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Weak magnetic field significantly enhances selenite removal kinetics by zero valent iron

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ABSTRACT

The effect of weak magnetic field (WMF) on Se(IV) removal by zero valent iron (ZVI) was investigated as functions of pH and initial Se(IV) concentrations. The presence of WMF significantly accelerated Se(IV) removal and extended the working pH range of ZVI from 4.0–6.0 to 4.0–7.2. The WMF induced greater enhancement in Se(IV) removal by ZVI at lower initial Se(IV) concentrations. The influence of WMF on Se(IV) removal by ZVI was associated with a more dramatic drop in ORP and a more rapid release of Fe^{2+} compared to the case without WMF. SEM and XRD analysis revealed that WMF accelerated the corrosion of ZVI and the transformation of amorphous iron (hdyr)oxides to lepidocrocite. XANES analyses showed that WMF expedited the reduction of Se(IV) to Se(0) by ZVI at pH 6.0 when its initial concentration was $\leq$20.0 mg L^{-1}. Se(IV) dosed at 40.0 mg L^{-1} was removed by ZVI via adsorption followed by reduction to Se(0) at pH 7.0 but via adsorption at 7.2 in the presence of WMF. Regardless of WMF, Se(IV) applied at 40.0 mg L^{-1} was removed by reduction at pH 4.0–6.0. The WMF-induced improvement in Se(IV) removal by ZVI may be mainly attributable to the Lorentz force and magnetic field gradient force. Employing WMF to enhance Se(IV) removal by ZVI is a promising and environmental-friendly method since it does not need extra energy and costly reagents.

1. Introduction

Zero-valent iron (ZVI) is a readily available, inexpensive, nontoxic and moderately strong reducing agent. Different classes of organic and inorganic compounds, e.g. halogenated organics, azoaromatics, chlorinated organics, nitroaromatics, arsenic, nitrate, chromate, and uranium, have been successfully removed from the aqueous phase by ZVI

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(Cundy et al., 2008). However, the iron filings or microscale iron powder has low reactivity toward contaminants and its reactivity decreased over time due to the formation of surface passivation layers or due to the precipitation of metal hydroxides and metal carbonates on the surface of iron (Wang and Zhang, 1997). Moreover, the reactivity of ZVI generally decreased significantly with increasing pH and remained inert or unreactive under neutral and alkaline conditions (Huang et al., 1998; Choe et al., 2004). The two most popular methods to enhance the reactivity of ZVI are to increase its surface area by synthesizing nano-sized ZVI (NZVI) (Liou et al., 2005a; Crane and Scott, 2012) and to alloy it with a noble metal (Pd, Pt, Ag, Ni, Cu, etc.) to form bimetals (Cwiertny et al., 2007). However, both methods bear some demerits. Although iron is inexpensive in bulk form, NZVI is much more expensive because the costly precursor reagents and complicated processes are needed to synthesize it (Crane and Scott, 2012). NZVI is very hard to be handled safely due to its very high reactivity (Noubactep et al., 2012) and it has low selectivity since it tends to react with non-target substances including dissolved oxygen and water (Comba et al., 2011). Furthermore, the toxicity of NZVI has arisen much concern (Phenrat et al., 2009; Chen et al., 2011) and Lee et al. (2008) reported that NZVI showed a strong bactericidal activity comparable to that of silver nanoparticles. With regard to the employment of bimetallic iron for contaminants removal, noble metals such as Pt, Pd and Ag are too costly and there are still considerable concerns over the ecotoxicity of some of the noble metals (Crane and Scott, 2012). Therefore, it is critical to explore an environmentally friendly method that can significantly improve the reactivity of ZVI to remove contaminants.

The kinetics of Se(IV) removal by zero valent iron (ZVI) as a function of pH and the involved mechanisms had been investigated in our previous study (Liang et al., 2013). In that study, the solution was completely mixed using a magnetic stirrer following the practice of Yoon et al. (2011). To our surprise, replacing the magnetic stirrer with a mechanical stirrer considerably decreased Se(IV) removal by ZVI. Careful examination of the literature implied that this phenomenon may be ascribed to the weak magnetic field (<70 mT) supplied by the magnetic stirrer and the magnetic rotor. Jiang et al. (2008) reported that there was a 30–50% improvement in SO_2 absorption by cast iron scraps due to the application of DC magnetic field (10–20 mT), which may be associated with the increased ZVI corrosion rate facilitated by the looser corrosion products. Kim et al. (2011) reported that the application of magnetic field (≤40 mT) on the ZVI slurry markedly enhanced 4-chlorophenol removal from 26% to 54% under air equilibrated condition, ascribed to the production of more OH radicals resulted from the easier transport of oxygen to ZVI surface in the presence of magnetic field. However, studies on the effect of magnetic field on reductive removal of contaminants by ZVI have not been reported. The objectives of this study were to 1) determine the effect of weak magnetic field, generated by permanent magnets, on Se(IV) removal by ZVI as functions of pH and initial Se(IV) concentrations; 2) shed a light on the ZVI corrosion process and corrosion products under a weak magnetic field; 3) understand the Se(IV) removal mechanism by ZVI in the presence of a magnetic field.

2. Materials and methods

2.1. Materials

All chemicals were of analytical grade and used as received. The ZVI employed in our previous study (Liang et al., 2013) was also used in this study. In brief, the D_{50} and BET surface area of the ZVI were ~7.4 μm and 0.3015 m^2/g, respectively (The particle size distribution and SEM image of ZVI are present in Fig. S1). All the other chemicals were purchased from Shanghai Qiangshun Chemical Reagent Company. The stock solutions were prepared by dissolving the corresponding salts in DI water generated from a Milli-Q Reference water purification system.

2.2. Batch experiments and chemical analysis

Two pieces of neodymium-iron-boron permanent magnets on an iron sheet, as illustrated in Fig. S2(b), were employed to offer magnetic field. The experimental setup was schematically illustrated in Fig. S2(a) and the axis line of the reactor (a 500-mL wide mouth bottle) and the center of the magnetic field coincided. The maximum magnetic field intensity was determined with a Teslameter (HT201, Shanghai Hengtong Magnetic & Electric Technology Co., Ltd) to be ~20 mT at the bottom of the reactor, much weaker than the case with a magnetic rotor on the magnetic stirrer (<70 mT). This magnetic field was weak and would be referred as weak magnetic field (WMF) hereafter.

Batch reduction tests were conducted by dosing 0.50 g ZVI to 0.50 L solution containing 40.0 mg L^{-1} Se(IV) and 0.01 M NaCl to investigate the effect of pH. The pH was varied from 4.0 to 7.2 for different tests. The influence of initial Se(IV) concentration was investigated by fixing pH at 6.0 while varying the initial Se(IV) concentration from 5.0 to 40.0 mg L^{-1}. Sodium acetate of 0.10 M, 2-(N-morpholino) ethanesulfonic acid (MES) of 0.10 M and tris(hydroxymethyl)aminomethane (TRIS) of 0.20 M were employed as buffers for the experiments conducted at pH 4.0–5.0, pH 6.0, and pH 7.0–7.2, respectively, to maintain pH almost constant (±0.1). If it was not otherwise specified, the experiments were carried out open to the air. Since ZVI is ferromagnetic, the presence of WMF can induce the aggregation of ZVI, which may subsequently affect Se(IV) removal by ZVI. The solution was mixed at 310 rpm using a mechanical stirrer (D2004W, Shanghai Sile Instrument Co., Ltd). With this stirring intensity, the aggregation of ZVI was avoided so that the influence of WMF on Se(IV) removal arisen from the aggregation of ZVI could be excluded. The experiments at pH 7.2 in the presence or absence of WMF lasted 47 h and 10 d, respectively, while all the other batch experiments lasted for 24 h. The variation of Se(IV) and Fe^{2+} with time and the change of Oxidation Reduction Potential (ORP) of the system were monitored. The collected solids were subject to X-ray absorption fine-structure (XAFS) and XRD analysis. The details of chemical analysis, solid