



# Article Can Selenium Be Removed in a Pilot Plant for Biological Iron and Manganese Removal?

Andrea Steuer <sup>1,2,\*</sup>, Urs Dippon-Deißler <sup>3</sup>, Daniel Mahringer <sup>1</sup> and Aki S. Ruhl <sup>1,2</sup>

- <sup>1</sup> Section II 3.3, German Environment Agency (UBA), Schichauweg 58, 12307 Berlin, Germany
- <sup>2</sup> Water Treatment, Technische Universität Berlin, KF 4, Straße des 17. Juni 135, 10623 Berlin, Germany
- <sup>3</sup> Section II 2.6, German Environment Agency (UBA), Wörlitzer Platz 1, 06844 Dessau-Roßlau, Germany

\* Correspondence: andrea.steuer@uba.de

**Abstract:** Selenium (Se) is essential to human health, yet harmful in high doses. Of the water-soluble Se redox species, Se(IV) readily adsorbs onto iron and aluminium oxides. Se(VI), the dominant form in oxygenated waters, is more mobile and less readily adsorbed. In this study, the removal of Se(VI) by reduction with Fe(II) to Se(IV) and subsequent adsorption onto iron hydroxides is investigated in a pilot plant for biological iron and manganese removal from groundwater to investigate an economical approach for Se removal during drinking water production. While Se(IV) is removed by up to 90%, Se(VI) shows no removal over 48 h. In batch-shaking tests, the adsorption of Se(IV) and Se(VI) onto iron hydroxides with and without addition of Fe(II) or dithionite as reducing agents was studied. Se(IV) was removed to a greater extent by adsorption than Se(VI) (7% and 2.6%, respectively, at a starting concentration of 0.1 mg/L) and the addition of reducing agents resulted in no significantly higher removal of Se(VI). Reducing Se(VI) with Fe(II) or dithionite and consequent adsorption onto iron hydroxides can therefore be excluded as viable removal mechanism for Se(VI).

Keywords: selenium removal; groundwater; iron hydroxide; pilot scale; drinking water



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# 1. Introduction

Selenium (Se) concentrations in soils and natural water strongly correlate with Se contents in the parent rock [1,2] but can also be influenced by anthropogenic activity such as agricultural run-off [3], through which Se can be transported into surface water and groundwater [4]. Groundwater concentrations typically range from 0.1–400  $\mu$ g/L [3]. Especially high concentrations of Se were found in Punjab, India (324  $\mu$ g/L) [1], and in the US states Colorado, New Mexico, and Utah (up to 4700  $\mu$ g/L) [5].

While low concentrations are necessary for human health, Se is highly toxic in elevated amounts [1–3]. Therefore, the WHO suggests a limit of 40  $\mu$ g/L [6], the European drinking water limit is 20  $\mu$ g/L [7], and the German limit value is 10  $\mu$ g/L [8].

Se naturally occurs in four redox states: selenate (Se(VI)), selenite (Se(IV)), elemental selenium (Se(0)), and selenide (Se(-II)) [9,10]. The speciation of Se is dependent on redox conditions and pH [3]. Reducing and acidic conditions favour the formation of Se(0) and Se(-II) [3,4], many of which are water insoluble. Oxidizing and alkaline conditions favour water-soluble Se(VI) and Se(IV) [3,4].

A large variety of methods for Se removal from water have been researched over the years. For Se(IV), various adsorption strategies have been proposed, including aluminiumbased water treatment residuals [11], manganese-aluminium hydroxides [12], iron oxyhydroxides [13], and carbon-substituted hydroxylapatite [14]. In most cases, Se(VI) is not as readily adsorbable as Se(IV). Therefore, alternative approaches such as co-precipitation with barite [15], removal with ion exchange resins [16], and reduction to Se(0) via zero-valent iron [17,18] and ferrous hydroxide [19] have been studied for Se(VI) removal. Most of the studies to date focus on laboratory set-ups. In pilot-scale and full-scale applications, Se(VI) removal is mainly investigated for the treatment of mining waste water. Biological treatment in plug flow biotreatment reactors [20], ion exchange resin [21], and nanofiltration [21] have been successfully implemented.

This study investigates the combination of chemical reduction, coagulation, and biological filtration as an economic, low-waste approach to Se(VI) removal from ground-water in a pilot plant for biological iron and manganese removal under Fe(II) dosage. Mahringer et al. [22] have shown that this process is an effective way to remove Cr(VI) from drinking water. As Fe(II) has the potential to reduce Se(VI), it is tested whether Se(VI) can be reduced to Se(IV) and subsequently adsorbed to in situ-produced iron hydroxides in a technical set-up. Therefore, the pilot plant was fed with iron- and manganese-free drinking water, and spiked with Se(VI). Fe(II) was added to act as a reducing agent and, after itself being oxidized to Fe(III) with dosed oxygen, to provide adsorption sites in the subsequent filter bed.

The reduction of Se(VI) and adsorption of Se(IV) were further studied in batch tests using Fe(II) and dithionite as reducing agents at different concentrations.

## 2. Materials and Methods

## 2.1. Modelling

Thermodynamic Se speciation was modelled using PHREEQC (2019) [23] with Phree-Plot (2022) [24] for batch processing and plotting of a Pourbaix diagram with the Lawrence Livermore National Laboratory (LLNL) dataset from 2017. Boundary conditions for the model were set to be 10 °C, carbonate available as  $CO_2$  at atmospheric pressure, a Se concentration of 1 µmol/L, and a sodium chloride background of 1 mmol/L in the pH range from 2 to 12 and Eh range from -0.75 V to 1.25 V. Only soluble species were considered for the model.

## 2.2. Chemicals and Stock Solutions

Se(IV) stock solution of 1 g/L was prepared from Na<sub>2</sub>SeO<sub>3</sub> (Sigma Aldrich, St Louis, MO, USA) in pure water, which was produced on-site by reverse osmosis and ion exchange. Se(VI) stock solution of 1 g/L was prepared from Na<sub>2</sub>SeO<sub>4</sub> (Carl Roth, Karlsruhe, Germany) in pure water, which was purged with nitrogen to remove oxygen.

Stock solutions (50 mg/L) for reducing agents were prepared using oxygen-free pure water and adding either  $FeSO_4 \cdot 7 H_2O$  (Th. Geyer, Renningen, Germany) or  $Na_2S_2O_4$  (Merck KGaA, Darmstadt, Germany).

Fe(II) solution for the pilot-scale experiments was prepared from FeSO<sub>4</sub>  $\cdot$  7 H<sub>2</sub>O, which was acidified to a pH below three to enhance the stability of Fe(II).

## 2.3. Pilot Plant Description

The experiments were conducted at a fully automated two-stage pilot plant for biological iron and manganese removal, which is described in detail elsewhere [22] and depicted in Figure 1. In short, the pilot plant consists of two filter columns (in row; 148 mm inner diameter, 1550 mm height, 20.64 L empty bed volume, 1200 mm filter bed height) filled with expanded polystyrene filter material and operated in up-flow. Due to the extended run time of the filters, these have been naturally converted into biofilters. The influent is aerated with technical oxygen before entering the first column and again before the second column. The oxygen flow is adjusted to remove iron mainly within the first column and manganese in the second column.

Oxygen dosage was set at 3 NmL/min (ca. 1.0 mg/L) resulting in a redox potential of 153 mV after the first column. During normal operation, the pilot plant treats groundwater at 250 L/h, which correspond to a filtration velocity of 15 m/h.



**Figure 1.** Simplified scheme of the pilot plant with dosing points for Se(VI) or Se(IV) and optional Fe(II), which was only dosed when Se(VI) removal was examined. Numbers depict the sampling ports.

#### 2.4. Pilot-Scale Experiments

Experiments were conducted within one filtration cycle until backwashing (50 h). Two experiments were conducted using iron- and manganese-free drinking water as raw water. Se(VI) was dosed into the pilot plant influent to achieve an influent concentration of 1.4 mg/L, a realistic concentration in highly contaminated areas [5]. To investigate adsorption of Se(VI), the filters were pre-loaded with precipitated iron for 4 h by treating iron- and manganese-containing groundwater before switching to the iron-free drinking water in the first experiment. Samples were obtained at different sampling points along the pilot plant to examine Se reduction during groundwater treatment. All samples were analysed for Fe(II) and total selenium (Se<sub>tot</sub>). Sampling was conducted daily.

To test potential reduction of Se(VI) to Se(IV) by Fe(II) and subsequent adsorption, Fe(II) was dosed at three different concentrations (1.0, 2.0, and 4.5 mg/L) to provide a reducing agent during the second experiment. Sampling was conducted in the same manner as without Fe(II) dosing. The filters were not pre-loaded for this experiment.

To verify and quantify Se(IV) adsorption within the pilot plant under natural conditions, a third experiment was run with natural groundwater as the raw water (ca. 2.5 mg/L Fe(II)) and Se(IV) was dosed into the pilot plant influent to achieve a concentration of 0.5 mg/L. The dosing tank of Se(IV) was purged with nitrogen to avoid oxidation. Sampling was conducted on the first and third day of the experiment.

All samples were filtered over 0.45  $\mu$ m PET filters (Chromafil, Macherey-Nagel, Düren, Germany). Fe(II) samples were analysed immediately, and Se samples (50 mL) were acidified with 300  $\mu$ L HNO<sub>3</sub> (65%, Merck KGaA, Darmstadt, Germany) for conservation.

## 2.5. Lab-Scale Batch Experiments

To further elucidate the reduction of Se(VI) and the adsorption behaviour of Se(IV) and Se(VI), batch-shaking tests were conducted in drinking water.

For reduction and adsorption tests, Se(VI) solutions were prepared at 1.0 mg/L and 0.1 mg/L. Dithionite was added as a reducing agent at concentrations of 5 mg/L and 25 mg/L. Fe(II) was also tested as a reducing agent at 5 mg/L. As an adsorbent, iron hydroxides were added in the form of backwash sludge from the first column of the pilot

plant in regular operation mode with unspiked reduced groundwater. The sludge was added as a suspension at a total suspended solid concentration of 12 mg/L in the batch.

To separate adsorption from reduction, in a separate trial, Se(IV) solutions of 1.0 mg/L and 0.1 mg/L were prepared from the stock solution. The adsorbent was added in the same manner to both Se(VI) and Se(IV) solutions at both concentrations.

All samples (50 mL) were shaken at 120 rpm for 30 min, filtered over 0.45  $\mu$ m PET filters, and acidified with 300  $\mu$ L HNO<sub>3</sub> (65%) for conservation.

#### 2.6. Analyses

Se(IV) and Se(VI) were measured as Se<sub>tot</sub> using inductively coupled plasma combined with mass spectrometry (ICP-MS; model NexION 300 D, Perkin Elmer, Waltham, MA, USA) according to ISO 17294-2.

Fe(II) samples were collected into 10 mL glass vials and analysed immediately. The photometric determination of Fe was carried out using the Spectroquant<sup>®</sup> Iron Test Kit (Merck KGaA, Darmstadt, Germany) with a UV/VIS spectrometer (Lambda 35, Perkin Elmer, Waltham, MA, USA). Measurements were carried out in a 10 mm quartz glass cuvette at a wavelength of 562 nm in a calibration range from 50 to 6000  $\mu$ g/L with a regression factor of 0.99.

## 3. Results

## 3.1. Modelling

The speciation of Se in dependence of pH and Eh was modelled with PHREEQC (2019) using the Lawrence Livermore National Laboratory (llnl.dat) 2017 database and is depicted in Figure 2. At a high oxidation redox potential (ORP), the very mobile [1,3,9,25] Se(VI) is the most dominant species over the entire pH range, present as  $SeO_4^{2-}$ . At moderate ORP, Se(IV) is the dominant speciation, changing from H<sub>2</sub>SeO<sub>3</sub> to HSeO<sub>3</sub><sup>-</sup> to  $SeO_3^{2-}$  with increasing pH. Se(IV) is considered to be more toxic than Se(VI) due to greater bioavailability [25–27], but is less mobile due to higher adsorption towards iron and aluminium oxides [3]. At low ORP, Se is present as Se(–II), in the form of H<sub>2</sub>Se at low pH and HSe<sup>-</sup> at moderate-to-high pH. Under strongly acidic and reducing conditions, Se is present as insoluble Se(0) [3] (not shown in Figure 2).



**Figure 2.** Pourbaix diagram of soluble Se species in an open system, computed with Lawrence Livermore National Laboratory dataset (llnl.dat). Dark grey field is Se(VI), light grey field is Se(IV), and white field is Se(-II).

The presented modelling results are consistent with literature investigating Se speciation under different conditions. Kumar et al. [25] investigated Se in groundwater in Chennai (India) and identified both Se(VI) and Se(IV) under slightly oxidizing to oxidizing conditions, with Se(VI) making up the majority of detected Se. Kuisi et al. [28] analysed total Se in eight different aquifers in Jordan, ranging from slightly oxidizing to oxidizing conditions depending on the aquifer depth. The speciation was not directly measured but assumed to be both Se(VI) and Se(IV) due to the prevailing conditions. It was further proposed that Se(VI) is more dominant due to its greater mobility [28]. In Berlin groundwater, Se levels tend to be below the limit of quantification (0.9  $\mu$ g/L), but there have been reports of up to 4.5  $\mu$ g/L [29]. Based on mean values for pH and ORP [29,30], Se(IV) would be expected.

Based on the thermodynamic calculation, it is hypothesized that Fe(II) can be used to reduce Se(VI) to Se(IV) at moderate-to-high ORP as would be expected for Se(VI)-containing groundwater.

## 3.2. Removal in the Pilot Plant

The adsorption of Se(VI) without Fe(II) dosing onto iron hydroxides and manganese oxides showed no significant removal over the duration of the filter cycle (Figure 3). While there is a small decrease in the Se(VI) concentration between sampling points 1 (influent) and 10 (effluent of the first filter) at the beginning of the experiment, adsorption stalled after 24 h, and after 48 h, the effluent concentration even exceeded influent concentration. As Fe(II) is completely removed by the filter, it can be assumed that ca. 1200 mg freshly precipitated Fe(III) was present in the filter at the start of Se(VI) dosing. This would indicate a Se(VI) loading of 114  $\mu$ g Se(VI) per mg Fe at the first sampling event after 2 h of Se(VI) dosing. This loading is about three orders of magnitude higher than loadings found by Kalaitzidou et al. [13] onto FeOOH in rapid small-scale column tests (RSSCT) with synthesized FeOOH (10  $\mu$ g Se(VI)/g FeOOH). Due to the high Se concentration of 1.4 (±0.1) mg/L, it is plausible that the initial adsorption capacity was quickly exhausted. As no further iron was introduced during the experiment, no further adsorption sites were created and were available, and Se(VI) was not removed.



**Figure 3.** Se(VI) concentrations in the pilot plant after dosing of Se(VI). Error bars indicate minimum and maximum concentrations from duplicate samplings per sampling point.

During continuous Fe(II) dosing, Fe(II) was removed to a great extent in the first column and further to values below the detection limit ( $50 \ \mu g/L$ ) in the second column independent of the feed concentration (Figure 4). Se(VI), on the other hand, was not significantly removed in either column of the pilot plant. As Se(VI) is poorly removable via adsorption to iron hydroxides [13], these results indicate that the reduction potential of Fe(II) is insufficient to reduce Se(VI) or reaction time between aeration and filter bed entry (approx. 13 min) is too short to achieve reduction. This confirms lab-scale results of Yoon at al. [18], who found Fe(II) insufficient to reduce Se(VI). Furthermore, no initial adsorption can be observed. The ratio of spiked Se to Fe(II) was lower after pre-loading (235 mg Se(VI) per g Fe(II) at the beginning of the experiment) than without pre-loading (ratio of Se to Fe was 300–1300 mg Se(VI) per g Fe(II) throughout the experiment), meaning the ratio of freshly produced adsorption sites to Se was higher, leading to the observed difference in Se removal during the first sampling of both experiments. Due to the high Se concentrations, the adsorption capacity was likely quickly exhausted, and the amount of Fe(II) dosed was not sufficient to remove Se consistently over the course of the experiment.



**Figure 4.** Se (**top**) and Fe (**bottom**) concentrations in the pilot plant after dosing of Se(VI) and Fe(II). Error bars indicate minimum and maximum concentrations from duplicate samplings per sampling point.

The high Se concentrations of 1.5 ( $\pm$ 0.2) mg/L are realistic in certain areas [5] and were therefore chosen to evaluate the efficiency of the treatment process, yet the dosed

Fe(II) concentrations are insufficient to remove such high concentrations. Previous studies dosed Se at an Se/adsorbent ratio of 0.1 to 5 mg/g [31,32], which is significantly lower than the ratio used in this study of 300 to 1300 mg Se per g Fe(II). Based on the mass balance of Se and Fe removed, an adsorbent loading of up to 113.6 mg Se per g Fe(II) (without Fe(II) dosing) and 22.35 mg/g (with continuous Fe dosing) was achieved. This is up to 100 times higher than adsorbent loadings found for hydroxide Fe<sub>3</sub>O<sub>4</sub> (1.4 mg Se(VI)/g) [31] and iron oxides (1.9 mg Se(VI)/g) [32]. For a better understanding of the removal capacity of the tested system, lower Se/Fe(II) ratios should be tested by either lowering the spiked Se concentration or further increasing the Fe(II) dosage.

As total Se was measured, the results can only indicate whether Se(VI) was reduced to Se(IV) based on the fact that Se(IV) is generally better adsorbable and would be expected to be removed in the pilot plant. To investigate this hypothesis, Se(IV) was dosed at 0.43 ( $\pm$ 0.03) mg/L in a third experiment using natural groundwater as influent.

Fe(II) was removed to concentrations below the limit of quantification within the first filter column (Figure 5). Se(IV) was removed by 85% within the first filter column and above 90% over the entire pilot plant shortly after the start of the experiment. Removals decreased to 43% in the first column and 57% overall by the end of the filtration cycle. These results show that Se(IV) can be effectively removed during the iron removal step of the pilot plant. This is in accordance with Kalaitzidou et al. [33], who demonstrated good removal of Se(IV) with FeOOH in RSSCT. At a dosing concentration of  $100 \,\mu\text{g/L}$  Se(IV), the adsorption capacity (defined as loading at residual concentrations of 10  $\mu$ g/L) was found to be 4.3 µg Se(IV) per mg FeOOH [33]. In this study, the amount of dosed Fe(II) was 5.8 times the amount of Se(IV), which resulted in a loading of 170  $\mu$ g Se(IV) per mg Fe(III) after the first two hours and 98  $\mu$ g Se(IV) per mg Fe(III) after 48 h of dosing. The decrease in the loading over the experimental period could indicate the exhaustion of the adsorptive sites. This seems unlikely despite the high Se dosage, as adsorption sites on iron hydroxides and manganese oxides are continuously produced during the filtration cycle, yet it is possible that iron hydroxides remaining in the filter after backwash could have enhanced Se(IV) adsorption at the beginning of the experiment. Potentially, Se(IV) might have been partially oxidized to Se(VI) in the dosage tank (despite purging with nitrogen), which might have led to decreased adsorption. As total Se was measured and no distinction between the species could be made, this cannot be ruled out entirely.

The results cannot unrefutably demonstrate to what extent Se(VI) can be removed and which underlying mechanism is responsible for the removal. The good removal of Se(IV) indicates that rapid reduction of Se(VI) before entering the filter column could present a solution for enhanced removal of Se(VI). Further investigations into Se(VI) reduction and adsorption are necessary to assess the feasibility of removal during groundwater treatment

The Se removal was investigated within one filter cycle. During continuous operation, groundwater treatment filters are periodically backwashed to remove the solids that accumulate in the filter bed. Adsorbed Se can therefore be expected to occur in the backwash sludge. There is some research on the reuse of Se from solids, for example, as a fertilizer in Se-poor soils [34,35], in the production of semi-conductors [36], or the adsorption of mercury [37]. Se might be recovered from solids using NaOH, which has been demonstrated to work well in extracting arsenic from hydroxyl-enriched CeO<sub>2</sub> [38].

If the selenium cannot be extracted and sludge cannot be reused, safe disposal to avoid secondary contamination is necessary. Staicu et al. [36] reported that Se-containing iron sludge has a low TCLP (toxicity characteristic leaching procedure) value and can be treated as non-dangerous waste. Se-containing sludge from groundwater treatment would need to be similarly tested before disposal options are discussed.



**Figure 5.** Se (**top**) and Fe (**bottom**) concentrations in the pilot plant after dosing of Se(VI). Fe(II) was provided from anoxic groundwater.

## 3.3. Reduction and Adsorption Tests

To examine the reducing potential of Fe(II) and dithionite, batch experiments were carried out with two initial Se concentrations and backwash sludge from the pilot plant as the adsorbent (Figure 6). At the initial concentration of 0.1 mg/L, Se(IV) was removed by 7% by the adsorbent alone, and Se(VI) was removed by 2.6%. The addition of dithionite resulted in slightly higher removals of 3% and 4% Se(VI) for 5 mg/L and 25 mg/L dithionite, respectively. Fe(II) did not result in significantly higher removals (0.4%). These removal rates translate to a loading of 0.007 µg Se(IV) per mg sludge and 0.002 µg Se(VI) per mg sludge only via adsorption, which is significantly lower than loadings achieved during pilot-scale removal. The addition of the reducing agents of Fe(II) at 5 mg/L and dithionite at 5 and 25 mg/L resulted in no significant increase in the Se(VI) loading (0.0004, 0.002, and 0.003 µg Se(VI) per mg sludge, respectively).



**Figure 6.** Se adsorption onto iron hydroxides in the presence of reducing agents for Se(IV) (blue) and Se(VI) (green) removals at Se starting concentrations of 0.1 mg/L (**left**) and 1.0 mg/L (**right**). Error bars indicate minimum and maximum values of two replicates.

At an initial Se concentration of 1 mg/L, removals were overall higher but showed larger variation. Se(VI) and Se(IV) were removed to a similar degree via adsorption. The addition of reducing agents resulted in no further Se(VI) removal, and on the contrary, the removals were lower. The addition of 5 mg/L Fe(II) and 25 mg/L dithionite resulted in a similar removal of approximately 13%, and the addition of 5 mg/L dithionite resulted in an even smaller Se(VI) removal. Calculated loadings due to adsorption are 0.008–0.015  $\mu$ g Se(IV) per mg sludge and 0.012–0.014  $\mu$ g Se(VI) per mg sludge. These are slightly higher than at lower initial Se concentrations. The impact of the reducing agents was negligible, indicating the ratio between Se(VI) and the reducing agents to be too low to achieve reduction.

Fe(II) has been shown to effectively reduce Cr(VI) to Cr(III), resulting in removal of Cr(III) via co-precipitation [22]. Although Se(VI) reduction by Fe(II) is thermodynamically possible [39], Fe(II) did not reduce Se(VI) to Se(IV) to a significant extent over time in this experiment. The increased contact time between Fe(II) and Se(VI) in the batch experiment in comparison to the pilot-scale experiment (30 min and 13 min, respectively) did not aid Se(VI) reduction. A previous study on the kinetics of Se(VI) reduction in the presence of iron oxides has shown that the reduction does not occur over the course of multiple hours [39], indicating an extension of the reaction time would not increase Se(VI) reduction in this set-up.

Dithionite also did not improve Se(VI) removal. It has been shown that dithionite can rapidly reduce selenious acid from weakly acidic sulphate solutions [40]. At neutral pH, dithionite is able to reduce Se(IV) and Se(VI) to Se(0) under UV radiation [41]. Therefore, the boundary conditions in this study might not have been optimal to utilize the reducing potential of dithionite for Se(VI) removal.

Further research is needed to identify adequate redox partners to reduce Se(VI) for subsequent Se(IV) adsorption. Other studies on the reduction of Se(VI) focus on the reduction to Se(0), either biologically [42–44] or using zero-valent iron [18], titanium dioxide [45], or granulated iron and organic carbon [16]. While employing these reducing agents and relying on co-precipitation of Se(0) can present an alternative to reduction to Se(IV) and consequent adsorption, they require additional chemicals or long operational times to achieve sufficient removal.

Unexpectedly, the removal of Se(VI) and Se(IV) were very low in this experiment. Other studies have also looked into Se adsorption onto iron-containing adsorbents. Jadhav et al. [46]

did a thorough investigation of Al-Fe mixed oxides and found an almost complete removal of both Se(IV) and Se(VI) at neutral pH values and a ratio 4  $\mu$ g Se per mg adsorbent. It was also shown that sulphate can significantly decrease Se adsorption [46]. In this study, the effect of competing anions in the water matrix was not studied and could be a factor in the observed poor removal.

Another factor impacting Se removal is the Se to adsorbent ratio. Qureshi et al. [47] demonstrated that ratios below and above the optimal ratio of 20  $\mu$ g Se(IV) per mg adsorbent resulted in decreased Se removal with Fe-Mn-based adsorbents. In this batch test, two ratios of 8.3  $\mu$ g Se per mg adsorbent and 83  $\mu$ g Se per mg adsorbent were tested. Both resulted in relatively low removals for Se(VI) and Se(IV) via adsorption alone, indicating that the dose was not optimal. In contrast to the pilot-scale experiments, the higher Se to adsorbent ratio resulted in better Se removal, but the achieved loading of the adsorbent was significantly lower than in the filter experiment. This effect highlights the importance of conducting pilot-scale experiments alongside batch experiments when looking for feasible treatment technologies.

## 4. Conclusions

The removal of the Se species, Se(IV) and Se(VI), during groundwater treatment in a pilot plant for biological iron and manganese removal was investigated. It was shown that up to 90% of Se(IV) was removed, while Se(VI) was not removed in significant amounts. This indicates that Fe(II) was not able to reduce Se(VI) within the given set-up. The removal of Se(IV) declined over the duration of the filtration cycle. Further investigations are needed to determine whether this is due to insufficient adsorption sites or an oxidation of Se(IV) to Se(VI) before entering the filtration column.

Batch experiments over 30 min confirmed the better adsorption of Se(IV) over Se(VI) onto backwash sludge. At a starting concentration of 0.1 mg/L, Se(IV) was removed by 7%, while Se(VI) was removed by less than 3%. The reducing agents dithionite and Fe(II) were not able to reduce Se(VI) over the duration of the experiment. Further research is needed to identify appropriate reducing agents and conditions to remove Se(VI) from water.

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#### References

- Bajaj, M.; Eiche, E.; Neumann, T.; Winter, J.; Gallert, C. Hazardous Concentrations of Selenium in Soil and Groundwater in North-West India. J. Hazard. Mater. 2011, 189, 640–646. [CrossRef] [PubMed]
- Fordyce, F.M. Selenium Deficiency and Toxicity in the Environment. In *Essentials of Medical Geology: Revised Edition*; Springer: Berlin/Heidelberg, Germany, 2012; pp. 375–416.
- 3. Gebreeyessus, G.D.; Zewge, F. A Review on Environmental Selenium Issues. SN Appl. Sci. 2019, 1, 55. [CrossRef]
- 4. Bailey, R.T. Review: Selenium Contamination, Fate, and Reactive Transport in Groundwater in Relation to Human Health. *Hydrogeol. J.* **2017**, *25*, 1191–1217. [CrossRef]

- 5. Morrison, S.J.; Goodknight, C.S.; Tigar, A.D.; Bush, R.P.; Gil, A. Naturally Occurring Contamination in the Mancos Shale. *Environ. Sci. Technol.* **2012**, *46*, 1379–1387. [CrossRef] [PubMed]
- 6. World Health Organization. *Guidelines for Drinking-Water Quality: Fourth Edition Incorporating First Addendum*, 4th ed.; +1st add.; World Health Organization: Geneva, Switzerland, 2017; ISBN 978-92-4-154995-0.
- Publications Office of the European Union. Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the Quality of Water Intended for Human Consumption (Recast); Publications Office of the European Union: Luxembourg, 2020; Volume 32020L2184, p. 62.
- 8. Bundesamt für Justiz. Verordnung über die Qualität von Wasser für den Menschlichen Gebrauch; Bundesamt für Justiz: Bonn, Germany, 2001.
- Elrashidi, M.A.; Adriano, D.C.; Workman, S.M.; Lindsay, W.L. Chemical Equilibria of Selenium in Soils: A Theoretical Developemnt. Soil Sci. 1987, 144, 141–152. [CrossRef]
- 10. Santos, S.; Ungureanu, G.; Boaventura, R.; Botelho, C. Selenium Contaminated Waters: An Overview of Analytical Methods, Treatment Options and Recent Advances in Sorption Methods. *Sci. Total Environ.* **2015**, *521–522*, 246–260. [CrossRef] [PubMed]
- Ippolito, J.A.; Scheckel, K.G.; Barbarick, K.A. Selenium Adsorption to Aluminum-Based Water Treatment Residuals. J. Colloid Interface Sci. 2009, 338, 48–55. [CrossRef] [PubMed]
- Constantino, L.V.; Quirino, J.N.; Monteiro, A.M.; Abrão, T.; Parreira, P.S.; Urbano, A.; Santos, M.J. Sorption-Desorption of Selenite and Selenate on Mg-Al Layered Double Hydroxide in Competition with Nitrate, Sulfate and Phosphate. *Chemosphere* 2017, 181, 627–634. [CrossRef]
- 13. Kalaitzidou, K.; Nikoletopoulos, A.-A.; Tsiftsakis, N.; Pinakidou, F.; Mitrakas, M. Adsorption of Se(IV) and Se(VI) Species by Iron Oxy-Hydroxides: Effect of Positive Surface Charge Density. *Sci. Total Environ.* **2019**, *687*, 1197–1206. [CrossRef]
- 14. Moore, R.C.; Rigali, M.J.; Brady, P. Selenite Sorption by Carbonate Substituted Apatite. *Environ. Pollut.* **2016**, *218*, 1102–1107. [CrossRef]
- 15. Tokunaga, K.; Takahashi, Y. Effective Removal of Selenite and Selenate Ions from Aqueous Solution by Barite. *Environ. Sci. Technol.* **2017**, *51*, 9194–9201. [CrossRef] [PubMed]
- Nishimura, T.; Hashimoto, H.; Nakayama, M. Removal of Selenium(VI) from Aqueous Solution with Polyamine-type Weakly Basic Ion Exchange Resin. Sep. Sci. Technol. 2007, 42, 3155–3167. [CrossRef]
- 17. Gibson, B.D.; Blowes, D.W.; Lindsay, M.B.J.; Ptacek, C.J. Mechanistic Investigations of Se(VI) Treatment in Anoxic Groundwater Using Granular Iron and Organic Carbon: An EXAFS Study. *J. Hazard. Mater.* **2012**, 241–242, 92–100. [CrossRef] [PubMed]
- Yoon, I.-H.; Bang, S.; Kim, K.-W.; Kim, M.G.; Park, S.Y.; Choi, W.-K. Selenate Removal by Zero-Valent Iron in Oxic Condition: The Role of Fe(II) and Selenate Removal Mechanism. *Environ. Sci. Pollut. Res.* 2016, 23, 1081–1090. [CrossRef] [PubMed]
- 19. Murphy, A.P. Removal of Selenate from Water by Chemical Reduction. Ind. Eng. Chem. Res. 1988, 27, 187–191. [CrossRef]
- 20. Maniatis, T.; Adams, D.J. Biological Treatment of Surface and Groundwater for Selenium and Nitrate. *ASMR* 2003, 2003, 749–764. [CrossRef]
- 21. Kratochvil, D.; Liang, H.C.; Baker, B.; Sundar, V. Industrial Scale Non-Biological Selenate Removal—Examples of Plants & Criteria behind Process Selection. In Proceedings of the Mine Water Solutions 2022, Vancouver, BC, Canada, 14–16 June 2022.
- 22. Mahringer, D.; Zerelli, S.S.; Dippon, U.; Ruhl, A.S. Pilot Scale Hexavalent Chromium Removal with Reduction, Coagulation, Filtration and Biological Iron Oxidation. *Sep. Purif. Technol.* **2020**, 253, 117478. [CrossRef]
- U.S. Geological Survey PHREEQC 2019. Version 3.7.3 Build-Number 15968. Available online: https://www.usgs.gov/software/ phreeqc-version-3 (accessed on 19 January 2022).
- 24. Kinniburgh, D.G.; Cooper, D.M. PhreePlot—Creating Graphical Output with PHREEQC 2011. Original Date June 2011, Last Updated 15 February 2023. 606p. Available online: http://www.phreeplot.org/ (accessed on 19 January 2022).
- Kumar, A.R.; Riyazuddin, P. Speciation of Selenium in Groundwater: Seasonal Variations and Redox Transformations. J. Hazard. Mater. 2011, 192, 263–269. [CrossRef]
- 26. Hamilton, S.J. Review of Selenium Toxicity in the Aquatic Food Chain. Sci. Total Environ. 2004, 326, 1–31. [CrossRef]
- 27. Fernández-Martínez, A.; Charlet, L. Selenium Environmental Cycling and Bioavailability: A Structural Chemist Point of View. *Rev. Environ. Sci. Bio/Technol.* 2009, *8*, 81–110. [CrossRef]
- 28. Kuisi, M.A.; Abdel-Fattah, A. Groundwater Vulnerability to Selenium in Semi-Arid Environments: Amman Zarqa Basin, Jordan. *Env. Geochem. Health* **2010**, *32*, 107–128. [CrossRef] [PubMed]
- 29. Senatsverwaltung für Mobilität, Verkehr, Klimaschutz und Umwelt Wasserportal: Gewässerkundliche Messdaten. (database). Last updated 6 December 2022. Available online: https://www.govdata.de/dl-de/by-2-0 (accessed on 19 August 2023).
- 30. Senatsverwaltung für Mobilität, Verkehr, Klimaschutz und Umwelt. In *Grundwasser in Berlin: Vorkommen, Nutzung, Schutz, Gefährdung*; Umwelt und Verbraucherschutz Berlin: Berlin, Germany, 2007.
- Gonzalez, C.M.; Hernandez, J.; Peralta-Videa, J.R.; Botez, C.E.; Parsons, J.G.; Gardea-Torresdey, J.L. Sorption Kinetic Study of Selenite and Selenate onto a High and Low Pressure Aged Iron Oxide Nanomaterial. *J. Hazard. Mater.* 2012, 211–212, 138–145. [CrossRef] [PubMed]
- 32. Sheha, R.R.; El-Shazly, E.A. Kinetics and Equilibrium Modeling of Se(IV) Removal from Aqueous Solutions Using Metal Oxides. *Chem. Eng. J.* 2010, *160*, 63–71. [CrossRef]

- Kalaitzidou, K.; Nikoletopoulos, A.; Bakouros, L.; Zouboulis, A.; Mitrakas, M. Selenite Removal from Water. In Proceedings of the 4th EWaS International Conference: Valuing the Water, Carbon, Ecological Footprints of Human Activities, Leftkada, Greece, 24 June–27 September 2020; MDPI: Basel, Switzerland, 2020; p. 23.
- Yan, J.; Chen, X.; Zhu, T.; Zhang, Z.; Fan, J. Effects of Selenium Fertilizer Application on Yield and Selenium Accumulation Characteristics of Different Japonica Rice Varieties. *Sustainability* 2021, 13, 10284. [CrossRef]
- 35. Zhang, X.; Li, X.; Jin, Z.; Tumrani, S.H.; Ji, X. Selenium in Wastewater Can Be Adsorbed by Modified Natural Zeolite and Reused in Vegetable Growth. *Sci. Prog.* **2021**, *104*, 003685042110198. [CrossRef] [PubMed]
- Staicu, L.C.; Van Hullebusch, E.D.; Lens, P.N.L. Production, Recovery and Reuse of Biogenic Elemental Selenium. *Environ. Chem.* Lett. 2015, 13, 89–96. [CrossRef]
- Fellowes, J.W.; Pattrick, R.A.D.; Green, D.I.; Dent, A.; Lloyd, J.R.; Pearce, C.I. Use of Biogenic and Abiotic Elemental Selenium Nanospheres to Sequester Elemental Mercury Released from Mercury Contaminated Museum Specimens. J. Hazard. Mater. 2011, 189, 660–669. [CrossRef]
- Hu, W.; Yang, L.; Shao, P.; Shi, H.; Chang, Z.; Fang, D.; Wei, Y.; Feng, Y.; Huang, Y.; Yu, K.; et al. Proton Self-Enhanced Hydroxyl-Enriched Cerium Oxide for Effective Arsenic Extraction from Strongly Acidic Wastewater. *Environ. Sci. Technol.* 2022, 56, 10412–10422. [CrossRef]
- Myneni, S.C.B.; Tokunaga, T.K.; Brown, G.E. Abiotic Selenium Redox Transformations in the Presence of Fe(II,III) Oxides. *Science* 1997, 278, 1106–1109. [CrossRef]
- Geoffroy, N.; Demopoulos, G.P. Reductive Precipitation of Elemental Selenium from Selenious Acidic Solutions Using Sodium Dithionite. *Ind. Eng. Chem. Res.* 2009, 48, 10240–10246. [CrossRef]
- 41. Duan, Y.; Kaushik, V.; Jung, B.; Batchelor, B.; Abdel-Wahab, A. Kinetic Study of Selenium Removal Using Advanced Reduction Process with Dithionite. *Environ. Eng. Sci.* **2018**, *35*, 169–175. [CrossRef]
- 42. Maiers, D.T.; Wichlacz, P.L.; Thompson, D.L.; Bruhn, D.F. Selenate Reduction by Bacteria from a Selenium-Rich Environment. *Appl. Environ. Microbiol.* **1988**, *54*, 2591–2593. [CrossRef] [PubMed]
- Sposito, G.; Yang, A.; Neal, R.H.; Mackzum, A. Selenate Reduction in an Alluvial Soil. Soil Sci. Soc. Am. J. 1991, 55, 1597–1602. [CrossRef]
- 44. Li, L.; Zhang, B.; He, C.; Zhang, H. Hydrodynamics- and Hydrochemistry-Affected Microbial Selenate Reduction in Aquifer: Performance and Mechanisms. *Sci. Total Environ.* **2021**, *768*, 145331. [CrossRef] [PubMed]
- Nguyen, V.N.H.; Beydoun, D.; Amal, R. Photocatalytic Reduction of Selenite and Selenate Using TiO2 Photocatalyst. J. Photochem. Photobiol. A Chem. 2005, 171, 113–120. [CrossRef]
- 46. Jadhav, A.S.; Ramteke, P.; Singh, S.K.; Labhasetwar, N.K. Sustainable Selenium Remediation from Water Using Aluminium–Iron Mixed Oxide: Batch and Column Adsorption Studies. *J. Water Process Eng.* **2022**, *48*, 102824. [CrossRef]
- 47. Qureshi, S.S.; Memon, S.A.; Rafi-ul-Zaman; Ram, N.; Saeed, S.; Mubarak, N.M.; Karri, R.R. Rapid Adsorption of Selenium Removal Using Iron Manganese-Based Micro Adsorbent. *Sci. Rep.* **2022**, *12*, 17207. [CrossRef]

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