



Understanding the positive effects of low pH and limited aeration on selenate removal from water by elemental iron



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ARTICLE INFO

Article history:

Received 28 January 2013

Received in revised form 9 May 2013

Accepted 22 May 2013

Available online 31 May 2013

Keywords:

Selenium

Zero valent iron

Wastewater

Green rust

ABSTRACT

Selenate (SeO_4^{2-}) is a toxic soluble compound and its presence in the environment should be minimized. Reduction of selenate ions by elemental iron is a promising approach for treating contaminated waters. However, uncertainty exists regarding both the favorable conditions required and the associated mechanisms. In this study, the kinetics and mechanisms of selenate removal using Fe^0 at different pH and aeration rates was investigated using quantitative measurement of reactants and products. Under acidic anaerobic conditions, selenate was reduced directly by Fe^0 . Limited aeration increased removal rates by up to four times due to formation of reactive Fe(II)-bearing solid intermediates on the iron surface. Further increase in aeration rate decreased removal rates but also decreased iron release and acid consumption. Under basic conditions, selenate by Fe^0 was negligible under anaerobic conditions and low under limited aeration. Selenate removal rates were shown to be dependent on Se concentration, on available reducing solid surface and on competition with oxygen over electrons.

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1. Introduction

Selenium (Se) is an essential micro nutrient but under elevated exposure levels is toxic to animals and humans [1,2]. Pollution of natural waters and ecosystems may be of geological origin or caused by various human activities such as mining, agriculture and industrial operations [1]. The presence of selenium in surface water, mainly in its soluble oxidized forms, selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}), is of major environmental concern [3,4] and was restricted in North America to 1–5 $\mu\text{gSe L}^{-1}$ [5]. A large number of technologies were proposed to address these regulations [5–11], although cost effectiveness remains a critical issue.

The reduction of selenate and selenite by low-cost elemental iron (Fe^0), also termed zero valent iron (ZVI), into immobilized Se^0 has been investigated both for active and passive (e.g., permeable reactive barrier) treatment of Se-contaminated waters [8]. This approach can achieve practically zero Se concentrations [12,13], while avoiding the reduction of the usually more abundant SO_4^{2-} (up to 10^8 S/Se) [8]. Reaction kinetics and sludge formation are main concerns associated with this approach [5]. The removal of selenate by ZVI was previously studied [4,12–16] under a variety of conditions (Table S1 in the supplementary material file (SM)). Although it is generally agreed that reaction rates increase at higher temperature, surface area and selenate concentration, disagreements exist regarding both the conditions under which selenate

removal is most favorable and the dominant mechanisms involved. For example, the best conditions for selenate removal were reported to be pH 9 and oxygenated environment [12], pH 6 and anoxic conditions [15] and pH 4 in the presence of oxygen [4]. While some studies [4,16] suggested that ZVI reacts directly with selenate, others [12,13] suggested that selenate and the intermediate selenite are actually reduced by Fe(II)-bearing corrosion products.

The current work was aimed at investigating the kinetic and mechanistic aspects associated with different pH and aeration rate on selenate removal from water by ZVI. Potential sludge formation and acid consumption were also assessed.

2. Experimental

2.1. Procedures

Four distinct sets of conditions were tested, namely pH 4.0 ± 0.1 and pH 9.0 ± 0.1 , each under anoxic (N_2) or oxygenated (air) environment. For each set, a “control” trial with only deionized water (DW, Milipore, 18 Mohm cm^{-1}), was conducted. The trial number and corresponding operational conditions are provided in Table 1. Two sets of experiments at different initial selenate (99% $\text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O}$, BDH Chemicals Ltd.) concentrations of ~ 300 and ~ 100 mgSe L^{-1} were conducted and denoted hereafter round 1 and round 2, respectively. These concentrations were chosen primarily to minimize interferences by side reactions, to evaluate the effect of Se concentration on the removal rate and to enable comparison with published data. Additional trials were conducted

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Table 1
Operational conditions and main results in round 1 ($\sim 300 \text{ mgSe L}^{-1}$).

Trial	Gas	pH	SeO_4^{2-}	Eh^a (mV)	Crystalline phases in SS ^b	Stable species ^c	Mean H^+/Fe (stdev)	Mean H^+/Se (stdev)
1	N_2	4.0	No	100	Fe_3O_4 , C	Fe^{2+} , FeSe_2^d	2.1 (0.26)	NA
2	N_2	4.0	Yes	-30	Fe_3O_4 , C	H_2Se , HSe^-	2.6 (0.31)	7.7 (2.95)
3	N_2	9.0	No	-550	Fe_3O_4 , C	Fe_3O_4 , FeSe	0.3 (0.52)	NA
4	N_2	9.0	Yes	-450	Fe_3O_4 , C	HSe^-	0.3 (0.41)	^e
5	Air	4.0	No	200	Fe_3O_4 , C	Fe^{2+} , Fe_2O_3	1.3 (0.34)	NA
6	Air	4.0	Yes	200	Fe_3O_4 , C	Se^0 , Fe_3O_4^d	2.4 (0.53)	3.0 (0.54)
7	Air	9.0	No	150	$\alpha\text{-Fe}_2\text{O}_3$, C	Fe_2O_3 , SeO_3^{2-}	-0.3 (0.12)	NA
8	Air	9.0	Yes	150	$\alpha\text{-Fe}_2\text{O}_3$, C	Se^0	0.1 (0.12)	0.65 (0.15)

NA = non applicable

^a Rounded steady-state values measured in the stirred container.

^b Based on Fig. S1 in the SM. Fe_3O_4 might be a solid solution with $\gamma\text{-Fe}_2\text{O}_3$.

^c Based on Pourbaix diagrams (Section 3.1.2).

^d Only inside the ZVI column.

^e Se removal was marginal in this trial (Section 3.2.1, Fig. S7 in the SM).

under pH 3.5 and 4.5, at variable low aeration rates, to expand reaction understanding under acidic conditions. Trial 6 was repeated at different initial ZVI mass to investigate the effect of Fe/Se on reaction kinetics. Trial 4 was repeated using selenite (99% $\text{Na}_2\text{SeO}_3 \cdot x\text{H}_2\text{O}$, Alfa Aesar) to compare removal rates with selenate (Section 3.2.1).

The experimental set up is represented schematically in Fig. 1. The placement of the ZVI filings (40 mesh, I-57, Fisher Scientific Co.) in a column was intended to (A) separate the Fe^0 reactant and products (anticipated to be released to the liquid phase), (B) prevent mixing problems associated with the magnetic stirring bar and the paramagnetic Fe^0 particles, (C) induce mechanical contact between ZVI particles to minimize passivation and improve solid-product release into solution and (D) reduce possible interference associated with the paramagnetic nature of both O_2 and Fe^0 [17].

A 1.82 L of either DW or selenate solution was placed in the 2 L (12 cm diameter) magnetically stirred container and circulation through the 30 mL ($\sim 30 \text{ cm}$ tall) glass column began at a rate of 1.8 L h^{-1} . Because of the short hydraulic residence time in the ZVI filled section of the column (about 20 s), the system was considered to be closely analogous to a continuous stirred tank reactor (CSTR). N_2 purging or aeration (200 mL min^{-1}) started approximately 0.5 h prior to addition of 17.2 g ZVI filings into the column and the pH was adjusted using 0.1 M HCl or 0.1 M NaOH solutions. The system was operated for 8 h after ZVI addition at a constant pH using 0.1 M HCl, a pH controller (Eutech 190 series) and a peristaltic pump. The HCl solution was stored in a 50 mL burette and its consumption was monitored along with Eh (Accumet pH meter, model 10). The solution temperature was $25 \pm 2 \text{ }^\circ\text{C}$. Samples were drawn from the container using a 10 mL syringe and filtered using

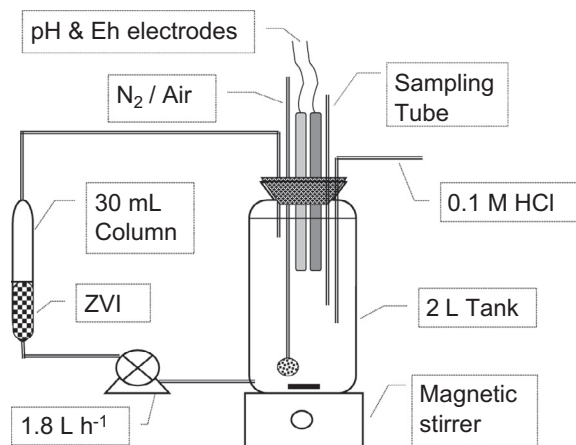


Fig. 1. Schematic representation of the experimental set up.

a replaceable membrane (Whatman Nuclepore, $0.4 \mu\text{m}$ pore size) filter. Determination of Se and Fe concentrations in the suspended solids (SS) was performed through dissolution of the SS attached to the membrane, filter plates and O-ring in a 37% HCl solution. At the end of each trial, SS were settled overnight in the container, extracted and dried at $40 \text{ }^\circ\text{C}$ for X-ray diffraction (XRD) analysis. The solids in the ZVI column were extracted at the end of each trial of round 2 ($\sim 100 \text{ mgSe L}^{-1}$) onto a filter paper (Whatman, #1), filtered and dried at $40 \text{ }^\circ\text{C}$ for Se detection by X-ray photoelectron spectrometry (XPS).

In order to identify solid phases present in the corrosion layer, a special trial was issued using sulfate instead of selenate to avoid the possible oxidation of iron intermediates by selenate [18]. H_2SO_4 ($\sim 250 \text{ mgS L}^{-1}$) and NaOH were introduced to the initial solution and operation followed exactly that of trial 6. After 5 h, operation was halted and a few N_2 bubbles were forced into the ZVI column, which was subsequently sealed. The column was then vigorously shaken to separate the corrosion layer from the ZVI filings. The solution with fine particles was quickly poured into a 15 mL test tube, which was sealed and centrifuged for 5 min. The test tube was opened in a glovebox under anoxic conditions and the concentrated solid phase was placed on a zero background quartz slide and left to dry in vacuum (-0.1 MPa) for 1 h. The dry powder was then mixed with two drops of glycerol, while in the glovebox, to prevent oxidation during XRD analysis [19]. The pH of the remaining supernatant at the end of this process was 6.1–6.2.

2.2. Analyses

Dissolved Fe and Se concentrations were determined by Inductively Coupled Plasma (ICP-AES, Perkin Elmer, Optima 7300 DV). XRD (Philips PW 3710) analyses were conducted using $\text{Cu K}\alpha$ radiation at 40 mA and 40 kV, scanning at a rate of $0.01 2\theta \text{ s}^{-1}$. XPS was conducted using a Thermo Scientific Al $\text{K}\alpha$ spectrometer (ThermoFisher, E. Grinstead, UK) and pass energy of 200 eV, followed by selected regions at higher resolution ($\text{PE} = 25 \text{ eV}$). Since the Se 3d feature overlaps completely with Fe 3p peak, the Se 3p region was also obtained. This region was also obtained at 50 eV pass energy to increase S/N and allow separation of the oxidized Se feature.

3. Results and discussion

3.1. End product characterization

Table 2 summarizes the most likely end products under each operational regime, according to visual observations (Section 3.1.1),

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