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# Kinetics and mechanisms of pH-dependent selenite removal by zero valent iron

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ABSTRACT

The kinetics of Se(IV) removal by zero valent iron (ZVI) open to the air as a function of pH and the involved mechanisms were investigated in this study. The specific rate constants of Se(IV) removal by ZVI decreased from 92.87 to 6.87 L $h^{-1}$ $m^{-2}$ as pH increased from 4.0 to 7.0. The positive correlation between the removal rate of Se(IV) and the generation rate of Fe(II) and the depression of Se(IV) removal in the presence of 1,10-phenanthroline indicated that both ZVI and adsorbed Fe(II) on ZVI surface contributed to the reductive removal of Se(IV). The soft X-ray STXM measurement confirmed the adsorption of Fe(II) on the surface of ZVI and freshly formed ferric (hydr)oxides. Se(IV) was removed by adsorption followed by reduction to Se(0) on ZVI surface at pH 4.0–7.0, as revealed by XANES spectra. A core-shell structure was observed when ZVI reacted with Se(IV)-containing solution for 3 h at pH 6.0. Se(IV) was reduced to Se(0) and co-precipitated with the freshly formed Fe(III), forming the shell surrounding the iron core. After reaction for 24 h, the generated Se(0) was surrounded by multiple layers of Fe(III) oxides/hydroxides. SEM images and XRD patterns revealed that the corrosion products of ZVI at pH 6.0 transformed from amorphous iron hydroxides to lepidocrocite (γ-FeOOH) as reaction proceeded. The final corrosion products of ZVI contained both lepidocrocite and goethite at pH 5.0 while they were X-ray amorphous at pH 4.0 and 7.0.

## 1. Introduction

Selenium is an important micronutrient for human and animal health, but at elevated concentration selenium toxicity is a concern. The range between essential and toxic concentrations in humans is narrow: below 40 mg $d^{-1}$ will result in Se deficiency whereas over 400 mg $d^{-1}$ can be toxic (Gibson et al., 2012). Selenium in water generally originates from either the

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run-off from mining operations and irrigation drainage from arid soils (Olegario et al., 2010) or the discharge from the industries such as electronics, fertilizers, fungicides, antidandruff shampoo, etc (Moore and Mahmoudkhani, 2011). Selenium contamination is not only a localized threat but also a global threat that is increasing as various industrial activities increase (Moore and Mahmoudkhani, 2011).

Selenium (Se) is a metalloid that exists in a variety of oxidation states including selenide (Se(-II)), elemental Se (Se(0)), selenite (Se(IV)), selenate (Se(VI)), as well as several organic (e.g., selenomethionine) and volatile Se compounds (e.g., dimethyl selenide, DMSe). The oxidized forms of Se, Se(VI) and Se(IV), are highly soluble and therefore bioavailable and potentially toxic (Zhang et al., 2008). According to the U.S. EPA report (FRL-5649-7), the acute toxicity of Se(IV) is almost 10 times superior to that of Se(VI) and both species exist simultaneously in aerobic surface water often incomparable concentrations (López de Arroyabe Loyo et al., 2008). Therefore, there is an urgent need to develop efficient, feasible methods to remove Se(IV) and Se(VI), particularly Se(IV), from water. On the other hand, the reduced forms, Se(0) and Se(-II), are insoluble, much less bioavailable, and can remain stable under anoxic conditions. Considering the redox-dependent solubility of Se, immobilizing Se(IV) by reducing it to insoluble Se(0) or Se(-II) is a wise choice for Se(IV) removal (Olegario et al., 2010).

Microbial reduction of Se(IV) to Se(0) has been investigated by several laboratory studies (Garbisu et al., 1996; Zhang and Moore, 1997). Various Fe(II)-containing minerals, i.e., pyrite ($FeS_2$) (Kang et al., 2011), siderite($FeCO_3$) (Badaut et al., 2012), pyrite/greigite composite ($FeS_2$/Fe(II)Fe(III)$_2S_4$) (Charlet et al., 2012), mackinawite (FeS) (Han et al., 2011), or magnetite ($Fe_3O_4$) (Scheinost and Charlet, 2008) have been employed for the reductive removal of Se(IV). Nguyen et al. (2005a and 2005b) reported that in the presence of formic acid as a hole scavenger, Se(IV) could be photo-reduced to Se(0) in illuminated $TiO_2$ suspensions at pH 3.5. Se(IV) could also be reduced by the Fe(II) adsorbed on freshly precipitated iron oxides, montmorillonite, and calcite (Chen et al., 2009; Charlet et al., 2007; Chakrabrty et al., 2010). However, the reduction rates of Se(IV) by the bacteria, Fe(II)-containing minerals, Fe(II) adsorbed on minerals are very low and high concentration of hole scavenger is necessary for Se(IV) reduction by electrons photo-generated in $TiO_2$ suspension. Compared to the above Se(IV) reduction methods, reduction by zero valent iron (ZVI) should be more favored since ZVI is a readily available, inexpensive, and moderately strong reducing agent. Although very few studies have been conducted to investigate the reductive removal of Se(IV) by ZVI, the limited information revealed that Se(IV) was reducible by ZVI. Puranen et al. (2010) showed that Se(IV) could be immobilized by iron covered by a magnetite corrosion layer at a greater rate than Se(VI) in the presence of uranyl, indicating that Se(IV) was more susceptible to reduction by ZVI than Se(VI). In addition, previous studies had confirmed that Se(VI) could be reduced by ZVI. Therefore, reductive removal of Se(IV) by ZVI should be a feasible choice. However, little work had been carried out to systematically investigate the interaction between Se(IV) and ZVI up to now. Thus, the objectives of this study were to determine the effectiveness of ZVI in removing Se(IV) from contaminated water as a function of pH and to investigate the kinetics and mechanisms involved in the reactions.

## 2. Materials and methods

### 2.1. *Materials*

All chemicals used were of analytical grade, and all stock solutions used were prepared with deionized (DI) water from a Milli-Q water system. The Se(IV) stock solutions were prepared by dissolving $Na_2SeO_3$ in DI water. ZVI with median particle size of ~7.4 μm and with a BET (Brunauer–Emmett–Teller) surface area of 0.3015 $m^2$/g was supplied by the Beijing Dk Nano technology Co., LTD.

### 2.2. *Batch reduction tests and chemical analysis*

Batch reduction tests were conducted by dosing 0.50 g ZVI (~7.4 μm) to 0.5 L solution containing 0.51 mM Se(IV) and 0.01 M NaCl to investigate the effect of pH varying from 4.0 to 8.0. Sodium acetate of 0.1 M, 2-(N-morpholino)ethanesulfonic acid (MES) of 0.1 M and tris(hydroxymethyl)aminomethane (TRIS) of 0.2 M were employed as buffers for the experiments conducted at pH 4.0–5.0, pH 6.0, and pH 7.0–8.0, respectively, to maintain pH almost constant (±0.1). These buffers were selected because they do not form complexes with Fe(II) or Fe(III) (Keenan and Sedlak, 2008). The experiments were carried out open to the air and the solution was completely mixed using a magnetic stir bar (5 cm length × 0.75 cm diameter). At a given time interval, 5 mL suspension was sampled and immediately filtered using 0.22 μm pore diameter membrane, which was then acidified with one drop of 65% $HNO_3$ followed by being analyzed for the concentrations of residual Se(IV) in the filtrate using a Perkin Elmer Optima 5300 DV ICP-OES. Fe(II) concentration was examined with the modified ferrozine method using a TU-1901 UV/visible spectrophotometer at a wavelength of 562 nm (Guan et al., 2011a). Standards containing known concentrations of ferrous ion were used as reference for each set of tests. The Oxidation Reduction Potential (ORP) was monitored with an ORP sensor connected to a pHS-3C pH meter.

The influence of 1,10-phenanthroline on Se(IV) removal by ZVI was carried out by applying 5.36 mM 1,10-phenanthroline to the reaction system before introducing ZVI. All experiments were run in duplicates or triplicates, and all points in the figures are the mean of the results and error bars represent standard deviation of the means. At the end of experiments, the precipitates were collected, washed with DI water, freeze-dried, and then kept in a desiccator for further analysis.

### 2.3. *Solid phase characterization*

Step-scanned XRD patterns were collected with a Rigaku DXR-8000 computer-automated diffractometer. XRD analysis was conducted at 40 kV and 40 mA using a diffracted beam graphite monochromator and Cu radiation. The XRD patterns were collected in the 2θ range of 5–90° with a step size of 0.02° and a count time of 2 s per step. Morphological analysis of the samples was performed by Field Emission Scanning Electron