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Iron anode mediated transformation of selenate in sand columns

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Ferrous hydroxide Chemical transformation Sand column Selenium

Abstract

Removal of aqueous selenate by iron electrolysis is investigated using sand-packed column experiments under a flowing condition. An iron anode generates ferrous ions, while cathode produces hydroxide, thus producing ferrous hydroxide capable of reducing selenate to elemental selenium. Additionally, siderite could reduce selenate or selenite to elemental selenium. The removal rate of selenate is proportional to the contact time and the yield of ferrous hydroxide or ferrous carbonate. At a sequence of anode–cathode, the transformation of selenate mostly occurs in the zone after cathode. An operation of 48 h electrolysis finally transforms 82.2% of selenate at 0.2 mM of initial concentration, 1.8 m/day of seepage velocity and 1.26 mA/cm² of current density. A longer reactive zone after cathode slightly increases the reduction of selenate to 84.1%, in comparison with 82.2% of a shorter residence time in the reactive zone after cathode. With shorter electrode spacing (approximately 27% shorter), the transformation rate of selenate decreased to 73.5%; however, the specific electrical energy consumption was saved by 78%. A sequence of cathode–anode was ineffective in removing selenate because of the lack of reducing agent in the column. The results indicate that the electrochemical system might be effective in removing selenate in a single well.

Keywords

Ferrous hydroxide; Chemical transformation; Sand column; Selenium

1. Introduction

Selenium is an essential trace element in the human body; however, the most suitable daily uptake is very narrow and slight differences in daily uptake may lead to either toxicity or deficiency (Charlet et al., 2007). In oxic environments, Se(VI) exists as an oxy-anionic form of selenate, which is generally soluble and weakly sorbed by mineral materials (Zhang et al., 2005b). As a consequence, selenate has high bioavailability to crops and fish and high

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mobility in soils and groundwater (Charlet et al., 2007; Zhang et al., 2005b). Traditionally, aqueous selenate has been treated by abiotic reduction, followed by co-precipitation with iron oxides and by biological reduction (Scheinost and Charlet, 2008; Zhang et al., 2008a). However, the costly chemicals required to achieve efficient removal of Se(VI) makes the processes impractical in reductive precipitation (Chen et al., 2009). Biological processes are highly sensitive to operating parameters and the transformation rate is relatively slow (Loyo et al., 2008). Previous studies have shown that selenate could be chemically reduced to elemental selenium or selenide by ferrous hydroxide or ferrous carbonate (Chen et al., 2009; Murphy, 1988; Scheinost and Charlet, 2008; Zingaro et al., 1997): selenate is first reduced to selenite, which is adsorbed onto iron oxides and finally reduced to elemental selenium. Similar reactions might also occur on green rusts (Myneni et al., 1997; Refait et al., 2000b), zero-valent iron (Yoon et al., 2011; Zhang et al., 2008b, 2005a), pyrite, and other iron oxides (Badaut et al., 2009; Banerjee et al., 2008; Charlet et al., 2007; Chen et al., 2009; Loyo et al., 2008; Qiu et al., 2000; Scheinost and Charlet, 2008; Scheinost et al., 2008).

In recent years, electrochemical processes for the remediation of contaminated groundwater have been reported (Alshawabkeh and Sarahney, 2005; Gent et al., 2009; Gilbert and Sale, 2005; Mao et al., 2011); however, few studies have focused on the electrochemical transformation of selenate in groundwater (Baek et al., 2013). Baek and colleagues reported that selenite could be reduced in an electrochemical batch reactor using iron anode (2013). They proposed that ferrous hydroxide generated by electrochemical reaction played a key role on the reduction of selenate.

In order to explore the feasibility of using iron electrolysis for the in-situ remediation selenate impacted groundwater, a flow-through sand column incorporating a pair of electrodes is designed for an in-depth study. The basic hypothesis of this study is that the ferrous hydroxide is electrochemically produced using a reactive iron anode in the system, and the ferrous hydroxide is responsible for the transformation of selenate. Additionally, the transformation rate of selenate in the silica sand-packed column, which mimics the in-situ application of the electrochemical system in a permeable aquifer, is evaluated at different operating variables.

2. Materials and methods

2.1. Column setup

As shown in Fig. 1, the test setups consist of 3 different sections of vertically mounted clear polyvinyl chloride (PVC) columns: inlet section prior to the electrode sets (zone 1, 10 cm in length and 3.18 cm in inner diameter), the central section between the two electrodes (zone 2), and the reactive zone after the electrode sets (zone 3). Silica sand (US Silica, 40/70 Ottawa white frac, IL, USA) with an effective size between 0.21 mm and 0.42 mm was packed in the column. The lengths of zone 2 and zone 3 were changeable, as indicated in Fig. 1a (Column A), Fig. 1b (Column B), and Fig. 1c (Column C). Cast iron (Macmaster-Carr, USA) was used as both the anode and cathode. The iron electrode was a perforated round disk (3.18 cm i.d. and 0.3 cm thick) with 15 holes (0.3 cm i.d.), allowing water to flow through. The active working area of the iron electrode was 6.9 cm³.

2.2. Experimental design

For a systematic study, the operating variables investigated in this study include current density, flow rate of simulated groundwater, length of zone 3, spacing between anode and cathode (length of zone 2), the packing status (packed with sand or without sand), and the sequence of electrodes (cathode–anode sequence or anode–cathode sequence). The experiments under different combinations of these operating variables are summarized in Table 1. Before each experiment, the iron electrode was polished with coarse emery cloths, washed with distilled water, and then assembled in the column. Simulated groundwater for experiments was aqueous solution containing 0.2 mM of selenate (analytic grade, VWR, USA) and 20 mM of sodium bicarbonate (analytic grade, JT Baker). The influent solution was pumped into the columns at constant seepage velocity until a stable concentration of selenate was achieved in the effluent. An electrical field was then applied and electrolysis was started. During the electrolysis, water samples were collected from the influent, effluent, and sampling ports along the column.

2.3. Analytical methods

The concentration of selenate and selenite in aqueous samples was analyzed using an ion chromatograph (IC, DIONEX 5000, USA). A concentration of 35 mM KOH was used as a mobile phase at a flow rate of 1.0 mL/min. The redox potential (ORP) and pH were measured using an ORP meter and pH meter, respectively (Microelectro, USA). The concentration of total iron was measured using a colorimetric method after dissolution of the iron from the sand column using 0.1 N HCl. The removal rate was calculated based on the concentration difference between the influent and the sampling points. The oxidation state of selenium on the solid surface was characterized using a Kratos Axis Ultra Imaging X-ray photoelectron spectroscopy (XPS) with monochromatic Al K α X-rays. A broad scan was obtained using 80 eV pass energy, while a narrow high resolution scan of Se 3d was obtained using 40 eV pass energy. XPS spectra were collected in the same manner for Se powder (Sigma–Aldrich) as a reference material. The charge effect was corrected using the C 1s line at 284.5 eV. The obtained spectrum was fitted using a curve-fitting program (XPSPEAK41). The spectrum was fitted using a least-squares procedure with peaks of 80% of the LorentzianGaussian peak shape after subtraction of a Shirley baseline.

3. Results and discussions

3.1. Current and flow rate effects

Fig. S1 shows the selenate concentration profiles along the column at different sampling times. As can be seen, the enhancing effect of current density on selenate removal rate appeared at all flow rates, but was considerably clearer at a lower flow rate (1.8 m/day). For experiments using an anode–cathode sequence, ferrous ions were generated in the vicinity of the anode. However, the free ferrous ion is not capable of reducing selenate effectively (Yoon et al., 2011). The standard redox potentials of a series of related reactions are listed as follows.

Based on our measurements, the actual pH_s of the pore water between the anode and the cathode were around 6.5. At this pH, both free ferrous ions, ferrous hydroxide and ferrous carbonate existed in the aqueous solution, with ferrous ions dominating. Based on the standard reduction potential at pH 6.5, the free ferrous ions could not directly reduce selenate to selenite or to elemental selenium, while the ferrous hydroxides or ferrous carbonate showed superior reducing capability. Therefore, IC analysis showed that only few amount of selenite was detected from the samples collected between the two electrodes (P2 in Fig. S1). It is also noted that a significant decrease of selenate mostly occurred downstream of the electrodes (P3 and effluent in Fig.S1), where ferrous hydroxide or ferrous carbonate formed due to the mixing of ferrous ions, hydroxyl ions and background electrolyte (bicarbonate). As a reducing agent, ferrous hydroxide or ferrous carbonate reduce the selenate to selenium based on the standard reduction potential (Baek et al., 2013; Scheinost and Charlet, 2008). The alkaline condition after the electrode sets apparently promotes the reducing capability of ferrous hydroxide or ferrous carbonate, resulting in the transformation of selenate.

At the slowest flow rate (1.8 m/day), the removal rate of selenate after 5 h operation increased to 24.8%, 70.8%, and 88.9% with current densities of 1.26, 2.53 and 3.79 mA/cm², respectively. Moreover, the removal rate increased from 36.7% to 73.6% and 88.8% when the flow rate decreased from 5.4 m/day to 3.6 m/day and 1.8 m/day, respectively. It is also noted that, at the lowest flow rate, the selenate concentration in effluent was higher than that of P3, until the completing of 5 h electrolysis. The selenate was removed from the system within 2 h and then gradually removed at a slow rate. In a batch experiment, the coulomb efficiency of iron anode dissolution was more than 90% in bicarbonate mediation (Ciblak et al., 2012). The mass transfer from the anode surface to the bulk phase was enhanced by complete mixing in the batch experiment; however, the transfer of ferrous to the bulk phase was limited in the column experiment, and the precipitation of iron oxides onto the iron anode surface decreased the generation of ferrous. Fig. S2 shows a contour plot of the selenate removal rate as a function of current density and seepage velocity. Apparently, selenate can be effectively removed by electrolysis in the sand column. Moreover, the removal rate of selenate was proportional to the current densities applied to the electrode and inversely proportional to the flow rate (Fig. S2). The highest removal rate of 80% occurred at the condition of low flow rate (<3 m/day) and high current density (>3 mA/cm²).

3.2. Longer time operation

An experiment with more time allocated was carried out using Column A under the operating condition of 1.8 m/day flow rate and 1.26 mA/cm² current density (Fig. 2). The selenate was effectively removed from P3 and the effluent, and the removal rates increased gradually with the progress of the operation. After 48 h operation, 82.2% of the selenate removal rate was achieved in the effluent. The electrolysis also induces the temporal changes of pH and ORP. The gradual pH decrease at P2 is probably due to the partial oxidation of ferrous to ferric and hydrolysis of ferric. The gradual increase of the pH at P3 resulted from the oxidation of ferrous hydroxide to ferric hydroxide because the oxidation reactions consumed free hydroxide ions. The oxidation of ferrous species by dissolved oxygen might be due to the competitive reactions to the reduction of selenate. The ORP at P1 does not show any apparent change compared to the influent; however, the values at other ports after the anode were negative (reducing) during the entire experiment. The effluent was in contact with the ambient air, and a slightly higher value of ORP compared to that at P2 and P3 was observed. However, the ORP at P2 increased gradually after the sudden decrease and the pH at P2 between the two electrodes decreased gradually. Some of the electricity was probably consumed for water oxidation to generate hydrogen ions and oxygen gas instead of iron oxidation at the anode, causing a gradual decrease in pH and gradual increase in ORP at P2.

The XPS spectrum of Se 3d is reported in Fig. 3. The spectrum was modeled with two Se 3d peaks and one Fe 3p peak since the Se 3d and Fe 3p spectra are overlapping. The Se 3d spectrum was modeled as doublets of 3d_{3/2} and 3d_{5/2}, separated by 0.68 eV, and the area of the Se 3d_{3/2} peak was two-thirds the area of the Se 3d_{5/2} peak. The major peak of the Fe 3p spectrum of the sample was found at 56.9 eV, which was consistent with the reported peak of Fe(III) oxyhydroxide (Refait et al., 2000a). The major peak of the Se 3d_{5/2} spectrum of the sample was attributed to elemental Se located at 55.2 eV, which was consistent with the peak of Se(0) reference material we studied. The Se 3d spectrum also contains smaller peaks at 58.5 eV, which was interpreted to be Se(IV) species (NIST). However, Se(VI)eO, which was initially added, was not observed in the Se 3d spectrum, suggesting that Se(VI) was mostly reduced to metallic Se(0) by the reaction. Table S1 shows the quantitative analysis of selenium speciation, which indicates that 90.5% of selenate was reduced to elemental selenium and 9.5% was reduced to selenite in the solid phase.

3.3. Effect of zone 3

The longer reactive zone is expected to achieve a higher removal of selenate in the sand column. Column B, with a longer reactive zone with 30 cm after the cathode, was used to evaluate this hypothesis. The position of P3 is equivalent to the sampling position of effluent shown in Fig. 1a. As can be seen in Fig. 4, the removal rate of selenate at P3 increased gradually up to 78.4%; however, it is still lower than the removal rate of effluent with a shorter reactive zone (82.2% in Fig. 1b). At P4 and in the effluent, the removal of selenate was 80.2% and 84.1%. The concentration profile at P2 was almost the same as that of the shorter reactive zone. The ferrous formed a large amount of ferrous hydroxide or ferrous carbonate near the cathode and some precipitates were transported by hydraulic flow from the cathode to the reactive zone through the column. Ferrous hydroxide and ferrous carbonate are major reducing agent of selenate to elemental selenium. The longer reactive

zone provided a longer residence time; however, the length of the reactive zone does not significantly influence the removal rate of selenate. However, the reaction rate by ferrous hydroxide is slow, and further removal from P3 to P4 and to the effluent was not significantly enhanced. Additionally, the ORP was maintained at a negative value, giving a reducing condition in the longer reactive zone.

3.4. Effect of electrode spacing

When inert silica sand was packed between the anode and cathode, the voltage of the electrochemical process under constant current operation was quite high (e.g. up to 71.5 V under a constant current density of 1.26 mA/cm²) due to the high electrical resistance between electrodes. One way to reduce the voltage and energy consumption is to shorten the spacing between the anode and cathode, since the zone between the anode and cathode did not substantially contribute to selenate removal (see Figs. 2 and 4). Therefore, a setup with a shorter electrode spacing (2.7 cm) was designed to investigate the voltage and energy consumption (Column C, Fig. 1c), the results of which are shown in Fig. 4. As can be seen, the selenate removal in the reactive zone was 65.7% at P2 (located immediately after the cathode, see Fig. 1c), 68.0% at P3 (located 10 cm from the cathode), 68.9% at P4 (located 20 cm from the cathode), and 73.5% at the effluent after 48 h (Fig. 5).

The pH at the reactive zone varied in the range of 8.3–9.2, and an effluent pH was around 8.7, a slightly higher value compared to the initial pH (8.4). The ORP decreased sharply at all ports in the reactive zone within the first 17 h and then fluctuated. During the first 17 h, the ORP near the cathode was more negative (reducing condition), and the value increased gradually downstream in the reactive zone. The ORP values are highly dependent on the amount of ferrous hydroxide and ferrous carbonate. The ferrous hydroxide and ferrous carbonate were oxidized gradually with operation time, which is the reason for the gradual increase in the ORP from the cathode to the effluent. The voltage between the anode and cathode was initially 20.6 V, increasing gradually to 27.9 V after 48 h, while the average value during the treatment was 24.9 V. In the experiment with a longer electrode spacing of 10 cm, the voltage changed from 33.9 to 76.7 V after 48 h, and the average voltage was 50.3 V. In comparison with a longer spacing, the average voltage of the shorter electrode spacing (2.7 cm) decreased by 49.5%, resulting in approximately 50% less energy consumption. Even though the removal of selenate decreased slightly from 78.4% (10 cm spacing) to 73.5% (2.7 cm spacing), there was a significant saving on the electrical energy.

3.5. Electrode arrangement

Even though the short electrode spacing reduced the energy consumption by 50%, the voltage remained high, which might be an obstacle for the application of this system to the actual field. The electrochemical system described above requires two separate wells to install an anode and a cathode. An alternative application is to install the electrodes in a single well and then to fill the space between the two electrodes with groundwater, then it is expected further reducing the cell voltage of electrolysis. An experiment without silica sand filled between the electrodes was used to simulate this situation (Column C, Fig. 1c). An initial voltage of 3.0 V was observed, which was 14.6% of the voltage of the column packed with silica sand. Afterward, the voltage increased to 8.0 V after 48 h operation, and the

average voltage for the duration of the experiment was 5.4 V. The selenate removal rate ranged from 62.2% to 65.4% in the reactive zone after the cathode, while the further removal downstream after the cathode was negligible (Fig. 6). The lower value of average voltage indicates that the energy consumption of the system decreased in proportion to the voltage in order to obtain the same removal of selenate. The pH in the reactive zone increased slightly, and the ORP was similar to the experiment with sand silica packing.

The electrode sequence is important to achieve the degradation of a specific target contaminant. Higher transformation of energetic compounds was observed in the reactors under sequential oxidation-reduction compared to under sequential reduction-oxidation (Gilbert and Sale, 2005). In the aforementioned experiments, we operated the system using a sequential anode (oxidation) – cathode (reduction) reaction. Oxidation of iron anode produces ferrous ions and ferrous hydroxide or ferrous carbonate reduces selenate. In order to evaluate the effect of the electrode arrangement, an experiment using cathode–anode electrode sets (in the flow direction of the liquid) and column C (Fig. 1c) was conducted, with the same experimental conditions as those shown in Fig. 4. The selenate removal increased gradually through the column after anode reaction, and the removal rates of selenate in the reactive zone (after anode reaction) were 41.2, 42.7, 41.5, and 46.3% downstream after anode reaction (Fig. 7). However, the removal of selenate was much lower than in the sequence of the anode–cathode shown in Fig. 6.

The transport of iron generated by electrochemical reactions was investigated by analyzing the total iron in the electrode spacing and reactive zone (Fig. S3). The fraction of iron remaining between the two electrodes was 63% (Exp.12), 53% (Exp.13), and 9.9% (Exp.14) of the total iron generated by electrochemical reaction, and the efficiency of iron generation was 24%, 25%, and 21% based on Faraday's law. Therefore, only 21–25% of the electrical energy was used to generate ferrous ions, and other fractions of energy were consumed by other reactions. In the case of the system packed with silica sand between two electrodes, iron transport was inhibited by the sand particles and retained at the electrode region. Ferrous ions were precipitated by the high initial pH and remained at the electrode region. However, in the sequential reduction-oxidation, more ferrous ions were transported toward the reactive zone by hydraulic flow before hydroxide ions were generated at the cathode. The remaining iron compounds might contribute to retain the selenate between electrodes.

4. Conclusions

The electrochemical transformation of selenate in a sand column was investigated. The transformation of selenate was inversely proportional to the flow rate in the column and proportional to the current applied to the system. The reactive zone for selenate removal was the downstream zone after the cathode, and the longer residence time in the reactive zone enhanced the removal of selenate. Additionally, a longer reactive zone (the zone after cathode) provided longer residence time, which slightly increased the removal of selenate. The energy consumption was highly dependent on the electrode spacing, and shorter spacing significantly reduced the electrical energy consumption. The silica sand packed between the anode and cathode increased the electrical resistance; however, the electrolyte solution, rather than the sand, decreased the resistance, indicating the reduced energy consumption. A

cathode–anode sequence significantly decreased the removal of selenate compared to that of an anode–cathode in the column.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1-
 Schema of flow-through electrochemical column system. (a) Column A, (b) Column B, and
 (c) Column C.

Fig. 2.-

Selenate removal in long time operation. Seepage velocity: 1.8 m/day; current density: 1.26 mA/cm²; electrode spacing packed with silica sand: 10 cm; length of reactive zone (from cathode to effluent): 10 cm; a sequence of anode–cathode.

Fig. 3-

Se 3d XPS spectra of the sample. Circles represent XPS data and thick solid curves represent the fit to the data. Thin solid curves represent Se 3d_{5/2} composite peaks and dotted curves are Se 3d_{3/2} composite peaks.

Fig. 4.

Influence of length of reactive zone on selenate removal. Seepage velocity: 1.8 m/day; current density: 1.26 mA/cm²; electrode spacing packed with silica sand: 10 cm; length of reactive zone (from cathode to effluent): 30 cm; a sequence of anode–cathode.

Fig. 5.-

Influence of electrode spacing on selenate removal. Seepage velocity: 1.8 m/day; current density: 1.26 mA/cm²; electrode spacing packed with silica sand: 2.7 cm; length of reactive zone (from cathode to effluent): 30 cm; a sequence of anode–cathode.

Fig. 6–.

Effect of silica sand between the electrodes. Seepage velocity: 1.8 m/day; current density: 1.26 mA/cm²; electrode spacing packed with electrolyte 2.7 cm; length of reactive zone (from cathode to effluent): 30 cm; a sequence of anode–cathode.

Fig. 7-.

Influence of electrode sequence. Seepage velocity: 1.8 m/day; current density: 1.26 mA/cm²; electrode spacing packed with electrolyte 2.7 cm; length of reactive zone (from cathode to effluent): 30 cm; a sequence of cathode–anode.

Table 1–

Summary of experimental variables and results.

Exp. no.	Current density (mA/cm ²)	Seepage velocity (m/day)	Electrode spacing (cm)	Length of reactive zone (cm)	Operation time (h)	Packing material between electrode	Average voltage (V)	% Removal at effluent	Ref.
1	1.26	5.4	10	10	5	Silica sand	51.2	17.2	Fig.S1a
2	1.26	3.6	10	10	5	Silica sand	48.9	27.9	Fig.S1b
3	1.26	1.8	10	10	5	Silica sand	31.4	24.8	Fig.S1c
4	2.53	5.4	10	10	5	Silica sand	58.7	37.2	Fig.S1d
5	2.53	3.6	10	10	5	Silica sand	56.8	27.9	Fig.S1e
6	2.53	1.8	10	10	5	Silica sand	86.1	70.8	Fig.S1f
7	3.79	5.4	10	10	5	Silica sand	89.9	36.7	Fig.S1g
8	3.79	3.6	10	10	5	Silica sand	99.7	73.6	Fig.S1h
9	3.79	1.8	10	10	5	Silica sand	92.7	88.8	Fig.S1i
10	1.26	1.8	10	10	48	Silica sand	48.7	82.2	Fig.2
11	1.26	1.8	10	30	48	Silica sand	47.0	84.1	Fig.4
12	1.26	1.8	2.7	30	48	Silica sand	24.9	73.5	Fig.5
13	1.26	1.8	2.7	30	48	Electrolyte	5.4	62.9	Fig.6
14	1.26	1.8	2.7	30	48	Electrolyte	15.3 ^a	46.3	Fig.7

^a sequential cathode–anode, others sequential anode–cathode.