Efficient selenate removal by zero-valent iron in the presence of weak magnetic field

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ABSTRACT

Se(VI) was very refractory to be removed by zero-valent iron (ZVI), therefore weak magnetic field (WMF) was employed to achieve efficient Se(VI) removal by ZVI. Batch experiments showed that negligible Se (VI) (<4%) was removed by ZVI without the application of WMF within 72 h. The presence of WMF dramatically enhanced Se(VI) sequestration by ZVI and complete removal of $10.0 \, mg \, L^{-1}$ Se(VI) was achieved by ZVI in 90 min. The main portion of kinetics of Se(VI) removal by ZVI in the presence of WMF followed zero-order rate law and the rate constants of Se(VI) sequestration by ZVI increased progressively with increasing the ZVI dosage. Fe K-edge XAFS spectra and synchrotron radiation-XRD analysis revealed that ZVI was transformed to X-ray amorphous Fe_3O_4 before finally transformed to lepidocrocite (γ-FeOOH). The LCF analysis of Se K-edge XANES spectra indicated that adsorptive removal of Se(VI) was minor but adsorption of Se(VI) to the corroded ZVI surface was the first step of Se(VI) removal. Se(VI) was rapidly reduced to Se(IV), which could be further transformed to Se(0). Comparison of the performance of Se(VI) removal in the literature suggested that employing WMF to enhance Se(VI) removal by ZVI under oxic conditions be a promising method.

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1. Introduction

Selenium is an environmental pollutant and ranks 147th on the Superfund Priority List of Hazardous Substances of the U.S. Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [1]. Depending on its concentration, selenium can act as an essential micro-nutrient protecting against reactive oxygen species damages, or as a toxic compound [2]. Se pollution is a worldwide problem and mainly originates from agricultural practices, manufacture processes, coal combustion and mining processes [3]. Se was found to be present in elevated concentrations in acid mine drainage which varied from 1 to $7000 \, \mu g \, L^{-1}$ [4].

Selenium (Se) is a metalloid that exists in a variety of oxidation states including selenide (Se(-II)), elemental Se (Se(0)), selenite (Se (IV)), and selenate (Se(VI)) [5]. The oxidized forms of Se, Se(VI) and Se(IV), are soluble and mobile and thus are potentially toxic [6]. Selenite is similar to phosphate in terms of mobility in the environment and tends to be adsorbed more strongly than selenate onto

adsorbents such as goethite and hematite [7,8]. However, selenate, similar to sulfate, is very difficult to be adsorbed on various minerals. Thus, it is the most mobile selenium species and very difficult to be removed by the conventional methods including coagulation, lime softening and adsorption [9]. Compared to the above Se(VI) removal methods, reductive removal by zero-valent iron (ZVI) should be more favored since ZVI is a readily available, inexpensive, and moderately strong reducing agent and can transform Se (VI) to the more immobile species, Se(IV), Se(0) or Se(-II) [3].

Several studies had been carried out to examine the performance of ZVI toward Se(VI) removal. However, the iron filings or microscale iron powder had low reactivity toward Se(VI) removal. A huge dosage of micron-sized ZVI ($50–100 \, g \, L^{-1}$) was necessary to sequester Se(VI) and the removal capacity of ZVI for Se(VI) was very low [2,10]. To improve the removal rate of Se(VI) by ZVI, nano-sized ZVI (nZVI) and NiFe bimetal were used [11]. Moreover, Tang et al. [12,13] proposed to apply Co^{2+}, Mn^{2+} or Fe^{2+} to improve Se(VI) removal by ZVI. However, both methods bear some demerits. Although iron is inexpensive in bulk form, nZVI and nano-sized NiFe bimetal were much more expensive because the costly precursor reagents and complicated processes are needed to synthesize them [14]. Furthermore, the toxicity of nanomaterial

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has arisen much concern [15] and Lee et al. [16] reported that nZVI showed a strong bactericidal activity comparable to that of silver nanoparticles. Although Tang et al. [12,13] did show that the application of Co^{2+}, Mn^{2+} or Fe^{2+} could greatly enhance Se(VI) by ZVI, a ZVI dosage as high as $50.0\,g\,L^{-1}$ was employed in their study to removal $20.0\,mg\,L^{-1}$ Se(VI) and the dosing of Co^{2+} or Mn^{2+} may induce secondary pollution. Therefore, it is critical to explore an environmentally friendly method that can significantly improve the reactivity of ZVI to remove Se(VI).

Our recent studies reported that the application of a weak magnetic field (WMF) could greatly accelerate ZVI corrosion and sequestration of Se(IV), As(III), and As(V) [17–19]. The primary role of WMF in the process of contaminants removal by ZVI was to enhance mass transfer [19]. Up to now, no study had been performed on the influence of WMF on Se(VI), which was much more refractory than Se(IV), removal by ZVI. However, two studies [11,20] on Se(VI) removal by ZVI, which employed magnetic stirrer to offer mixing, showed much more efficient Se(VI) removal by ZVI than other studies. The magnetic field generated by the magnetic stirrer was stronger than the WMF applied in our previous studies [18], thus it was expected that WMF had promoting effect on Se (VI) removal by ZVI. Therefore, the current work was aimed at investigating the kinetics and mechanisms of Se(VI) removal from water by ZVI in the presence of WMF.

2. Materials and methods

2.1. Materials

All chemicals were analytical grade and used as received. The high purity ZVI powders (99.8–99.9% Fe^0), with d_{50} of 7.4 μm and BET specific surface area (a_s) of $0.3015\,m^2\,g^{-1}$, were purchased from Beijing Dk Nano technology Co., LTD, and used in this study without further treatment. Chemicals including $Na_2SeO_4 \cdot 10H_2O$, HCl, NaOH and 2-(N-morpholino)ethanesulfonic acid (MES) were purchased from Shanghai Qiangshun Chemical Reagent Company and were used as received in this study. The stock solutions were prepared by dissolving the corresponding salts in ultrapure water generated from a Milli-Q Reference water purification system.

2.2. Batch experiments and chemical analysis

To investigate the feasibility of Se(VI) removal by ZVI in the presence of WMF, the experimental setup employed in our previous study was also used here [18]. In brief, two cylindrical neodymium–iron–boron permanent magnets with diameter of 30 mm and height of 5 mm on an iron sheet were placed under the reactor, which provided a maximum magnetic field intensity of 20 mT at the bottom of the reactor throughout the course of the experiment [18]. Batch tests were carried out in 500 mL glass bottles and the solutions were open to the air or purged with nitrogen gas during continuous mixing with mechanical stirring (310 rpm). The aqueous medium consisted of Se(VI), 0.01 M NaCl and 0.1 M MES as buffer to keep pH constant (6.0 ± 0.1). MES was employed as buffer because it did not form complexes with Fe^{2+} or Fe^{3+} [21]. The tests were initiated by adding $1.0\,g\,L^{-1}$ of ZVI. All experiments were performed at 25 °C, which was controlled with a water bath. At fixed time intervals, aliquots of 5 mL sample were periodically withdrawn from the center of the reactor by a Teflon tube connected to a plastic syringe and immediately filtered with a 0.22 μm pore diameter membrane. Hereafter the extracted samples were acidified and analyzed for residual Se(VI) concentration with Perkin Elmer Optima 5300 DV ICP–OES. Fe^{2+} concentration in the filtrate was determined by the modified ferrozine method using a TU-1901 UV/visible spectrophotometer at a wavelength

of 562 nm following the procedure of Stookey [22]. The Oxidation Reduction Potential (ORP) of each sample was monitored with an ORP sensor connected to a pHS-3C pH meter. All experiments were carried out in triplicates for a given condition, and all points in the figures are averaged and error bars represent the standard deviation.
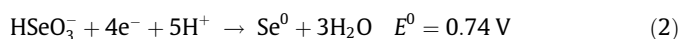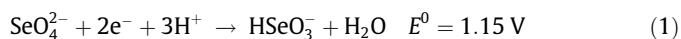
2.3. Solid phase characterization

The reacted ZVI samples were collected at different intervals, washed with distilled water, freeze-dried and put into zippered bags before subjecting to Se K-edge and Fe K-edge X-ray Absorption Fine Structure (XAFS) analysis. XAFS analysis was performed at BL14 W Beam line at Shanghai Synchrotron Radiation Facility (SSRF) (Shanghai, China). The details of XAFS analysis are present in Text S1 of Supporting Information [23].

The X-ray diffraction data of the ZVI samples reacted with Se (VI) were obtained at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF) at a wavelength of 1.2398 Å. BL14B1 is a beamline based on bending magnet and a Si(111) double crystal monochromator was employed to monochromatize the beam. The size of the focus spot is about 0.5 mm and the end station is equipped with a Huber 5021 diffractometer. NaI scintillation detector was used for data collection.

3. Results and discussion

3.1. Effect of initial Se(VI) concentrations

As illustrated in Fig. 1(a), negligible Se(VI) (<4%) was removed by ZVI without the application of WMF within 72 h, regardless of the initial Se(VI) concentration varying from 10.0 to $100.0\,mg\,L^{-1}$. Similar phenomenon had been reported by Tang et al. [13] although ZVI dosage as high as $50\,g\,L^{-1}$ was employed in their study. In our previous study [18], it took only 60 min to achieve almost complete removal of Se(IV) of $40.0\,mg\,L^{-1}$ by the same ZVI sample under similar conditions. Obviously, the reductive removal of Se(IV) was much more facile than that of Se(VI) although the redox potential of the $SeO_4^{2-}/HSeO_3^-$ couple was larger than that of the $HSeO_3^-/Se^0$ couple, as shown in Eqs. (1) and (2) [24]. Selenite is a softer base than selenate [25] and thus has smaller resistance to electron transfer and is more reactive with Fe^0 [26].

$$SeO_4^{2-} + 2e^- + 3H^+ \rightarrow HSeO_3^- + H_2O \quad E^0 = 1.15\,V \quad (1)$$

$$HSeO_3^- + 4e^- + 5H^+ \rightarrow Se^0 + 3H_2O \quad E^0 = 0.74\,V \quad (2)$$

The superimposed WMF remarkably improved Se(VI) sequestration by ZVI, as illustrated in Fig. 1(b). It was surprising to find that $10.0\,mg\,L^{-1}$ Se(VI) could be completely sequestered by $1.0\,g\,L^{-1}$ ZVI in 90 min in the presence of WMF. The removal efficiencies were 96.3%, 67.6% and 36.9% after 12 h of reaction, respectively, when the initial Se(VI) concentrations were 20.0, 40.0, and $100.0\,mg\,L^{-1}$. Moreover, Se(VI) removal by ZVI with WMF was almost completed within 5 h when the initial Se(VI) concentration was in the range of $20.0–100.0\,mg\,L^{-1}$ and negligible removal of Se (VI) was observed with prolonged reaction time. The main portion of each data set in Fig. 1(b) could be well described by the zero-order kinetics. The fitting results are presented with dotted lines in Fig. 1(b). It was found that the zero-order rate constants (k_{obs}) were in the range of $0.094–0.141\,mg\,L^{-1}\,min^{-1}$, no obvious dependence on the initial concentration of Se(VI).

The variations of Fe^{2+} concentration and ORP with time in the process of Se(VI) removal by Fe^0 were also examined and present in Fig. 1(c) and (d), respectively. ZVI reacted with Se(VI) solution