glass vials, each of which contained 20 mL of arsenic-bearing groundwater. These vials were sealed immediately and placed on a bench, without mixing during the reaction. A small permanent magnet, with a diameter of 18 mm and a thickness of 1 mm, was placed under the glass vial to provide magnetic field. After 24 h, the supernatant was collected and analyzed following the aforementioned procedures.

RESULTS AND DISCUSSION

WMF Effects on As(V) Removal from Water and the Corresponding ZVI Corrosion. Figure 1 depicts the influence of WMF on As(V) removal by ZVI and the corresponding variations in dissolved Fe^{2+} and solution pH at various initial pH values. Obviously, As(V) removal was highly pH dependent in the absence of WMF. Approximately 87.5% of As(V) was removed by ZVI in 3 h at $\text{pH}_{\text{ini}} 3.0$, whereas only 24.7–39.4% of As(V) was removed at $\text{pH}_{\text{ini}} 5.0$ –9.0 within the same time period. This pH-dependent trend of As(V) removal by ZVI had also been reported by other researchers and was always explained by the decreasing ZVI corrosion rate and/or the ionization of adsorbates and adsorbents with increasing pH.^{26,30–32}

At $\text{pH}_{\text{ini}} 3.0$, the kinetics of As(V) removal by ZVI, without WMF, could be roughly divided into three stages: fast adsorption (0–10 min), slow adsorption (10–80 min), and sustained rapid adsorption (80–180 min). The fast As(V)

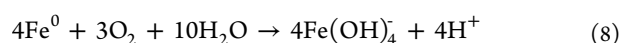
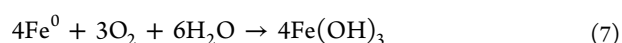
removal at the initial stage should be ascribed to the oxide film coated on the pristine ZVI particles. It was found that the concentration of Fe^{2+} increased progressively in the first 80 min without WMF at pH_{ini} 3.0, resulting from the rapid release of Fe^{2+} from Fe^0 (reaction 1) but slow oxidation of Fe^{2+} by oxygen (reaction 2) at low pH values.²⁶ Therefore, the slow removal of As(V) without WMF during the second stage should be associated with the minor accumulation of ferric (hydr)oxides. The drop in the Fe^{2+} release rate after 90 min should be ascribed to the increased oxidation rate of Fe^{2+} by oxygen, which resulted in the formation of ferric (hydr)oxides. Consequently, the continuous generation of iron oxides accounted for the sustained rapid adsorption observed in the third stage at pH_{ini} 3.0 without WMF.³³ When pH_{ini} was elevated to 5.0–9.0, the kinetics of As(V) removal, in the absence of WMF, could be divided into two stages: a fast arsenic removal stage in the first 10 min, followed by a slow arsenic removal stage that lasted for hours. Likewise, the oxide film coated on the pristine ZVI particles accounted for the adsorption behavior of As(V) in the first stage, whereas the subsequent slow As(V) removal should be associated with the slow ZVI corrosion rate, which was proved by the XAFS analysis.

The Fe *K*-edge XANES spectra and k^3 -weighted EXAFS spectra of As(V)-treated ZVI samples (collected at different pH_{ini} levels, without WMF) and the reference materials are shown in Figure 2. Without WMF, the XANES and EXAFS spectra of As(V)-treated ZVI samples were analogous to those of pristine ZVI. Furthermore, to identify the composition of ZVI corrosion products, linear combination fitting (LCF) analysis was carried out based on the Fe k^3 -weighted EXAFS spectra (Figure 2b); corresponding fit results are summarized in SI Table S2. Metallic Fe^0 was the major Fe species (81.3–96.0%) with minor magnetite/maghemite (4.0–18.7%) that was identified in the As(V)-treated ZVI samples collected at pH_{ini} 5.0–9.0 without WMF. The above discussion suggested that As(V) removal by ZVI at pH_{ini} 5.0–9.0, in the absence of WMF, was mainly limited by the ZVI corrosion rate. It should be noted that the samples obtained at pH_{ini} 3.0 could not be identified by LCF due to the limited number of XAFS references and data compromised by the strong signal from metallic Fe^0 .²⁵

The application of WMF substantially enhanced the As(V) removal rate and efficiency over a pH_{ini} range of 3.0–9.0, as shown in Figure 1. At pH_{ini} 3.0, the application of WMF markedly shortened the reaction time from 180 to 50 min to achieve an 87.5% removal rate for As(V). The WMF-induced enhancement in As(V) removal by ZVI was even more significant within the pH_{ini} range of 5.0–9.0, which successfully reduced 1000 $\mu\text{g/L}$ As(V) to below 10 $\mu\text{g/L}$ within 60 min. The application of WMF reduced the necessary reaction time for efficient As(V) removal with micrometer ZVI from hours (even days) to minutes.¹³

The improvement in As(V) removal by ZVI, in the presence of WMF, should be associated with accelerated ZVI corrosion. According to reaction 1, two protons are consumed per Fe^{2+} produced, thus a pH increase during the corrosion can be expected. Indeed, at pH_{ini} 3.0, the pH experienced a gradual increase with time but was lower than 3.4 at the end of 3 h, without WMF, as shown in Figure 1. While with WMF, the solution pH increased dramatically from 3.0 to 4.7 within 30 min and eventually reached 5.6 after 3 h. The significant pH change, upon the application of WMF, was accompanied by a

rapid release of Fe^{2+} in solution, which reached a plateau within 30 min and then remained almost constant. A sharp increase in pH, from 5.0 to 7.2 during the first 20 min in the presence of WMF, was also observed at pH_{ini} 5.0. However, not much Fe^{2+} release occurred because of its fast oxidation by dissolved oxygen at high pH values.²⁹ These results provided direct evidence that ZVI corrosion rates were accelerated at pH_{ini} 3.0 and 5.0, upon the application of WMF. However, when the pH_{ini} values were further elevated to 7.0 and 9.0, the influences of WMF on pH variation and Fe^{2+} generation were minor. The ZVI overall corrosion reactions were restated, taking into account the dominant Fe species at pH_{ini} values of 7.0 (reaction 7) and 9.0 (reaction 8).²⁶ According to reaction 7, no proton consumption takes place at pH 7.0, which corresponds well with the nearly constant pH values observed in this study, regardless of the application of WMF. The small pH elevation in the first 30 min in the ZVI/WMF system at pH_{ini} 7.0 may be because the ZVI corrosion rate is greater than the oxidation rate of Fe^{2+} and the subsequent Fe^{3+} hydrolysis rate at the beginning of reaction.



At pH_{ini} 9.0, protons are produced via reaction 8, leading to a decrease in pH during the process. However, when the pH falls to near 7.0, the ZVI corrosion process may change their pathway from reaction 8 to reaction 7, and then the pH will not change markedly with elapsing time, as illustrated in Figure 1. Compared to the case without WMF, it was observed that the ZVI suspension became yellow more quickly and eventually got a darker yellow with WMF at pH_{ini} 7.0–9.0. This resulted from accelerated ZVI corrosion and more iron (oxyhydr)oxides being generated in the presence of WMF. The iron corrosion products generated with WMF at pH_{ini} 3.0–9.0 were also analyzed by XAFS. As shown in Figure 2a, the positions of the absorption maximum (7131.5 eV) of ZVI corrosion products formed in the presence of WMF were close to those of the Fe(III) reference compounds, implying that these solids were mainly composed of nonmetallic Fe. This was further confirmed by the Fe k^3 -weighted EXAFS spectra (Figure 2b). The small peaks at $k = 7.0$ – 7.5 \AA were observed in the samples collected from the ZVI/WMF system, which were always considered to be the typical spectra feature of Fe(III) (oxyhydr)oxides and dominantly derived from the edge-sharing FeO_6 octahedral linkages.³⁴ Furthermore, as summarized in SI Table S2, LCF analysis revealed that Fe in the solid phases, collected at pH_{ini} 5.0–9.0, was predominantly present as lepidocrocite (80.8–92.6%) in the presence of WMF, whereas goethite and magnetite/maghemite were rejected. This is in agreement with our previous study.¹⁹ These XAFS data provided further evidence that ZVI corrosion was largely accelerated upon the application of WMF, which contributed to the enhanced As(V) removal. In the presence of the WMF, the Lorentz force gives rise to convection in the solution which narrows the diffusion layer and enhances mass transport²⁰ while the field gradient force tends to drive paramagnetic ions (esp. Fe^{2+}) to the region where the magnetic field gradient is higher at the ZVI particle surface.²¹ Both of the two sources of magnetic forces could be operative in the tests of arsenic removal by ZVI with WMF and contribute to the accelerated corrosion of ZVI.³⁵ In addition, lepidocrocite has a looser and more porous structure than magnetite or maghemite. Thus,

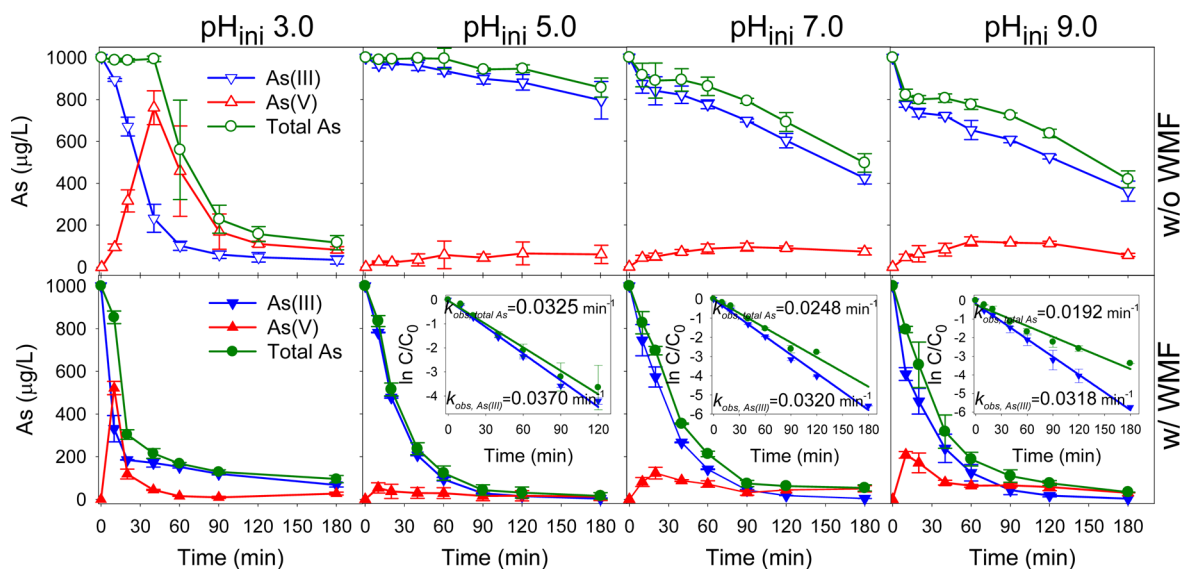


Figure 3. Influence of WMF on the depletion of total arsenic and As(III) as well as the evolution of As(V) in the process of As(III) removal by ZVI at various initial pH values (ZVI = 0.10 g/L, initial As(III) = 1000 $\mu\text{g/L}$, $T = 25^\circ\text{C}$). Inset: simulation of the rates of total arsenic and As(III) removal in the presence of WMF with pseudo-first-order model.

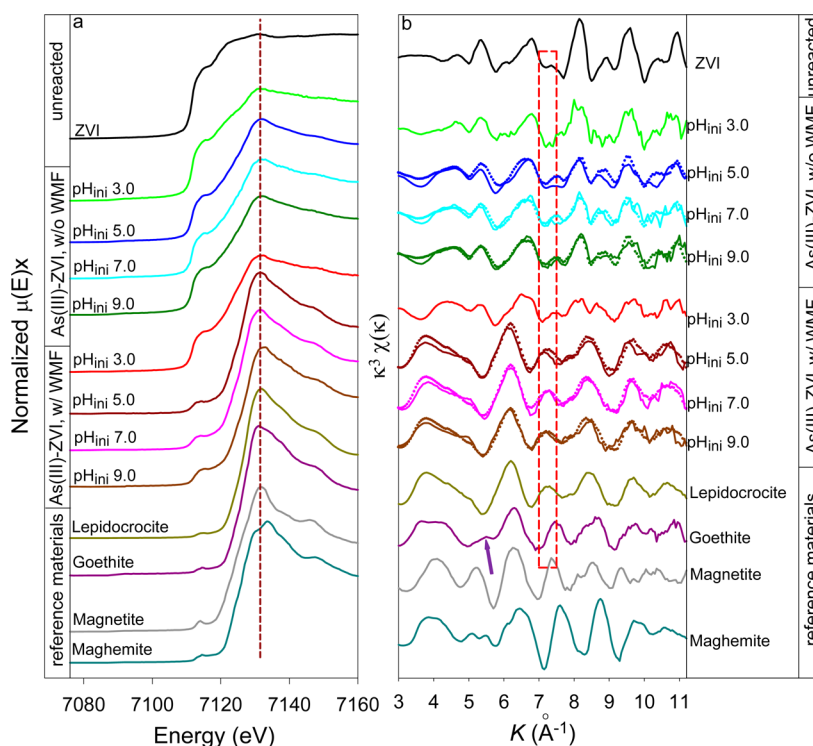


Figure 4. Fe K-edge XANES spectra (a) and k^3 -weighted EXAFS spectra (b) of As(III)-treated ZVI corrosion products and reference materials (ZVI = 0.10 g/L, initial As(III) = 1000 $\mu\text{g/L}$, reaction time: 180 min, $T = 25^\circ\text{C}$). Experimental data is shown as thick solid lines. The dashed lines and the arrow ($k \approx 5.7 \text{ \AA}^{-1}$) in (b) represent the linear combination fits and the line shape feature of goethite, respectively.

favorable mass transport between the solid phase and aqueous phase could be expected, which may also partially account for the WMF accelerating effect.^{25,36}

Although WMF can accelerate ZVI corrosion, it has no effect on Fe^{2+} oxidation by oxygen (reaction 2). As(V) sequestration by ZVI, without WMF, was mainly limited by ZVI corrosion at $\text{pH}_{\text{ini}} 5.0$ – 9.0 while controlled by both ZVI corrosion and subsequent Fe^{2+} oxidation at $\text{pH}_{\text{ini}} 3.0$. Consequently, the application of WMF, that had enhanced As(V) removal at $\text{pH}_{\text{ini}} 5.0$ – 9.0 to a greater extent than it had at $\text{pH}_{\text{ini}} 3.0$, weakened

the influence of pH on As(V) removal. In the presence of WMF, As(V) was removed at a lower rate at $\text{pH}_{\text{ini}} 3.0$ than it was at $\text{pH}_{\text{ini}} 5.0$ – 9.0 . Although the ZVI corrosion rate dropped with increasing pH, the As(V) removal at $\text{pH}_{\text{ini}} 3.0$ with WMF was limited by the slow Fe^{2+} oxidation rate under acidic conditions.

WMF Effects on As(III) Oxidation and Removal from Water. Figure 3 shows the influence of WMF on the depletion of total As and As(III), as well as the evolution of As(V) in the process of As(III) removal by ZVI at different pH_{ini} levels.

Without WMF, the total removal efficiency of As in 3 h was 88.4%, 14.4%, 50.4%, and 58.1%, at pH_{ini} of 3.0, 5.0, 7.0, and 9.0, respectively. The removal of aqueous As(III) by ZVI at pH_{ini} 3.0, in the absence of WMF, obviously consisted of two periods. During the first period (the first 40 min of reaction), the decrease in As(III) concentration was accompanied by an elevation in As(V), whereas the concentration of total As remained almost constant. This indicated the quick transformation of As(III) to As(V), although negligible sequestration of As(V) was involved during this period. During the second stage, the concentration of total As decreased progressively, which was mainly associated with the generation of iron (oxyhydr)oxides and the resulting As(V) removal. Within the pH_{ini} range of 5.0–9.0, the time plots of total As concentrations, in the absence of WMF, were very similar to those of As(III), and the total removal of As increased with elevating pH. Furthermore, a more rapid As uptake was achieved in the first 10 min at pH_{ini} 9.0 than it did at pH_{ini} 7.0, and no fast As removal was observed in the first 10 min at pH_{ini} 5.0 without WMF. Little As(V) was detected in solution under these conditions. All of the above phenomena implied that As(III) was primarily removed by the oxide film coated on the pristine ZVI and/or the newly formed iron oxides without oxidizing to As(V) in the absence of WMF at pH_{ini} 5.0–9.0.^{27,37}

Without WMF, more arsenic was removed at pH_{ini} 7.0–9.0 in the process of As(III) removal by ZVI than from As(V), which is consistent with the phenomenon reported by Su and Puls.¹³ It was elaborated that As(V) was more effectively removed by coprecipitation than As(III) was at an equilibrium pH lower than 7.4.³⁸ Therefore, the more efficient removal of As(III) than of As(V) may be associated with the formation of more ZVI corrosion products when the As(III) species was present at pH_{ini} 7.0–9.0 (the equilibrium pH range was 6.6–7.2 for removal of both As(V) and As(III) by ZVI in this work). This was supported by the Fe *K*-edge XAFS analysis of As(III)-treated ZVI samples. According to the best LCF fit results (Figure 4b and SI Table S2), the metallic Fe fraction in the As(III)-treated samples collected at pH_{ini} 5.0–9.0, without WMF, was 46.2–64.1%, which is much smaller than that in As(V)-treated samples (75.6–96.0%). Triszc et al.³⁹ revealed that, compared to As(III), As(V) depressed ZVI corrosion at pH_{ini} 7.1, which is in agreement with our observations. The above discussion also indicated that when As(III) was the initial arsenic species, the inefficient arsenic removal at pH_{ini} 5.0 without WMF was primarily ascribed to the low affinity of As(III) for an iron oxide surface under acidic conditions.

The application of WMF remarkably enhanced the removal of both As(III) and total As at all tested pH values, as illustrated in Figure 3. The removal efficiencies of total As, with WMF, were as high as 90.5–98.4%. Upon the introduction of WMF at pH_{ini} 3.0, it was observed that the lag period of time for total As removal disappeared, the depletion rate of As(III) increased, and the accumulation of As(V) was alleviated. Since As(III) has a low affinity for iron (oxyhydr)oxides due to its electric neutrality, whereas As(V) is much more easily adsorbed or entrapped under acidic conditions,^{6,40} acceleration of the disappearance rate of As(III) indicated that its conversion to As(V) in solution was improved by WMF at pH_{ini} 3.0. The oxidizing $\cdot\text{OH}$ produced by the Fenton reaction is generally believed to be responsible for As(III) oxidation at a low pH,^{26,41} thus, WMF may favor the Fenton reaction (via reaction 5) involved in the ZVI system by accelerating ZVI corrosion. Although As(III) was oxidized at a greater rate in the

presence of WMF, a drop in As(V) accumulation was observed, as compared to its counterpart in the absence of WMF, which could be explained by the quick generation of iron (oxyhydr)oxides. These results provided strong evidence that As(III) was first oxidized to As(V) before As depletion at pH_{ini} 3.0, and the oxidation mainly occurred in solution.^{26,42,43}

The removal kinetics of aqueous As(III) and total As by ZVI with WMF at pH_{ini} 5.0–9.0 are well simulated with the pseudo-first-order reaction model, as demonstrated by the insets in Figure 3. The observed rate constants (k_{obs}) of total As removal were 3.25×10^{-2} , 2.48×10^{-2} , and $1.92 \times 10^{-2} \text{ min}^{-1}$ at pH_{ini} 5.0, 7.0, and 9.0, respectively, and the corresponding surface normalized rate constants (k_{SA}) were determined to be 25.7, 19.6, and $15.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, respectively. The drop in k_{obs} of total As removal with increasing pH_{ini} could be due to the decreased ZVI corrosion rate with elevating pH_{ini} . Kanel et al. reported that the k_{SA} of As(III) sequestration by Nano-ZVI ($\sim 15 \text{ nm}$) ranged from 0.252 to $0.690 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$,⁸ which were 1–3 orders of magnitude higher than those of micrometer ZVI as reported by Su and Puls.¹³ Upon the application of WMF, the k_{SA} of As(III) removal by micrometer ZVI obtained in this work was 20–100 times higher than that of Nano-ZVI, highlighting the superiority of WMF in enhancing the reactivity of ZVI. The WMF-induced enhancement in As(III) removal by ZVI at pH_{ini} 5.0–9.0 can be ascribed to the accelerated ZVI corrosion (reaction 1) and the subsequent elevated As(III) oxidation rate. Figure 4 and SI Table S2 unravel that WMF significantly facilitated ZVI corrosion in the process of As(III) removal by ZVI at pH_{ini} 5.0–9.0. The fraction of Fe^0 in the As(III)-treated ZVI samples was lowered to 8.7–11.3%, and the dominant corrosion product was lepidocrocite (88.7–91.3%) in the presence of WMF. As(III) oxidation could also occur at $\text{pH}_{\text{ini}} \geq 5.0$, since previous studies have suggested that the Fenton reaction (via reaction 6) could take place at a neutral pH with Fe(IV) rather than $\cdot\text{OH}$ as the predominant products.^{23,26} Indeed, the generation of As(V) was observed in the process of As(III) removal at pH_{ini} 5.0–9.0, regardless of the application of WMF. Although the concentration of soluble As(V), after 3 h at pH_{ini} 5.0–9.0 with WMF, was smaller than its counterpart without WMF, the appearance of As(V) in the first 10–20 min in the presence of WMF was more pronounced and increased with increasing pH_{ini} . The observed phenomena implied that the introduction of WMF facilitated the oxidation of As(III) to As(V) in an aqueous phase at pH_{ini} 5.0–9.0. The rate of As(III) oxidation by Fe^0/O_2 in the presence of WMF exceeded that of As(V) adsorption by the corrosion products, resulting in the accumulation of As(V) in the solution, as illustrated in Figure 3.

Arsenic Speciation in the As(III)-treated ZVI Corrosion Products. Although many studies have been conducted on As(III) removal by ZVI, there is still a debate on the mechanism of As(III) oxidation and the removal at circum-neutral pH. Some argue that As(III) is first oxidized in aqueous solution by the Fenton reagent, and then As(V) is adsorbed onto the newly formed hydrous ferric oxides.^{26,42,43} Other researchers believe that the oxidation of As(III) occurs on or near the solid surface, which involves surface-mediated redox transformations instead of adsorption of reaction products formed in the solution phase.^{27,37,41,44} All of them agree that Fenton reactions can take place at a neutral pH range and are responsible for the As(III) oxidation.

To clarify the As(III) oxidation and removal mechanism, As *K*-edge XANES spectra of As(III)-treated ZVI samples were collected (Figure 5) for analysis of the evolution of arsenic

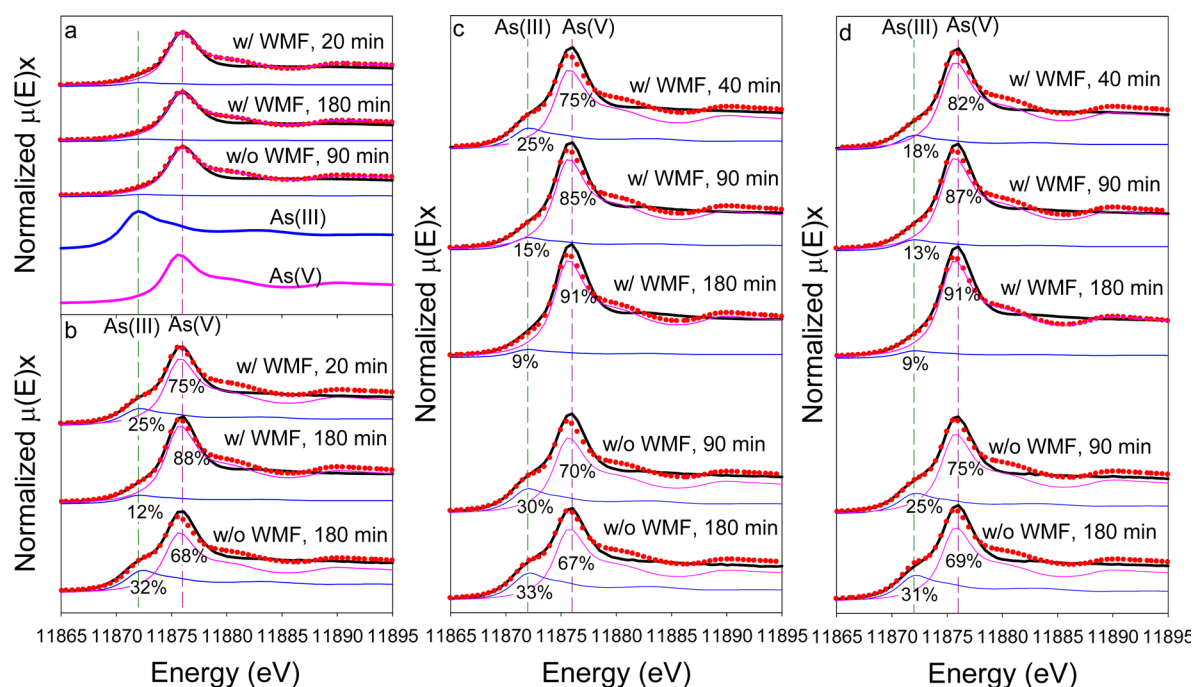


Figure 5. Time-series As K-edge XANES spectra and linear combination fits of the As(III)-treated ZVI at initial pH 3.0 (a), 5.0 (b), 7.0 (c), and 9.0 (d) (ZVI = 0.10 g/L, initial As(III) = 1000 $\mu\text{g/L}$, $T = 25^\circ\text{C}$). Experimental XANES data is shown as thick black solid lines and red dashed lines represent the linear combination fits.

species in the solid phase. At pH_{ini} 3.0, the arsenic speciation in the solution phase demonstrated that As(III) was oxidized to As(V), followed by adsorption, and the LCF analysis confirmed that only As(V) was detected in the solid phase, regardless of the application of WMF. Although the trends of aqueous As(III) removal by ZVI at pH_{ini} 5.0–9.0 without WMF indicated that As(III) was primarily removed without oxidizing to As(V), LCF analysis showed that the major arsenic species in As(III)-treated ZVI samples without WMF was As(V). Thus, it could be inferred that there was not enough oxidant present in the aqueous phase and the oxidation of As(III) mainly occurred on or near the solid surface at pH_{ini} 5.0–9.0, without WMF.^{27,37,41,44} However, upon the introduction of WMF, As(III) was oxidized to a larger extent in solution, indicating that the solution-oxidation/adsorption mechanism also played an important role. The dynamic transformations of arsenic species in the solid phase were also investigated by analyzing the corrosion products collected at various time intervals (Figure 5). The fraction of As(III) in the As(III)-treated ZVI samples with WMF decreased progressively and remained $\sim 10\%$ at 3 h while those without WMF remained almost constant. This implied that the rate of surface-mediated As(III) oxidation in the presence of WMF was greater than that in the absence of WMF. Combining the results of arsenic removal behavior and arsenic speciation in solution and solid phase, it can be confirmed that both As(V) adsorption following As(III) oxidation to As(V) in solution and As(III) adsorption preceding its conversion to As(V) in solid phase occurred in the process of As(III) removal by ZVI at pH_{ini} 5.0–9.0. Moreover, the transformation of As(III) to As(V) at pH_{ini} 5.0–9.0 in both aqueous and solid phases was improved by applying WMF.

Application for As Removal from Groundwater Samples and Environmental Implications. The WMF effect on arsenic removal from real arsenic-contaminated

groundwater was investigated by checking the residual As at different ZVI dosages, as demonstrated in SI Figure S3. As expected, the color of the ZVI suspension with WMF was darker than its counterpart without WMF, indicating the formation of more iron (oxyhydr)oxides in the presence of WMF. In all of the examined ZVI loadings, much higher arsenic removal efficiency was obtained upon the application of WMF, an advantage that became greater at lower ZVI loadings. The removal efficiency of arsenic by 0.5 g/L ZVI ($\sim 82.3\%$) with WMF was even greater than that of 2.0 g/L ZVI ($\sim 71.6\%$) without WMF. Reducing ZVI loading would be a great advantage in achieving efficient arsenic removal from groundwater. Nevertheless, a much larger dosage of ZVI was necessary to remove arsenic from a real groundwater sample than from a synthetic water sample. This was possibly due to the solutes present in water which could not only compete with arsenic for reactive sites but also inhibit ZVI corrosion.^{45,46} Therefore, further research is necessary to investigate and determine the effect of water chemistry on arsenic removal by ZVI in the presence of WMF.

This study offers an innovative alternative approach to substantially improve the reactivity of ZVI for As(V)/As(III) removal by providing a WMF with a permanent magnet. Upon the introduction of WMF, the removal of As(V) and As(III) from deionized water or real groundwater by ZVI could be significantly accelerated over a wide pH range. Most studies on ZVI have mainly focused on using its reducing capacity, while few studies on contaminants removal by the oxidants generated in the process of ZVI corrosion have been carried out, possibly due to the low generation of Fenton reagents and the pH limitation (it only works well in an acidic pH range).^{47,48} Given that the application of WMF accelerated the Fenton reaction and favored As(III) oxidation under both acidic and neutral pH, it can be expected that the oxidative removal of many organic contaminants by ZVI may also be improved with the

aid of WMF. Since there is a challenge to apply WMF in ZVI columns for arsenic removal from water, efforts are being made both on ZVI particles pretreatment by magnetic field and on designing a continuous flow reactor to take advantage of the magnetic field effect.

■ ASSOCIATED CONTENT

● Supporting Information

One text, three figures, and two tables are provided in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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