01 May 2015

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ARTICLE INFO

ABSTRACT

Weak magnetic field (WMF) was employed to improve the removal of Cr(VI) by zero-valent iron (ZVI) for the first time. The removal rate of Cr(VI) was elevated by a factor of 1.12–5.89 due to the application of a WMF, and the WMF-induced improvement was more remarkable at higher Cr(VI) concentration and higher pH. Fe^{2+} was not detected until Cr(VI) was exhausted, and there was a positive correlation between the WMF-induced promotion factor of Cr(VI) removal rate and that of Fe^{2+} release rate in the absence of Cr(VI) at pH 4.0–5.5. These phenomena imply that ZVI corrosion with Fe^{2+} release was the limiting step in the process of Cr(VI) removal. The superimposed WMF had negligible influence on the apparent activation energy of Cr(VI) removal by ZVI, indicating that WMF accelerated Cr(VI) removal by ZVI but did not change the mechanism. The passive layer formed with WMF was much more porous than without WMF, thereby facilitating mass transport. Therefore, WMF could accelerate ZVI corrosion and alleviate the detrimental effects of the passive layer, resulting in more rapid removal of Cr(VI) by ZVI. Exploiting the magnetic memory of ZVI, a two-stage process consisting of a small reactor with WMF for ZVI magnetization and a large reactor for removing contaminants by magnetized ZVI can be employed as a new method of ZVI-mediated remediation.

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Introduction

Chromium can be present in different oxidation states in aquatic environments, of which the most stable states are the hexavalent (Cr(VI)) and trivalent Cr(III) states. Chromium and its compounds are extensively used in many industrial processes and products, such as metallurgy (as a corrosion inhibitor), paint pigments, antifouling agents, fungicides,

leather tanning, and electroplating (Baron et al., 1996; Hug et al., 1997; Naftz et al., 2002; Pratt et al., 1997; Puls et al., 1994). Leakage, poor storage practices and improper disposal of chromium waste have released Cr(VI), a potential carcinogen, into groundwater and surface water (Zazo et al., 2008). The high mobility of Cr(VI) in soils and aquifers (Guan et al., 2011) makes its environmental effect more significant. On the other hand, Cr(III) is much less toxic, and a trace level of Cr(III) is

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needed as an essential trace nutrient for animals and humans (Cespon-Romero et al., 1996; Guertin et al., 2004). The World Health Organization (WHO) and the Ministry of Health of China have established a provisional guideline of 50 μg/L for Cr(VI) in drinking water (Guan et al., 2011). Thus, Cr(VI) should be effectively removed from industrial wastewater before discharge, or from Cr(VI)-contaminated natural water when it is used as a source for potable water (Gheju, 2011).

Cr(VI) removal by reduction to Cr(III) and subsequent precipitation, coprecipitation, or coagulation is well documented. Many chemical, electrochemical and biological methods have been proposed to reduce Cr(VI) to Cr(III) (Barrera-Díaz et al., 2012). In particular, zero-valent iron (ZVI) has been widely used as a reducing agent, especially for *in-situ* treatment of Cr(VI)-contaminated groundwater, since iron is readily available, relatively inexpensive, and nontoxic (Blowes et al., 1997; Liang et al., 2013). However, due to the formation of a passive layer of iron oxides on the surface of ZVI during the high-temperature manufacturing process (Ritter et al., 2002), ZVI has low reactivity toward Cr(VI). Moreover, the reduction of Cr(VI) by ZVI is a self-inhibiting process in near natural groundwater because the generation of (oxy)hydroxide films on the ZVI surface may block further access of Cr(VI) to the iron surface (Hu et al., 2010). Some methods including ZVI pretreatment (acid washing, H_2-reduction), dosing with complexing agents, and sonication have been applied to improve the removal of Cr(VI) by ZVI (Hung et al., 2000; Lai and Lo, 2008; Zhou et al., 2008). Although the aforementioned methods were able to enhance Cr(VI) removal by ZVI, the inconvenience and cost of these measures are major drawbacks in applying them. Moreover, the effectiveness of polishing pretreatments is problematic because iron (hydr)oxides will be rapidly produced on the ZVI surface before its contact with contaminants (Lai and Lo, 2008). One way to overcome this deficiency is to coat a small amount of another metal, nobler than iron (*e.g.*, Cu, Ag), onto the surface of ZVI. It has been reported that coating the surface of ZVI with copper not only significantly enhanced the Cr(VI) reduction rate but also increased the Cr(VI) removal capacity per unit weight of ZVI (Hu et al., 2010). However, there are still considerable concerns over the ecotoxicity and material cost of the noble metals (Crane and Scott, 2012), and the bimetals may be more inactive than pure ZVI (Kim and Carraway, 2000). Therefore, it is critical to explore an environmentally friendly method to significantly improve the reactivity of ZVI for Cr(VI) removal.

Our previous studies observed that Se(IV) removal by pristine or aged ZVI could be significantly improved by applying a weak magnetic field (WMF) (B_{max} < 20 mT) and the accelerated Se(IV) sequestration was accompanied with the accelerated corrosion of ZVI with a faster release of Fe^{2+} (Liang et al., 2014a, 2014b). Moreover, As(III)/As(V) removal by ZVI could also be considerably enhanced over a wide pH range upon the application of a WMF (Sun et al., 2014), ascribed to the improved ZVI corrosion in the presence of WMF. Cr(VI) is different from Se(IV), As(III) and As(V) because ferric (oxy)hydroxide generated in the process of Cr(VI) removal by ZVI can easily passivate ZVI. Although it is expected that the Cr(VI) removal by ZVI can also be accelerated in the presence of WMF, this speculation needs verification. It was proposed in our previous study that the enhanced contaminant removal by ZVI in the presence of WMF could be mainly ascribed to the enhanced mass transport and localized corrosion induced by WMF. If this speculation is correct, the activation energy of contaminant removal by ZVI would not be affected by WMF, which has not yet been confirmed. Besides affecting the mass transport *via* the Lorentz force and field gradient force, the applied WMF may affect the morphology of corrosion products (Hinds et al., 2001) and thus affect the process of contaminant removal by ZVI.

Therefore, the major objectives of the present study were: (1) to investigate the effect of WMF on Cr(VI) removal by ZVI as a function of ZVI dosage, initial Cr(VI) concentration, pH, and magnetizing time; and (2) to understand the role of WMF in Cr(VI) removal process by determining the influence of WMF on the activation energy and corrosion products.

1. Materials and methods

1.1. Chemicals and materials

All chemicals used in this research were of analytical grade and used as received. All stock solutions were prepared with deionized (DI) water obtained from a Milli-Q water system. The Cr(VI) stock solutions were prepared by dissolving $K_2Cr_2O_7$ in DI water. Iron powder with a median size of 32.1 μm was obtained from Beijing Dk Nano technology Co., Ltd., China and used as received. All other chemicals were purchased from Shanghai Qiangshun Chemical Reagent Company. The magnetic field was provided by two pieces of neodymium–iron–boron permanent magnet on an iron sheet placed under the reactor. The magnetic flux density was measured by a Teslameter (Shanghai Hengtong Magnetic & Electric Technology Co., Ltd., Shanghai, China) and the maximum magnetic flux density was ca. 20 mT at the bottom of the reactor. This magnetic field was weak, and is referred as weak magnetic field or WMF hereafter. The experimental setup and details were schematically illustrated in our previous study (Liang et al., 2014b).

1.2. Batch experiments

Batch experiments were carried out to investigate the effect of WMF on Cr(VI) removal by ZVI as a function of ZVI dosage, pH, initial Cr(VI) concentration and temperature. The test solutions of Cr(VI) with varying concentrations were prepared freshly for each batch test in 0.01 mol NaCl and 0.10 mol sodium acetate. Sodium acetate was employed as a buffer to maintain constant pH conditions (±0.1) in the range of 4.0–5.5. Batch tests were started by adding ZVI to 500 mL of test solution, and the solution was mixed at 400 r/min with a mechanical stirrer (the aggregation of ZVI induced by the WMF could be avoided with intense stirring). The experiments were carried out in open reactors in the presence of WMF for 3 hr and at room temperature ((25 ± 0.1)°C) unless otherwise specified. To estimate the activation energy of Cr(VI) removal by ZVI, batch experiments were conducted in the temperature range of 15 to 35°C at pH 5.0 by fixing the initial Cr(VI) concentration at 3.12 mg/L and ZVI dosage at 0.10 g/L. The permanent magnets placed under the reactor were immediately withdrawn after a specified magnetizing time (0, 3, 5, 10, or 120 min) to examine the effects of magnetizing time on Cr(VI) removal. At a fixed

time interval, 6 mL suspension was sampled and immediately filtered through a 0.22 μm membrane filter, which was then acidified with one drop of 65% HNO₃, and then followed by residual Cr(VI) analysis using a TU-1901 UV/visible spectrophotometer (absorbance measured at 540 nm). Fe^{2+} concentration was measured using a colorimetric method with o-phenanthroline. The absorbance of the colored Fe^{2+}-o-phenanthroline complex was recorded at 510 nm using the TU-1901 UV/visible spectrophotometer. All batch experiments were performed in duplicate, and all data points in the figures are the mean of the results and the error bars represent the standard deviation. At the end of experiments, the precipitates were collected, washed with DI water, freeze-dried, and then kept in a desiccator for further analysis.

1.3. Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) analyses

Morphological analysis of the Cr(VI)-ZVI reaction products was performed by SEM using a Hitachi 4700 microscope (at 15 kV). The XPS analysis was conducted using a RBD (RBD Enterprises, USA) upgraded PHI-5000C ESCA system (Perkin Elmer) with Al $K\alpha$ radiation ($h\nu$ = 1486.6 eV). Samples were directly pressed to form a self-supported disk and mounted on a sample holder then transferred into the analyzer chamber. All Cr(VI)-ZVI reaction product samples were stored under N₂ atmosphere to avoid oxidation prior to the analysis.

2. Results and discussion

2.1. WMF effects by different ZVI dosages

The WMF effects on Cr(VI) removal by ZVI at different ZVI dosages were investigated at pH 5.0, as shown in Fig. 1. Since the increase of ZVI dose led to the increase of available ZVI surface area, the rate of Cr(VI) removal by ZVI increased with increasing ZVI dosage, regardless of WMF application. Without WMF, ca. 27% of Cr(VI) was removed by 0.05 g/L ZVI in 3 hr while it took 90 min to achieve 100% Cr(VI) removal by 0.30 g/L ZVI. The introduction of WMF greatly accelerated Cr(VI) removal by ZVI. Almost complete Cr(VI) removal was achieved by 0.05 g/L ZVI in 3 hr or by 0.30 g/L ZVI in 30 min in the presence of WMF. Thus, the necessary reaction time to achieve complete Cr(VI) removal was greatly shortened by introducing WMF. Under different experimental conditions, the kinetics of Cr(VI) removal in ZVI slurry was reported to be first-order, zero-order or less than unity-order (Gheju, 2011). The kinetics of Cr(VI) removal by ZVI in the absence or presence of WMF could be well described by a zero-order kinetic model (d[Cr(VI)]/dt = −k_{obs}) in our study, as illustrated in Fig. S1. The regression coefficient R^2, zero-order rate constants in the absence of WMF k_{obs1}, the rate constants in the presence of WMF k_{obs2}, and the promotion factor f_2, which is defined as (k_{obs2}/k_{obs1} − 1), are summarized in Table S1. Melitas et al. (2001) also reported that Cr(VI) removal kinetics by
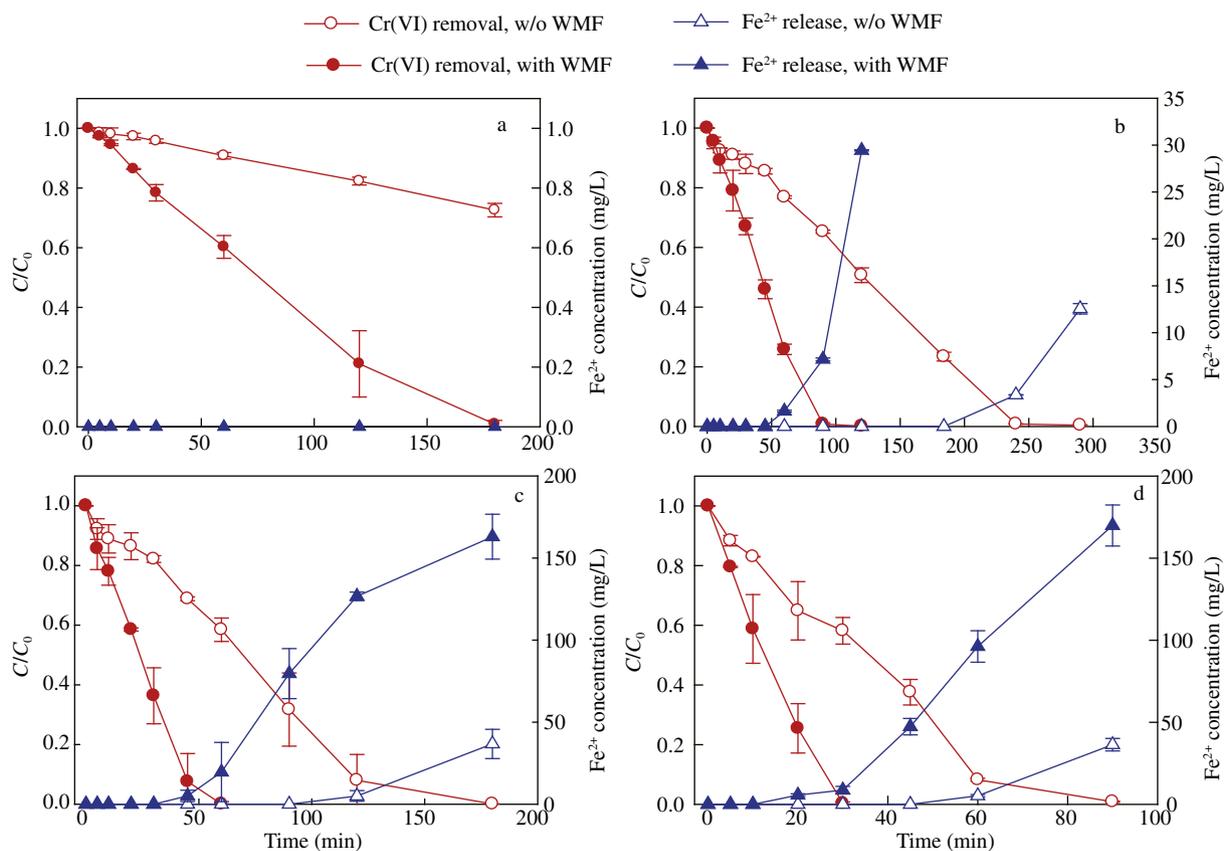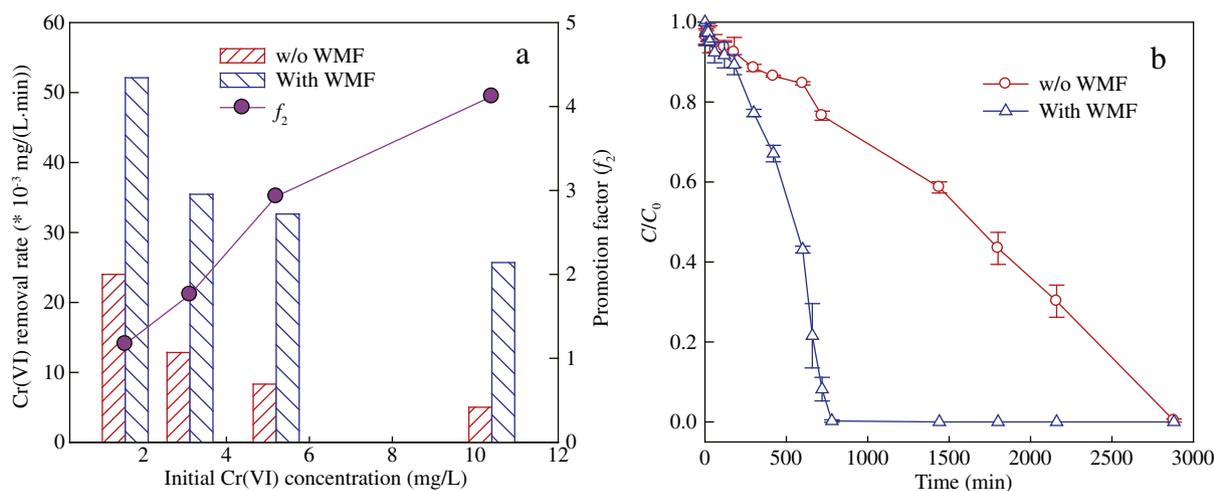

Fig. 1 – Influence of WMF on Cr(VI) removal by ZVI and Fe^{2+} release at different ZVI dosages. ZVI dosage at (a) 0.05 g/L, (b) 0.1 g/L, (c) 0.2 g/L, and (d) 0.3 g/L. Reaction conditions: [Cr(VI)]₀ = 3.12 mg/L, pH = 5.0, background ionic strength 0.01 mol/L. C and C₀ are Cr(VI) concentration at time t and initial.

high-purity ZVI wires fit well with the zero-order kinetic model. It was found that the application of WMF elevated the rate constants of Cr(VI) removal by ZVI by a fraction of 1.33–3.32 at pH 5.0 when the ZVI dosage varied from 0.05 to 0.30 g/L. Moreover, the rate constants of Cr(VI) removal were linearly dependent on ZVI dosage regardless of the application of WMF, as shown in Fig. S2. A linear relationship between k_{obs} and ZVI dosage had also been observed for Cr(VI) reduction by laboratory-synthesized ZVI, reagent grade ZVI and ZVI filings (Alidokht et al., 2011; Ponder et al., 2000; Scherer et al., 2000; Shi et al., 2011). In the presence of WMF, ZVI had a Cr(VI) removal capacity ranging from 10.4–62.4 mg Cr(VI)/g ZVI, much larger than the literature value (Li et al., 2008).

The study of Cr(VI) removal by ZVI in the presence of organic or inorganic complexing reagents reveals that a pathway of Cr(VI) reduction to Cr(III) by ZVI may involve the corrosion of ZVI to release Fe^{2+}, which then reduces Cr(VI) to Cr(III), rather than the direct electron transfer between ZVI and Cr(VI) (Zhou et al., 2008). Therefore, the concentration of Fe^{2+} generated in the process of Cr(VI) removal by ZVI was also monitored and shown in Fig. 1. It was found that Fe^{2+} was not detected until Cr(VI) was completely removed at each ZVI dosage with or without WMF, indicating that Fe^{2+} released from iron corrosion was instantaneously oxidized by Cr(VI) and that ZVI corrosion was the limiting step in the reaction between ZVI and Cr(VI). Yoon et al. reported that Cr(VI) removal was faster under oxic conditions than under anoxic conditions (Yoon et al., 2011), supporting the hypothesis that Fe^{2+} release from ZVI was the limiting step of the reaction of Cr(VI) with ZVI, because the anoxic corrosion of iron was slow whereas aerobic corrosion was rapid as long as O_2 was available. Under aerobic conditions, when Cr(VI) was depleted, dissolved oxygen was the electron acceptor and Fe^{2+} was released following Eq. (1), as shown in Fig. 1.

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \qquad (1)$$

2.2. WMF effects at different Cr(VI) concentrations

Fig. 2a shows the influence of WMF on the zero-order rate constants of Cr(VI) removal by ZVI at pH 5.0 at initial Cr(VI) concentrations ranging from 1.56 to 10.40 mg/L. The rate constants dropped from 24.01×10^{-3} to 5.02×10^{-3} mg/(L·min) in the absence of WMF as the initial Cr(VI) concentration increased from 1.56 to 10.40 mg/L. Most of the studies investigating the effect of Cr(VI) concentration reported that an increase in Cr(VI) concentration had a detrimental effect on Cr(VI) reduction rate by ZVI (Gheju and Iovi, 2006; Lee et al., 2003). This inhibitory behavior at high Cr(VI) concentration can be attributed to the increasing iron surface passivation with increasing Cr(VI) concentration because of the passivating effect of a corrosion inhibitor like Cr(VI) (Melitas et al., 2001). The formation of the $(Cr_xFe_{1-x})(OH)_3$ or $Cr_xFe_{1-x}OOH$ layer on the ZVI surface increases the resistance for the electron transfer from ZVI to oxidants like Cr(VI) or oxygen and hinders the reduction of Cr(VI) by ZVI at high initial Cr(VI) concentrations (Li et al., 2008). Imposing a WMF could remarkably improve Cr(VI) removal by ZVI at various Cr(VI) concentrations, and the rate constants varied from 52.10×10^{-3} to 27.01×10^{-3} mg/(L·min). Moreover, the WMF-induced improvement was greater at a higher initial Cr(VI) concentration since the promotion factor increased with increasing Cr(VI) concentration, as depicted in Fig. 2a. Thus, the inhibitory effect of passivation layers at a higher initial Cr(VI) concentration could be greatly alleviated by imposing a WMF. The rate constants of Cr(VI) removal by ZVI with WMF were determined at various ZVI dosages when the initial Cr(VI) concentration was 10.4 mg/L, shown in Fig. S2. Cr(VI) was always removed at a slower rate by ZVI at 10.4 mg/L than that at 3.12 mg/L in the presence of WMF, attributable to the inhibitory effect of Cr(VI). However, the removal rate constants of Cr(VI) by ZVI in the presence of WMF when the initial Cr(VI) was 10.4 mg/L were much higher than those in the absence of WMF when the initial Cr(VI) was 3.12 mg/L, confirming the promoting effect of WMF on Cr(VI) removal. To further test the positive effects of WMF on

Fig. 2 – WMF effects on Cr(VI) removal rate by ZVI (a) at various initial Cr(VI) concentrations with a ZVI dosage of 0.1 g/L and (b) at an initial Cr(VI) concentration of 20.8 mg/L with a ZVI dosage of 0.2 g/L. The line in (a) shows the promotion factor (f_2) at various initial Cr(VI) concentrations. Reaction conditions: pH = 5.0, background ionic strength 0.01 mol/L.

Cr(VI) removal by ZVI at high initial Cr(VI) concentrations, an experiment with initial Cr(VI) concentration of 20.8 mg/L was conducted. The results revealed that Cr(VI) could be completely removed by ZVI within 13 hr in the presence of WMF while only ~25% Cr(VI) was removed within 13 hr without WMF, as shown in Fig. 2b, which verified the advantageous effect of WMF on Cr(VI) removal by ZVI, especially at a high initial Cr(VI) concentration.

2.3. WMF effects at different pH levels

The WMF effects on Cr(VI) removal by ZVI at different pH were investigated over the pH range of 4.0–5.5 since negligible Cr(VI) was removed by ZVI even in the presence of WMF at pH 6.0 in 3 hr. Fig. 3a shows the WMF effects on Cr(VI) removal rates by ZVI at various pH levels. In the absence of WMF, the Cr(VI) removal rate increased with increasing pH from 4.0 to 5.0 but declined with a further elevation in pH. Yoon et al. (2011) showed that the kinetics of Cr(VI) removal by ZVI over the pH range of 4.0–6.0 was fastest at pH 5.0, consistent with our observation. After the application of WMF, the Cr(VI) removal rates were increased considerably over the pH range of 4.0–5.5 and the removal rates at pH 4.5 and 5.0 were very similar, much higher than those at pH 4.0 and 5.5.

The influence of WMF on Fe^{2+} release from ZVI in the absence of Cr(VI) at various pH levels was examined, as shown in Fig. S3. It was found that Fe^{2+} generation was accelerated due to the application of a WMF at various pH levels, which may be ascribed to the enhanced diffusion of paramagnetic oxygen molecules to ZVI surface (Kim et al., 2011) and the improved transport of generated Fe^{2+} from ZVI surface to the bulk solution in the presence of WMF (Lioubashevski et al., 2004). The Fe^{2+} generation followed zero-order kinetics with or without WMF and the zero-order rate constants of Fe^{2+} generation were determined and shown in Fig. 3. Without WMF, the rate of ZVI corrosion (k'_{obs1}), following Eq. (1), decreased progressively with increasing pH from 4.0 to 5.5. If

the removal of Cr(VI) by ZVI follows Eq. (2), the removal rates will drop with increasing pH levels since protons are consumed in this reaction.

$$HCrO_4^- + Fe^0 + 3H_2O \rightarrow 2Fe_{0.5}Cr_{0.5}(OH)_3 + OH^- \tag{2}$$

$$HCrO_4^- + 3Fe^{2+} + 8H_2O \rightarrow 4Fe_{0.75}Cr_{0.25}(OH)_3 + 5H^+ \tag{3}$$

However, the maximum Cr(VI) removal rate was observed at pH 5.0, implying that homogeneous reduction of Cr(VI) by Fe^{2+}, shown in Eq. (3), was the dominant mechanism for Cr removal. The reduction rate of Cr(VI) by Fe^{2+} increased progressively as pH increased from 4.0 to 5.0 (Buerge and Hug, 1997), while the Fe^{2+} generation rate decreased with increasing pH in the absence of WMF. Therefore, the overall removal rate of Cr(VI) was optimized at an intermediate pH level around 5.0. Cr(VI) removal was limited by the slow reaction between Cr(VI) and Fe^{2+} at pH 4.0 while it was limited by the slow Fe^{2+} generation rate at pH 5.5 in the absence of WMF. Furthermore, the corrosion rates of ZVI in the presence of WMF (k'_{obs2}) showed little difference in the pH range of 4.0–5.5, which indicated that the introduction of WMF significantly enhanced iron corrosion, and the enhancement was greater at higher pH. However, the rate of Cr(VI) removal by ZVI in the presence of WMF did not show a monotonic increasing trend with increasing pH, which should be associated with the passive layer formed in the presence of Cr(VI) at higher pH (Yoon et al., 2011). The Fe^{2+} release monitored in the absence of Cr(VI) should be very different from that in the presence of Cr(VI), especially when WMF is applied and much Cr(VI) is removed. If Cr(VI) were stoichiometrically reduced by the Fe^{2+} released from ZVI following Eq. (3) and the inhibitive influence of the passive layer is neglected, Cr(VI) would be removed much more rapidly than what was observed. Therefore, the observed decline in Cr(VI) removal rate as pH increased from 5.0 to 5.5 should be mainly associated with the formation of a passive layer, which blocked the electron transfer from ZVI to Cr(VI) (Yoon et al., 2011). The WMF-induced improvement in
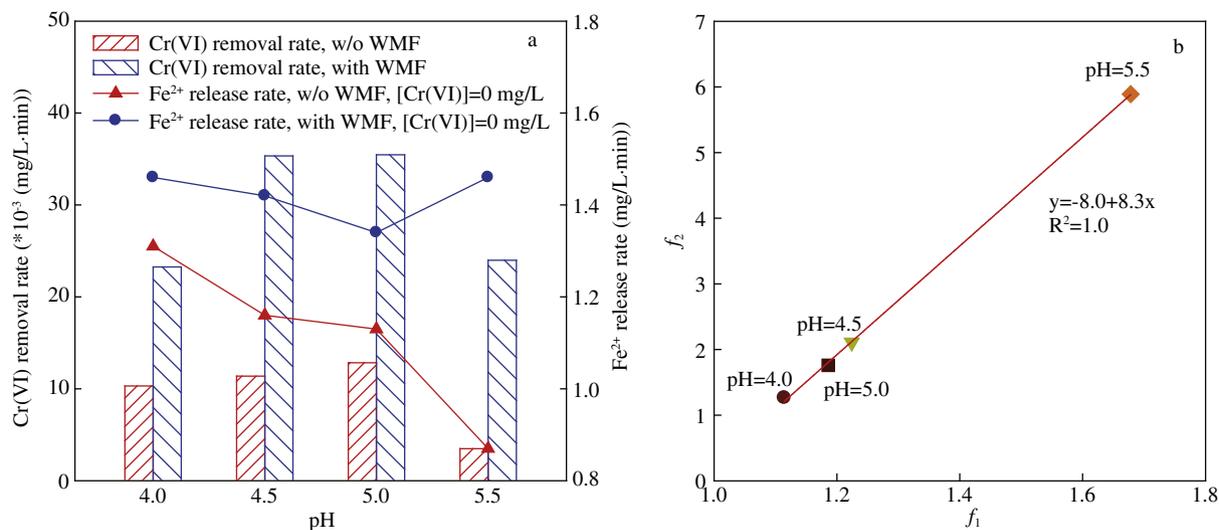

Fig. 3 – (a) WMF effects on Cr(VI) removal rate by ZVI and Fe(II) release rate (in the absence of Cr(VI)) at various pH; (b) the correlation between the promotion factor of Cr(VI) removal rate (f_2) with that of Fe(II) release rate (f_1) at various pH. Reaction conditions: $[Cr(VI)]_0 = 3.12$ mg/L, $[ZVI]_0 = 0.1$ g/L, background ionic strength 0.01 mol/L.

the rate constant of Cr(VI) removal by ZVI was most pronounced at pH 5.5 over the pH range of 4.0–5.5, and the Cr(VI) removal at pH 5.5 in the presence of WMF was much more rapid than that at pH 4.0 in the absence of WMF, which would be of great significance in real practice. Decreasing the pH of the Cr(VI)-ZVI system may accelerate Cr(VI) removal, but it will result in a pH decrease in the treated effluent, which must be neutralized before discharge to the aquatic environment (Gheju et al., 2008).

It is interesting to find that there is a close correlation between the promotion factor of Cr(VI) removal rate (f_2) with that of Fe^{2+} release rate (f_1, defined as k'_{obs2}/k'_{obs1}) at various pH, as illustrated in Fig. 3b. Furthermore, our experiments revealed that the application of WMF had no influence on Cr(VI) reduction by Fe^{2+} over the pH range of 4.0–5.5 (data not shown). This implies that the WMF-enhancement effect on Cr(VI) removal by ZVI can be largely ascribed to the accelerating effect of WMF on ZVI corrosion and supports the hypothesis that Cr(VI) is mainly removed *via* the homogeneous mechanism (*i.e.*, reduction by Fe^{2+} (Eq. (3))).

2.4. Influence of magnetizing time on WMF effects

Imposing a WMF to enhance the removal of contaminants by ZVI is effective, energy-saving, and environmentally friendly, in comparison to the methods of reducing the ZVI size to nanometers or forming bimetals by alloying it with another noble metal to increase the reactivity (Liang et al., 2014b). However, it may be difficult to supply the magnetic field throughout the entire process during the treatment. Therefore, we examined the influence of magnetizing duration on Cr(VI) removal by ZVI and the results are shown in Fig. 4. It is interesting to find that the zero-order reaction rates increased for magnetizing duration in the range of 0–10 min, whereas further increase in the magnetizing duration did not induce an additional enhancement in Cr(VI) removal rate. The remarkable "memory effect" of WMF on Cr(VI) removal by ZVI should be ascribed to the well-known ferromagnetic property of ZVI, which is magnetized in an external magnetic field and has
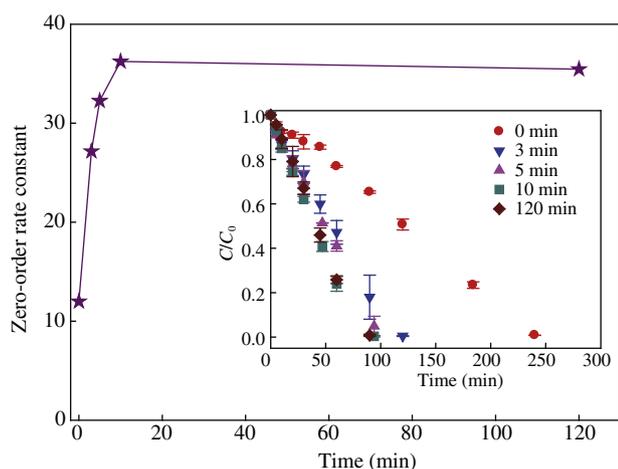
remanent magnetism after the external magnetic field is removed. The result indicates that a two-stage process consisting of a small reactor for ZVI magnetization and a large treatment reactor for removing contaminants by magnetized ZVI can be employed as a new method of ZVI-mediated remediation. This two-stage process is much easier to apply in real practice and much less expensive than the case where the magnetic field is supplied throughout the whole treatment process.
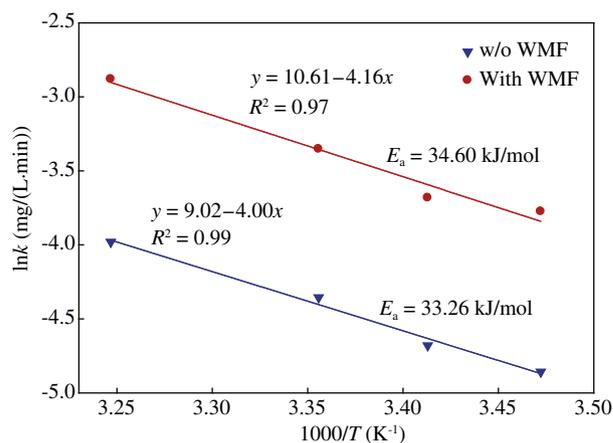
2.5. Role of WMF in Cr(VI) removal by ZVI

Fig. S4 shows the influence of WMF on the kinetics of Cr(VI) removal by ZVI over the temperature range of 15 to 35°C. The removal rates of Cr(VI) by ZVI considerably increased with increasing temperature regardless of WMF and employing WMF can markedly enhance the Cr(VI) removal rate by ZVI. The effect of temperature on degradation rates can be quantified using Arrhenius equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

where, k is the degradation rate constant, A is the pre-exponential factor, E_a is the activation energy, R is the ideal gas constant, and T is the absolute temperature. By plotting $\ln k$ *versus* $1/T$, as shown in Fig. 5, the apparent activation energies of Cr(VI) removal by ZVI in the absence and presence of WMF were determined to be 33.26 and 34.60 kJ/mol, respectively. The influence of WMF on the activation energy of Cr(VI) removal by ZVI was negligible, indicating that the application of WMF did not change the mechanism of Cr(VI) removal. The pre-exponential factor for Cr(VI) removal in the presence of WMF was much larger than its counterpart in the absence of WMF, suggesting that the application of WMF increased the number of active sites on ZVI to react with Cr(VI) (Xie et al., 2009).

The Cr 2p and Fe 2p XPS spectra of Cr(VI)-ZVI reaction products at an initial Cr(VI) concentration of 20.8 mg/L with a

Fig. 4 – Influence of application duration of WMF on Cr(VI) removal by ZVI. Reaction conditions: [Cr(VI)]₀ = 3.12 mg/L, [ZVI]₀ = 0.1 g/L, pH = 5.0, background ionic strength 0.01 mol/L.

Fig. 5 – Arrhenius plots for the reaction rate constants (activation energies, Ea) with or w/o WMF in the temperature range of 15–35°C. Reaction conditions: [Cr(VI)]₀ = 3.12 mg/L, [ZVI]₀ = 0.1 g/L, pH = 5.0, background ionic strength 0.01 mol/L.

ZVI dosage of 0.2 g/L are presented in Fig. 6. Regardless of WMF, the photoelectron peaks of Cr $2p_{1/2}$ and Cr $2p_{3/2}$ are centered at 587.3 and 577.5 eV, respectively, as shown in Fig. 6a and the spin-orbit splitting between the two peaks is 9.8 eV, which is characteristic of Cr(III) (Manning et al., 2007). Thus, the XPS results suggest that all of the removed Cr(VI) was reduced to Cr(III) either in the presence or absence of WMF. The photoelectron peaks at 711.3 and 725 eV, shown in Fig. 6b, corresponded to the binding energies of $2p_{3/2}$ and $2p_{1/2}$ of oxidized iron [Fe(III)] (Li et al., 2008). The absence of Fe^{2+} and Fe^0 components demonstrated that the ZVI surface was completely oxidized, regardless of WMF. The above analysis revealed that the application of WMF had no influence on the mechanisms of Cr(VI) removal by ZVI and all the removed Cr(VI) was reduced to Cr(III) by ZVI, consistent with the activation energy analysis.

Fig. 7 shows the SEM images of Cr(VI)-ZVI reaction products at initial Cr(VI) concentration of 3.12 mg/L with ZVI dosage of 0.3 g/L after different reaction times to examine the influence of WMF on the morphology of the generated passive layer. As can be observed in the images, ZVI was covered by a compact passive layer in the absence of WMF, while the corrosion products were very loose in the presence of WMF. Our previous study also revealed that the application of WMF could affect the morphology of corrosion products (Liang et al., 2014b). The compact passive layer formed in the absence of WMF may inhibit the access of Cr(VI) to the ZVI surface and the release of Fe^{2+} from ZVI. On the other hand, the mass transfer of Cr(VI) to the ZVI surface and Fe^{2+} to the Cr(VI) solution would be much easier when the corrosion products were very porous. As presented in Fig. 3b, the influence of WMF on Cr(VI) removal by ZVI was much greater than that on Fe^{2+} release from ZVI in the absence of Cr(VI), verifying that WMF could alleviate the negative effect of the passive layer formed in the process of Cr(VI) removal by ZVI. Therefore, the enhancement effect of WMF on Cr(VI) removal by ZVI should

be mainly attributable to the accelerated mass transfer of oxygen and Cr(VI) to ZVI surface and Fe^{2+} to the Cr(VI) solution in the presence of WMF.

3. Conclusions

The kinetics of Cr(VI) removal by ZVI with or without WMF could be well described by a zero-order kinetic model. The rate constants of Cr(VI) removal increased with increasing ZVI dosage and temperature while decreasing progressively with increasing initial Cr(VI) concentration. The effects of pH on Cr(VI) removal by ZVI were determined by both the Fe^{2+} generation rate and the reduction rate of Cr(VI) by Fe^{2+}. The removal rate of Cr(VI) by ZVI was enhanced by a factor of 1.12–5.89 due to the application of WMF. Moreover, the improvement in Cr(VI) removal induced by WMF was more significant at higher Cr(VI) concentration and higher pH, when the inhibitory effect of the passive layers formed at the surface of ZVI was obvious.

The Fe^{2+} release rate was greatly improved in the presence of WMF at various pH levels. Fe^{2+} was not detected until Cr(VI) was completely removed at each ZVI dosage regardless of WMF, indicating that Fe^{2+} released from iron corrosion was instantaneously oxidized by Cr(VI). There was a positive linear correlation between the promotion factor of Cr(VI) removal rate and that of Fe^{2+} release rate in the absence of Cr(VI). The apparent activation energy and the XPS results revealed that WMF accelerated Cr(VI) removal by ZVI but did not change the mechanism. The SEM results showed that the passive layer formed in the presence of WMF was much more porous than that formed in the absence of WMF, indicating that mass transport was facilitated by imposing a WMF. This research indicated that WMF could facilitate ZVI corrosion and Fe^{2+} release, alleviate the detrimental effects of the passive layer and thus accelerate Cr(VI) removal by ZVI. Applying
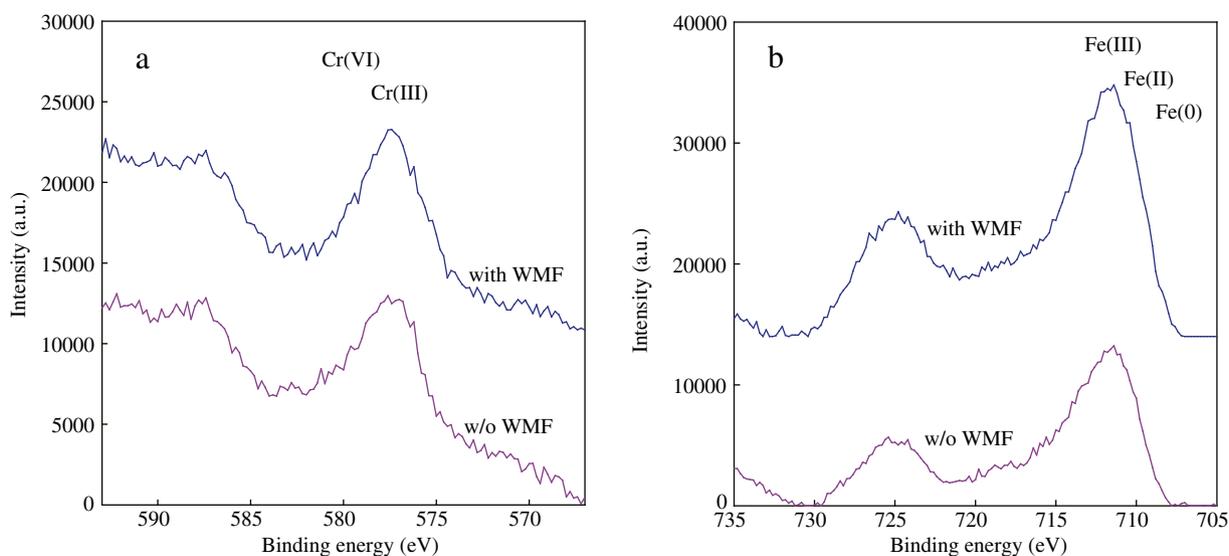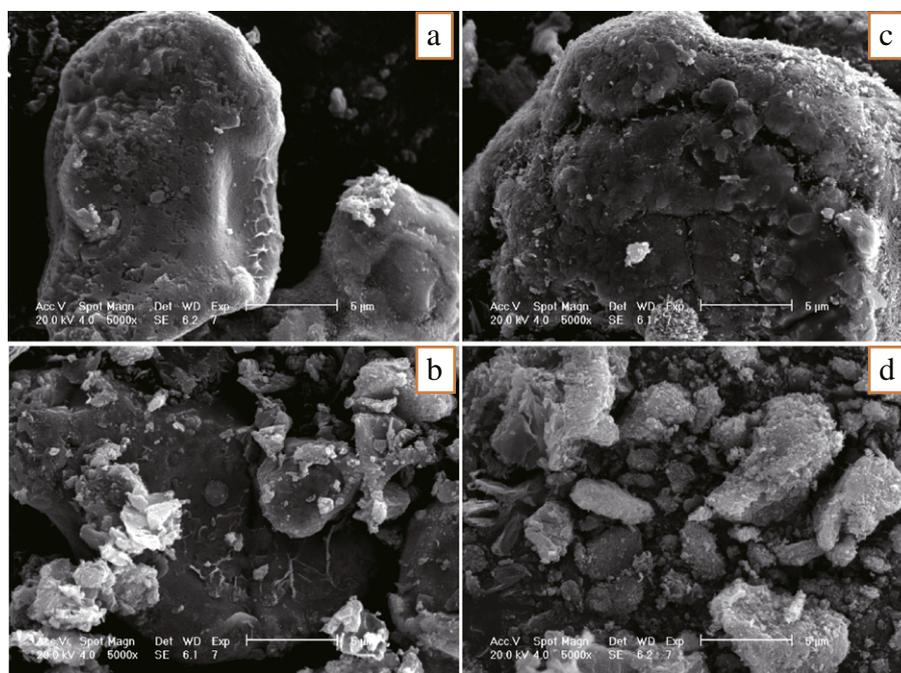

Fig. 6 – (a) Cr 2p and (b) Fe 2p XPS spectra of Cr(VI)-ZVI reaction products with or w/o WMF. Reaction conditions: $[Cr(VI)]_0$ = 20.8 mg/L, $[ZVI]_0$ = 0.2 g/L, pH = 5.0, background ionic strength = 0.01 mol/L, reaction time = 13 hr.

Fig. 7 – SEM images of Cr(VI)-ZVI reaction products obtained using 3.12 mg/L Cr(VI) with a ZVI dosage of 0.3 g/L in 0.01 mol/L NaCl at pH 5.0 w/o WMF after reacting at 30 min (a) and 90 min (b), or with WMF after reacting at 30 min (c) and 90 min (d).

WMF to promote Cr(VI) removal by ZVI is promising and environmentally friendly, since it is energy- and chemical-free. Moreover, this method is easily applicable since applying WMF for a short duration is enough to induce a significant improvement in Cr(VI) removal by ZVI.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2014.10.017.

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