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Adsorption of Se(IV) and Se(VI) species by iron oxy-hydroxides: Effect of positive surface charge density

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Abstract

Batch and continuous mode experiments were used to determine the influence of physic-chemicals characteristics of iron oxy-hydroxides (FeOOHs) on selenium adsorption. Batch experiments and continuous flow rapid small-scale column tests (RSSCTs) at pH 7 and NSF (National Sanitation Foundation) water matrix, showed that the adsorption capacity of FeOOHs for Se(IV) is strongly related to positive surface charge density (PSCD), and gradually increases when synthesis pH is lowered. The highest PSCD value of 3.25 mmol [OH⁻]/g was observed at synthesis pH 2.5 (FeOOH/2.5) and the lowest, 0.45 mmol [OH⁻]/g was observed at synthesis pH 9 (FeOOH/9). A thermodynamic study verified the endothermic (ΔΗ° 21.4 kJ/mol) chemisorption of Se(IV) by the qualified FeOOH/2.5. EXAFS data showed that Se(IV) is involved in three types of surface complexes: bidentate mononuclear edge-sharing (¹E) and two types of binuclear inner-sphere (¹C) linkage between the SeO₃²⁻ pyramids, and Fe(O,OH)₆ octahedra. The FeOOHs were evaluated by their adsorption capacity (Q₁₀) at residual concentrations equal to the EU drinking
water regulation limit of 10 µg/L, e.g. in conditions implemented in full-scale water treatment plants. The qualified FeOOH/2.5 was found to be the most effective for Se(IV) adsorption with a $Q_{10}$ value 4.3 mg Se(IV)/g. In contrast, the $Q_{10}$ value for Se(VI) was almost three orders of magnitude lower (10 µg Se(VI)/g) than that for Se(IV). Finally, regeneration experiments showed that FeOOHs reuse for Se(IV) removal is economically feasible and the recovery of selenium by precipitation as elemental Se contributes to green chemistry.

Keywords
selenium; adsorption; iron oxy-hydroxides; structural/sorbed sulfates; positive surface charge density

1. Introduction

Although selenium is one of the most important elements for human biology, it is toxic if consumed excessively. Consumption of low concentrations of selenium in drinking water can cause dermatological problems while, excessive consumption leads to severe health effects (Jordan et al., 2014). Setting a Drinking Water Regulation Limit (DWRL) for selenium is complex because the selenium content of local foodstuffs should also be taken into account (WHO, 2017). Although WHO has set a regulation limit of 40 µg/L, most European countries have set the regulation limit as 10 µg/L, while the upper limit set by the U.S. Environmental Protection Agency is 50 µg/L. Limited epidemiological data on the effects of selenium on human health has resulted in the DWRL being a controversial issue (WHO, 2017; EPA, 2018; EU, 1998).

Selenium recorded in groundwater is of either natural or anthropogenic origin. Mining, petroleum refining, construction waste rocks of sedimentary origin release, and fossil fuel combustion all contribute to selenium pollution, while other human activities, such as irrigation, enhance the corrosion of selenium-ferrous rocks (Leblanc et al., 2018; Tabelin et al, 2014; Tamoto et al, 2015) and lead to the leaching of selenium into aquifers in the forms of soluble Se(IV) (HSeO$_3^-$) and Se(VI) (SeO$_4^{2-}$) oxyanions. Water
chemistry determines the dominant species of selenium present in a water body. Oxic conditions favor the presence of Se(VI), and Se(IV) dominates in anoxic environments (Kumkrong et al., 2018).

Many treatment processes have been studied for their ability to remove Se(IV)/Se(VI) from water and wastewaters (Table S1 Supplementary Material). These treatment technologies include: chemical reduction techniques (Ling et al., 2015; Geoffroy and Demopoulos, 2011); co-precipitation (Francisco et al., 2018; Börsig et al., 2017; Tokunaga and Takahashi, 2017); coagulation-flocculation (Hue et al., 2015); electrocoagulation (EC)-membrane filtration (Mavrov et al., 2006); electrochemical methods (Baek et al., 2013); adsorption (Wang et al., 2019; Ma et al., 2018; Kongsri et al., 2013; Tian et al., 2017; Kwon et al., 2015; Fu et al., 2014; Seyed Dorraji et al., 2017; Awual et al., 2015a; 2015b; Gezer et al., 2011); membrane technologies (He et al., 2018; Gui et al., 2015); biological removal (Mal et al., 2017; Dessì et al., 2016); bioremediation (Cantafio et al., 1996); and phytoremediation (Carvalho and Martin, 2013).

Although versatile treatment methods have been examined for selenium removal, most of them are not applicable for drinking water purification due to certain drawbacks. Research is focused on high initial concentrations in distilled water matrix without the respective crucial evaluation of co-existing ions. In addition, these methods are only efficient at acidic pH ranges meaning a post-treatment stage is required, have long residence times, high operating costs, strongly modify water quality, and, moreover, do not achieve residual concentrations below the strict European Union regulation limit of 10 μg/L for drinking water (Table S1 Supplementary Material). However, adsorption treatment technologies are now being focused on due to their simple operation, minimal labor cost, and residence times of below 6 min (Simeonidis et al., 2016).

The high affinity of iron oxy-hydroxides (FeOOHs) with selenium oxyanions renders them strong potential candidates for selenium removal from drinking water in full-scale water treatment plants. FeOOHs show higher uptake capacities for Se(IV) than for Se(VI) since they form inner-sphere complexes with Se(IV), while the corresponding complexes formed with Se(VI) are outer-sphered (Sun et al., 2015). However, the adsorption capacities of various FeOOH, presented in reported studies (Jacobson and Fan, 2019; Ma et al., 2018; Lounsbury et al., 2016; Das et al., 2013; Mitchell et al., 2013; Sharrad et al.,
2012; Rovira et al., 2008; Duc et al., 2003; Peak and Sparkles, 2002; Balistrieri and Chao, 1990) are not applicable in full scale drinking water purification plants because of the aforementioned drawbacks (Table S1, Supplementary Material).

This study aims to determine the parameters that affect adsorption of Se onto iron oxy-hydroxides and evaluate the process according the following criteria: Ability to achieve residual concentrations \(C_e<10 \mu g/L\), uptake capacity \(Q_{10}\) at \(C_e\ 10 \mu g/L\), fixed-bed continuous flow process, empty bed contact time (EBCT) <4 min, retain the physical and chemical characteristics of drinking water, ability for full-scale implementation and, lastly, estimate operating costs. To the best of our knowledge, the evaluation of FeOOH adsorbents according to the above-mentioned criteria has not been previously reported. For this research a series of FeOOH adsorbents were prepared by the precipitation of iron salts under different pH and oxidation reduction potential (ORP) values according to Tresintsi’s procedure (Tresintsi et al., 2012). By applying batch reactor and continuous flow experimental protocols the adsorption capacity of these adsorbents and their corresponding commercially available products was evaluated for Se(IV) and Se(VI) species and also correlated with their physicochemical characteristics.

2. Materials and Methods

2.1 Adsorbents production

To study the effect of their surface charge density and structure on selenium species adsorption FeOOHs were synthesized following the procedure of Tresintsi et al., 2012 by oxidation-hydrolysis of FeSO₄·H₂O under high ORP and pH values in the range of 2 - 9 using a laboratory, two-stage, continuous flow reactor (Fig. S1, Supplementary Material). During the synthesis, ORP potential and pH were regulated drop-wise by H₂O₂ (50% w/w) and NaOH (30% w/w), respectively. Moreover, a FeOOH was synthesized by FeCl₃ hydrolysis at pH 3 to estimate the contribution of sulfate to surface charge density. The collected dried adsorbent, was ground and sieved to obtain either a fine powder form (<63 mm) used for the batch adsorption experiments or granules (0.25 - 0.50 mm) for the column tests. Furthermore,
commercially available FeOOH products approved for arsenic treatment, such as GEH (comprising akagaenite) and Bayoxide (comprising goethite), were also examined.

2.2 Adsorbents characterization

Iron content of adsorbents was determined by sample dissolution in HCl as measured by flame atomic absorption spectroscopy using a PerkinElmer AAnalyst 800 instrument. The crystalline structure of each produced powder was identified by X-ray diffractometry (XRD) using a water-cooled Rigaku Ultima+ diffractometer with CuKα radiation, a step size of 0.05° and step time of 3 s, operating at 40 kV and 30 mA. Surface area and porosity of the adsorbent samples was estimated by nitrogen gas adsorption at liquid N₂ temperature (77 K) using a micropore surface area analyzer according to the Brunauer-Emmett-Teller (BET) model. The isoelectric point (IEP) in a water dispersion of oxy-hydroxide solid was determined by the curve of zeta-potential at 20 ± 1°C. Sample preparation included the suspension of 50 mg fine oxy-hydroxide powder into 1 L of electrolyte solution (0.01 M NaNO₃). Quantities of 100 mL were equilibrated at different pH values (4 - 10) for 60 min by adding either HNO₃ or NaOH while stirring. The electrophoretic velocity of at least 20 particles was then determined through a digital camera using a Rank Brothers Micro-Electrophoresis Apparatus Mk II device and the ζ-potential value was calculated. The surface charge density of the adsorbents and the point of zero charge (PZC) were estimated using the potentiometric mass titration method (Kosmulski, 2009). Physically sorbed sulfate was extracted with water and both physically and chemically sorbed sulfate was extracted with 5mM NaOH and determined by an Alltech 600 ion chromatography system with a Transgenomic ICSep AN1 column using a 1.7 mM NaHCO₃/1.8 mM Na₂CO₃ solution as eluent (Tresintsi et al., 2014b). Total sulfate content of the FeOOHs was determined gravimetrically by precipitation as BaSO₄ (Mendham et al., 2000). A 200 mg sample was dissolved in 8 mL HCl (6N) applying mild heating. 150 mL of hot distilled water was then added, followed by drop-wise addition of 50 mL BaCl₂ solution (5g/L). The white precipitate of BaSO₄ was aged under heating for at least 2h, filtered through a 0.45 μm pore-size fiberglass filter, dried and weighed.
2.3 Reagents

Stock solutions of Se(IV) and Se(VI) were prepared from analytical grade reagents Na$_2$SeO$_3$ and NaSeO$_4$, respectively, dissolved in distilled water. Working standards were freshly prepared by proper dissolution of the stock solutions in NSF water containing interfering ions commonly encountered in natural waters. NSF challenge water is prepared according to National Sanitation Foundation protocols, because it simulates the natural waters providing a common evaluation basis for water treatment at full scale (Amy et al., 2005), by dissolving 252 mg NaHCO$_3$, 12.14 mg NaNO$_3$, 0.178 mg NaH$_2$PO$_4$·H$_2$O, 2.21 mg NaF, 70.6 mg NaSiO$_3$·5H$_2$O, 147 mg CaCl$_2$·2H$_2$O, and 128.3 mg MgSO$_4$·7H$_2$O in 1 L of distilled water.

2.4 Batch experiments

Batch experiments were initially carried out to preliminary evaluate adsorbents efficiency for Se(IV)/Se(VI) removal. The kinetics of Se(IV) adsorption was evaluated by dispersing 200 mg of adsorbent in 1 L of 1000 μg/L in NSF water matrix at pH 7 and 20°C, while the influence of water pH was evaluated by dispersing 200 mg of adsorbent in 1 L of 500 μg/L in NSF water matrix at pH range 5 – 11 and 20°C. To record the respective adsorption isotherms, 50 - 300 mg/L of fine adsorbent powder (<63 μm) was dispersed in 200 mL selenium-containing solutions (100 – 1000 μg/L) in 300 mL conical flasks. The flasks were placed on an orbital shaker for 24 h at 20°C. Similar experiments were carried out at different temperatures 5 – 35°C and equilibrium pH 7 to study the thermodynamic parameters of the process. The examined pH range was 6-8, representing that commonly encountered in natural waters. At the end of each experiment, the suspensions were filtered through a 0.45 μm pore-size membrane filters. Initial and residual concentrations were determined by Graphite Furnace Atomic Absorption Spectrophotometry using a Perkin-Elmer AAnalyst 800 instrument. The detection limit was calculated from seven (7) replicates of 2 - 10 μg Se/L, and was estimated to be 1 μg/L. The results were tested to fit the Langmuir and Freundlich models and adsorbent efficiency was evaluated according to their adsorption capacity at residual concentration equal to DWRL of 10 μg/L, which is abbreviated as Q$_{10}$ henceforth.
2.5 Rapid Small-Scale Column Tests

Rapid small-scale column tests (RSSCT) were performed in glass columns of 1.1 cm diameter and 50 cm height with polytetrafluoroethylene (PTFE) valves and caps, and a glass frit at the base of each column. The columns were filled with FeOOH adsorbents of particle size 0.25 - 0.50 mm to the height of 20 cm and were fed from the top with 100 μg/L selenium solution in NSF water at pH 7 ± 0.1 via a dosing pump. Effluent samples were collected periodically and analyzed for residual selenium concentration. A schematic diagram along with a photograph of the RSSCTs set up is presented in Fig. S2 (Supplementary Material). The laboratory experiment simulates full-scale processes and was designed to achieve an Empty Bed Contact Time (EBCT) of 3 - 4 min at 20°C.

Selenium leaching tests were performed on the spent RSSCT adsorbents according to the standard test EN 12457 (BSI, 2002) and the U.S. Toxicity Characteristic Leaching Procedure (USEPA, 1992) to evaluate their compliance with the current regulations for environmentally safe disposal.

2.6 X-Ray Absorption Spectroscopy

X-Ray Absorption Fine Structure Spectroscopy (XAFS) was implemented to identify the oxidation state and adsorption mechanism of selenium onto FeOOH. The Near-Edge (XANES) and Extended (EXAFS) X-ray measurements were carried out using the BESSY-II storage ring of a Helmholtz Zentrum Berlin instrument. The Se-K XAFS spectra of two FeOOH samples synthesized at pH 2.5 and 8 were recorded at the KMC2 beamline in the fluorescence yield mode using an energy dispersive (Bruker X-Flash) detector. The spectrum of one powder Se(IV) reference sample (Na₂SeO₃), was acquired in the transmission mode simultaneously with the FeOOH samples and used for energy calibration of the XANES spectra. Subtraction of the atomic absorption in the EXAFS spectra was performed using ATHENA (Ravel and Newville, 2005) and the theoretical phase and amplitude functions for the scattering paths were calculated by FEFF8.2 (Ankudinov et al., 1998). Curve fitting of the $k^3 \chi(k)$ EXAFS spectra was carried out in both $R$- and $k$-space using FEFFIT, assuming that Se chemisorbs at the edges and corners of Fe(O,OH)₆ octahedra in three types of geometries. The Debye-Waller ($\sigma^2$) factors were iterated for the oxygen atoms in the 1st nearest neighbor (nn) shell, while in the Fe-comprised nn shells, due to high correlation among
the fitted parameters, the $\sigma^2$ factors were constrained to be equal although allowed to vary during the fitting.

2.7 Adsorbent regeneration

Based on preliminary experiments, on-site adsorbent regeneration was achieved by pumping at up-flow configuration 600 mL/h of 0.011 N NaOH solution (pH = 12 ± 0.5) for 3.5 h.

3. RESULTS AND DISCUSSION

3.1 Materials characterization

The physicochemical characteristics of adsorbents synthesized by FeSO$_4$/H$_2$O$_2$ were strongly influenced by the synthesis pH, an observation also reported by Tresintsi et al., 2012. Fig. 1 presents XRD diagrams of the samples produced within the pH range 2–9. The observed broadened peaks indicated the amorphous structure of the materials produced. The application of Scherer’s equation showed that the synthesized FeOOHs are nano-materials with an average crystal size of less than 5 nm. Low pH and the corresponding highly oxidizing environments favored fast nucleation, slow growth rate, and surface protonation, which led to the incorporation of sulfate at diffuse layer relatively away from the surface electrostatic influence, onto Stern layer where they are strongly bound to the solid’s surface (chemisorbed) and into the crystal structure of the oxy-hydroxide captured during material’s growth (Table 1), which was also verified by the FT-IR data (Fig. S3, Supplementary Material).

Comparing the resulting XRD patterns to the those in the JCPDS database, the main phase identified at synthesis pH range 2-4 is oxy-hydroxy-sulfate schwertmannite (Fe$_{16}$O$_{16}$(OH)$_{10}$(SO$_4$)$_3$·10H$_2$O (PDF#47-1775). At synthesis pH values 5.7 and 8, lepidocrocite (g-FeOOH) becomes the dominant product (PDF#29-0713), while at alkaline values (pH 9) the more crystalline iron oxide hematite (a-Fe$_2$O$_3$) was identified (PDF#33-0664). In contrast, the hydrolysis of FeCl$_3$ at pH 3 in the absence of sulfate resulted in the formation of ferryhydrite (PDF#29-0712) (Fig. 1).
Fig. 1. XRD diagrams of the iron oxy-hydroxides (a) FeOOH/2, (b) FeOOH/2.5, (c) FeOOH/3, (d) FeOOH/4, (e) FeOOH/5.7, (f) FeOOH/8, (g) FeOOH/9, (h) FeOOH/FeCl₃, (i) Bayoxide, and (j) GEH. Symbols indicate the expected diffraction peaks for the following structures ▼ schwertmannite (PDF#47-1775), ◆ lepidocrocite (PDF#44-1415), ○ hematite (PDF#33-0664), ● ferrihydrite (PDF#29-0712), ▼ goethite (PDF#29-0713), □ akaganeite (PDF#34-1266).

The positive surface charge density (PSCD) gradually increased when synthesis pH was lowered. For example, the highest PSCD of 3.25 mmol [OH⁻]/g was recorded at synthesis pH 2.5, while the lowest, 0.45 mmol [OH⁻]/g, was observed at synthesis pH 9 (Table 1). This tendency to counterbalance the positive surface charge leads to sulfate incorporation in the crystal structure and Stern layer, which gradually increased when synthesis pH is decreased. Adsorbed SO₄²⁻ anions in the Stern layer are exchangeable and therefore contributed to surface charge density which, in turn, improved adsorption capacity (Tresintsi et al., 2012). The lower PSCD value of 2.7 mmol [OH⁻]/g recorded at synthesis pH 2 (Fe: 38.6 wt.%) compared to the FeOOH synthesized at pH 2.5 (Fe: 44.8 wt.%) is attributed to lower iron content due to the incorporation of a higher percentage of sulfate in the FeOOH structure (Table 1). The contribution of
exchangeable sulfate in surface density was verified by comparing the PSCD (2.45 mmol \([\text{OH}^-]/g\)) of FeOOH/3 to that of FeOOH/FeCl\(_3\) (1.5 mmol \([\text{OH}^-]/g\)) that was also synthesized at pH 3 by hydrolysis of FeCl\(_3\) but in the absence of SO\(_4^{2-}\) anions.

**Table 1.** Main physicochemical characteristics of laboratory synthesized and commercial FeOOHs evaluated for Se(IV) adsorption.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Synthesis parameters</th>
<th>Fe wt. %</th>
<th>Surface area ((m^2/g))</th>
<th>IEP(^1)</th>
<th>ZPC(^2)</th>
<th>PSCD(^3) mmol ([\text{OH}^-]/g)</th>
<th>Physically sorbed SO(_4^{2-}) wt. %</th>
<th>Chemically sorbed SO(_4^{2-}) wt. %</th>
<th>Total SO(_4^{2-}) wt. %</th>
<th>Main crystal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeOOH/2</td>
<td>FeSO(_4)/H(_2)(_2)O</td>
<td>2</td>
<td>38.6</td>
<td>100</td>
<td>5.7</td>
<td>2.6</td>
<td>2.80</td>
<td>3.4</td>
<td>8.3</td>
<td>17.9</td>
</tr>
<tr>
<td>FeOOH/2.5</td>
<td>FeSO(_4)/H(_2)(_2)O</td>
<td>2.5</td>
<td>44.8</td>
<td>48</td>
<td>6.9</td>
<td>2.7</td>
<td>3.25</td>
<td>1.9</td>
<td>9.1</td>
<td>17.0</td>
</tr>
<tr>
<td>FeOOH/3</td>
<td>FeSO(_4)/H(_2)(_2)O</td>
<td>3</td>
<td>44.9</td>
<td>53</td>
<td>7.2</td>
<td>3.2</td>
<td>2.45</td>
<td>1.9</td>
<td>8.7</td>
<td>15.1</td>
</tr>
<tr>
<td>FeOOH/4</td>
<td>FeSO(_4)/H(_2)(_2)O</td>
<td>4</td>
<td>50.4</td>
<td>120</td>
<td>7.1</td>
<td>3.2</td>
<td>2.23</td>
<td>4.0</td>
<td>7.2</td>
<td>14.0</td>
</tr>
<tr>
<td>FeOOH/5.7</td>
<td>FeSO(_4)/H(_2)(_2)O</td>
<td>5.7</td>
<td>50.1</td>
<td>168</td>
<td>7.3</td>
<td>4.2</td>
<td>1.42</td>
<td>4.4</td>
<td>3.7</td>
<td>8.1</td>
</tr>
<tr>
<td>FeOOH/8</td>
<td>FeSO(_4)/H(_2)(_2)O</td>
<td>8</td>
<td>50.2</td>
<td>226</td>
<td>6.6</td>
<td>7.9</td>
<td>1.04</td>
<td>0.8</td>
<td>1.1</td>
<td>1.9</td>
</tr>
<tr>
<td>FeOOH/9</td>
<td>FeSO(_4)/H(_2)(_2)O</td>
<td>9</td>
<td>51.4</td>
<td>140</td>
<td>5.8</td>
<td>7.9</td>
<td>0.45</td>
<td>1.8</td>
<td>&lt;0.2</td>
<td>1.8</td>
</tr>
<tr>
<td>FeOOH/FeCl(_3)</td>
<td>FeCl(_3)</td>
<td>3</td>
<td>50.5</td>
<td>158</td>
<td>7.1</td>
<td>2.6</td>
<td>1.50</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Bayoxide</td>
<td></td>
<td></td>
<td>52.0</td>
<td>135</td>
<td>7.4</td>
<td>7.8</td>
<td>0.80</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>GEH</td>
<td></td>
<td></td>
<td>54.2</td>
<td>237</td>
<td>7.2</td>
<td>5.2</td>
<td>1.00</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>

\(^1\) Isoelectric point (Fig. S4, Supplementary Material).

\(^2\) Point of zero charge.

\(^3\) Positive surface charge density.

### 3.2 Batch adsorption experiments

Preliminary batch adsorption experiments indicated that all adsorbents tested for Se(VI) uptake resulted in zero efficiency to decrease an initial Se(VI) concentration of 100 μg/L, with adsorbent dose 100 mg/L, pH 7, 20°C and NSF water matrix (Table S2, Supplementary Material). These results revealed that Se(VI) adsorption by FeOOHs is not efficient and the only approach to meet the DWRL of 10 μg/L requires its reduction to Se(IV). Therefore, this study focused on Se(IV) removal.
3.3 Influence of pH on Se(IV) adsorption

Most studies have examined adsorbent efficiency at pH values ranging from 4 to 5, where selenium occurs as an oxy-anion HSeO$_3^-$ / HSeO$_4^-$ (Fig. S5, Supplementary Material) and adsorbents surface are positively charged. This pH range also results in severe water quality degradation. Concerning Se(IV) adsorption by FeOOHs, their adsorption capacity exponential decreased when water pH exceeded values of 7 (Fig. 2), while at pH >10, adsorption capacity neared zero. This data was used for the on-site regeneration of spent adsorbents experiments. However, the results of Fig. 2 indicated that FeOOHs could achieve residual Se concentrations lower than the regulation limit of 10 μg/L when pH was around 7, the value commonly encountered in drinking water, with commercially viable adsorption capacity. The quantification of pH influence on Se(IV) adsorption by FeOOH/2.5 at pH range 6 - 8 is shown by the adsorption isotherms in (Fig. S6, Supplementary Material).

![Fig. 2. Influence of water pH on Se(IV) adsorption by FeOOH/2.5 with initial Se(IV) concentration 500 μg/L, adsorbent dose 100 mg/L, NSF water matrix, T 20°C.](image)

The data showed a better fit to the Freundlich model which was used to calculate adsorption capacity ($Q_{10}$) at equilibrium/residual concentration equal to a DWRL of 10 μg/L (Table 2). The $Q_{10}$ value decreased nearly 10% when water pH increased from 6 to 7, and decreased by one order of magnitude
when pH was raised to 8. The observation that the $Q_{10}$ value reduces as the equilibrium pH increases from 6 to 8 can be attributed to: (a) a gradual decrease in FeOOH positive charge density, (b) predomination of $\text{SeO}_3^{2-}$ in the equilibrium solution relative to the monovalent $\text{HSeO}_3^-$, with the former demanding two active adsorption sites on the oxy-hydroxide surface, (c) predomination of $\text{HPO}_4^{2-}$ relative to $\text{H}_2\text{PO}_4^-$ that also demands two active adsorption sites, and (d) increased concentrations of $\text{OH}^-$ that competes strongly with selenium for adsorption sites.

Table 2. Adsorption data of FeOOH/2.5 for Se(IV) uptake at pH range 6 - 8.

<table>
<thead>
<tr>
<th>Water pH</th>
<th>$Q_{10}$</th>
<th>$K_F$</th>
<th>$n$</th>
<th>$R^2$</th>
<th>$K_L$</th>
<th>$Q_{max}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>3.55</td>
<td>1.1</td>
<td>0.51</td>
<td>0.986</td>
<td>0.0133</td>
<td>23.0</td>
<td>0.960</td>
</tr>
<tr>
<td>7</td>
<td>2.95</td>
<td>0.86</td>
<td>0.53</td>
<td>0.986</td>
<td>0.0081</td>
<td>19.6</td>
<td>0.956</td>
</tr>
<tr>
<td>8</td>
<td>0.33</td>
<td>0.07</td>
<td>0.67</td>
<td>0.989</td>
<td>0.0051</td>
<td>5.1</td>
<td>0.994</td>
</tr>
</tbody>
</table>

3.4 Evaluation of FeOOH adsorption capacity

The efficiency of laboratory synthesized and commercially available FeOOHs for Se(IV) uptake was evaluated using the adsorption isotherm data (Fig. S6, Fig. S7 Supplementary Material). The adsorption data fitted well to both the Freundlich and Langmuir models (Table 3), probably due to the low equilibrium concentrations which were related to partial coverage of adsorption sites. However, it must be clarified that the $Q_{max}$ values resulted from the Langmuir equation are only indicative as they were calculated by extrapolation of the experimental data. These experimental data focused on low residual concentrations in order to better evaluate the $Q_{10}$-values that are required for the implementation of full scale water treatment plants, while no data are available for residual concentrations when adsorbents are in saturated conditions.
The $Q_{10}$ values for Se(IV) uptake were also determined from the adsorption data (Table 3). The FeOOH/2.5 resulted in the highest $Q_{10}$ value, although it had the lowest specific surface area of those examined. Since FeOOH/2.5 showed the best efficiency was the qualified adsorbent of this study. Isotherm data resulted to one of the most important observations of this study which is the strong correlation of adsorption capacity ($Q_{10}$ value) with PSCD of FeOOHs (Fig. 3). Conclusively, this result verifies that the most important parameter in adsorption is the surface charge density and not the specific surface area of the adsorbent.

**Table 3.** Adsorption capacities $Q_{10}$ for FeOOHs at pH 7.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$Q_{10}$ (mg Se(IV)/g)$^\text{ads}$</th>
<th>$K_F$ (mg Se(IV)/g$^\text{ads}$/ (μg/L)$^n$)</th>
<th>$n$</th>
<th>$R^2$</th>
<th>$K_L$ (L/μg Se(IV))</th>
<th>$Q_{\text{max}}$ (mg Se(IV)/g FeOOH)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeOOH/2</td>
<td>2.35</td>
<td>0.48</td>
<td>0.69</td>
<td>0.984</td>
<td>0.0090</td>
<td>24.0</td>
<td>0.989</td>
</tr>
<tr>
<td>FeOOH/2.5</td>
<td>2.95</td>
<td>0.86</td>
<td>0.53</td>
<td>0.986</td>
<td>0.0081</td>
<td>19.6</td>
<td>0.956</td>
</tr>
<tr>
<td>FeOOH/3</td>
<td>2.70</td>
<td>0.75</td>
<td>0.56</td>
<td>0.985</td>
<td>0.0089</td>
<td>23.3</td>
<td>0.962</td>
</tr>
<tr>
<td>FeOOH/4</td>
<td>2.10</td>
<td>0.59</td>
<td>0.55</td>
<td>0.982</td>
<td>0.0166</td>
<td>11.6</td>
<td>0.952</td>
</tr>
<tr>
<td>FeOOH/5.7</td>
<td>1.60</td>
<td>0.31</td>
<td>0.71</td>
<td>0.981</td>
<td>0.0052</td>
<td>23.9</td>
<td>0.971</td>
</tr>
<tr>
<td>FeOOH/8</td>
<td>1.45</td>
<td>0.31</td>
<td>0.68</td>
<td>0.993</td>
<td>0.0159</td>
<td>10.1</td>
<td>0.997</td>
</tr>
<tr>
<td>FeOOH/9</td>
<td>0.95</td>
<td>0.21</td>
<td>0.66</td>
<td>0.976</td>
<td>0.0064</td>
<td>12.2</td>
<td>0.994</td>
</tr>
<tr>
<td>FeOOH/FeCl$_3$</td>
<td>1.60</td>
<td>0.43</td>
<td>0.57</td>
<td>0.996</td>
<td>0.0126</td>
<td>10.7</td>
<td>0.993</td>
</tr>
<tr>
<td>Bayoxide</td>
<td>1.10</td>
<td>0.16</td>
<td>0.85</td>
<td>0.986</td>
<td>0.0039</td>
<td>28.5</td>
<td>0.992</td>
</tr>
<tr>
<td>GEH</td>
<td>1.35</td>
<td>0.34</td>
<td>0.60</td>
<td>0.996</td>
<td>0.0129</td>
<td>12.0</td>
<td>0.989</td>
</tr>
</tbody>
</table>
3.5 Kinetics

One significant adsorption parameter is the uptake rate as derived from contact time. The evaluation of adsorption in relation to contact time for the qualified adsorbent FeOOH/2.5 showed that at least four (4) hours were required to reach 90% removal (Fig. 4). Kinetics data are expressed by the pseudo-second order Equation 1 (Fig. S7, Supplementary Material):

\[
\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}
\]  

(Equation 1)

where \( t \) is the contact time (min), \( Q_t \) is the adsorption capacity at this time (mg/g), \( Q_e \) is the adsorption capacity at equilibrium, and \( k_2 \) is the corresponding pseudo-second order adsorption constant (g/mg-min).
Fig. 4. Kinetics data for Se(IV) adsorption by FeOOH/2.5 in NSF water and pH 7 ($C_o = 1000 \mu g \text{Se(IV)}/L$, FeOOH/2.5 dose 200 mg/L, $C_e = 12 \mu g \text{Se(IV)}/L$, $T = 20^\circ C$).

The fitting parameters $Q_e$ and $k_2$ were estimated to be 4.95 mg/g and 0.0041 g/(mg·min), respectively. Since FeOOH/2.5 consists of porous particles that are vigorously agitated during adsorption, it is reasonable to assume that the uptake rate is not limited by mass transfer from the bulk liquid to the external surfaces of the particles. One might then assume that the rate limiting step may be film or intraparticle diffusion. To verify this assumption the amount of Se(IV) adsorbed, $Q_t$, at time $t$ was plotted (Fig. 4 insert) according to the parabolic diffusion law:

$$Q_t = k_i \cdot t^{1/2}$$  \hspace{1cm} (Equation 2)

The linear portion is attributed to the effect of intraparticle diffusion and the plateau to the equilibrium. The fact that the linear part of the curve does not pass through the origin, indicates that intraparticle diffusion is not the only rate controlling parameter for the adsorption of Se(IV) onto FeOOH/2.5. The $k_i$ value (0.6499 μg mg$^{-1}$ min$^{-1/2}$) was estimated from the slope of the linear portion of the curve (Fig. 7 insert). The significantly high diffusion rate constant at $C_e = 12 \mu g \text{Se(IV)}/L$ indicates the good affinity of Se(IV) with FeOOH/2.5, which may be attributed to sulfate replacement. The $k_i$ value recorded in this research is higher than those recorded for As(V) adsorption by FeOOH/4 (0.55 μg mg$^{-1}$ min$^{-1/2}$ - Tresintsi PhD thesis, 2014a), and Se(IV) adsorption by binary Fe-Mn hydrous oxides (0.542 μg
mg⁻¹ min⁻¹/₂ – Szlachta and Chuba, 2013), and more than double that recorded by Simeonidis et al., 2017 for Sb(III) adsorption by FeOOH/4 (0.26 μg mg⁻¹ min⁻¹/₂).

3.6 Thermodynamic study

The effect of temperature on Se(IV) adsorption was estimated for the qualified adsorbent FeOOH/2.5 at temperature range 278 - 308 K. The type of adsorption process was determined by the thermodynamic parameters Gibbs free energy (ΔG⁰), enthalpy (ΔH⁰) and entropy (ΔS⁰). Gibbs free energy change of the adsorption reaction ΔG⁰ (J/mol) was calculated using Equation 3:

\[ \Delta G^0 = -RT \ln K_{ads} \]

(Equation 3)

where R is the ideal gas constant 8.314 J/mol K, T is the absolute temperature in K, and K_ads is the equilibrium adsorption constant, as approximated by the Langmuir equilibrium constant K₁ (Table 4) determined from the fitting to the respective adsorption isotherms (Fig. S9a, Supplementary Material). Although the setting of the correct distribution coefficient is an ambiguous topic in the literature, the applied K_ads should be just equal to the Langmuir’s constant, when expressed in L/mol, by multiplying L/μg Se with 78.96x10⁶. This is because equilibrium constants become dimensionless after dividing the participating concentration terms by 1 mol/L referring to the definition of the standard state of the substance (the reference point used to calculate its properties under different conditions). ΔH⁰ and ΔS⁰ were calculated using the Van’t Hoff equation (Equation 4):

\[ \ln K_{ads} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \]

(Equation 4)

by plotting ln(K_ads) versus 1/T and calculating ΔH⁰ and ΔS⁰ from the slope and intercept, respectively (Fig. S9b, Supplementary Material). Table 4 presents the isotherms and thermodynamic data at the different adsorption temperatures. The positive ΔH⁰ value of 21.4 kJ/mol indicates an endothermic chemisorption of Se(IV) by FeOOH/2.5, which is also verified by the EXAFS data. Furthermore, the increase of randomness at the adsorbent/solution interface during adsorption is verified by the positive ΔS⁰, while the negative values of ΔG⁰ indicate the spontaneous nature of the Se(IV) adsorption process. The Q₁₀ values revealed the strong influence of temperature between 278 K (Q₁₀ 1.1 mg Se(IV)/g_ads) and 293 K (Q₁₀
2.95 mg Se(IV)/g$_{ads}$, i.e., an increase of adsorption capacity close to 280%, while a further temperature increase to 308 K ($Q_{10}$ 3.6 mg Se(IV)/g$_{ads}$) resulted in a 20% improvement in adsorption capacity.

**Table 4.** Adsorption isotherms and thermodynamic data for Se(IV) adsorption by FeOOH/2.5 at pH 7 and temperature range 278 - 308 K.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$Q_{10}$ mg Se(IV)/g$_{ads}$</th>
<th>$K_F$ mg Se(IV)/g$_{ads}$/ (μg/L)$^n$</th>
<th>$n$</th>
<th>R$^2$</th>
<th>$R$ L/mol Se(IV) mg Se(IV)/g$_{ads}$</th>
<th>$Q_{max}$ mg Se(IV)/g$_{ads}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>278</td>
<td>1.10</td>
<td>0.35</td>
<td>0.50</td>
<td>0.978</td>
<td>268.5x10$^3$</td>
<td>12.6</td>
<td>0.968</td>
</tr>
<tr>
<td>293</td>
<td>2.95</td>
<td>0.86</td>
<td>0.53</td>
<td>0.986</td>
<td>655.3x10$^3$</td>
<td>19.6</td>
<td>0.956</td>
</tr>
<tr>
<td>308</td>
<td>3.60</td>
<td>0.90</td>
<td>0.60</td>
<td>0.982</td>
<td>742.2x10$^3$</td>
<td>20.2</td>
<td>0.952</td>
</tr>
</tbody>
</table>

**Thermodynamic parameters**

<table>
<thead>
<tr>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>$\Delta S^\circ$ (J/mol*K)</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.4</td>
<td>183</td>
<td>278 K 293 K 308 K</td>
</tr>
</tbody>
</table>

-28.9  -32.6  -34.6

**3.7 Column Experiments**

The adsorption of SeO$_3^{2-}$ and SeO$_4^{2-}$ ions was also evaluated in rapid small-scale column tests (RSSCTs) (Fig. 5). The resulting adsorption capacities ($Q_{10}$) at residual concentration equal to a DWRL of 10 μg/L are shown in Table 5. Contrary to the adsorption isotherm results, the FeOOHs in column configuration achieved residual Se(VI) concentrations below the DWRL. However, the $Q_{10}$ values recorded ranged from 0.0 (for Bayoxide) to 17 μg Se(VI)/g (for FeOOH/2), and are therefore considered not suitable for commercial use. In contrast, the $Q_{10}$ values for Se(IV) were almost three orders of magnitude greater
than those observed for Se(VI), ranging between 0.7 mg Se(IV)/g for GEH and 4.3 mg Se(IV)/g for FeOOH/2.5. The adsorption capacities of FeOOH/2 (3.5 mg Se(IV)/g), FeOOH/2.5 (4.3 mg Se(IV)/g), and FeOOH/5.7 (3.5 mg Se(IV)/g), are considered commercially exploitable. The $Q_{10}$ values recorded in the RSSCTs (Table 5) are generally higher than their corresponding batch experiment values (Table 3). This can be attributed to the better exploitation of intraparticle adsorption sites since the RSSCTs were run for over two months.

![Fig. 5. Breakthrough curves of: (a) Se(VI), and (b) Se(IV) adsorption by FeOOHs in RSSCTs (initial concentrations: 50 μg Se(VI)/L and 100 μg Se(IV)/L, NSF water matrix, pH = 7, T = 20°C, EBCT = 3.5 ± 0.5 min).](image)

**Table 5.** Adsorption capacities ($Q_{10}$) of FeOOHs for Se(VI) and Se(IV) removal in RSSCTs.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Bulk Density (g/mL)</th>
<th>$Q_{10}$ Se(VI) (μg Se(VI)/g$_{ads}$)</th>
<th>$Q_{10}$ Se(IV) (mg Se(IV)/g$_{ads}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeOOH/2</td>
<td>0.54</td>
<td>17.0</td>
<td>3.5</td>
</tr>
<tr>
<td>FeOOH/2.5</td>
<td>0.46</td>
<td>10.0</td>
<td>4.3</td>
</tr>
<tr>
<td>FeOOH/3</td>
<td>0.49</td>
<td>4.4</td>
<td>2.5</td>
</tr>
<tr>
<td>FeOOH/4</td>
<td>0.54</td>
<td>1.6</td>
<td>2.3</td>
</tr>
<tr>
<td>FeOOH/5.7</td>
<td>0.49</td>
<td>4.0</td>
<td>3.6</td>
</tr>
<tr>
<td>FeOOH/8</td>
<td>0.48</td>
<td>1.4</td>
<td>2.7</td>
</tr>
</tbody>
</table>
Fig. 6 shows results of the correlation of $Q_{10}$ values with PSCD. The adsorption capacity is primarily related to PSCD, while influenced by both molecular structure and bulk density, since in fixed bed adsorption the adsorbent particle size ranged from 0.25 mm to 0.50 mm. The lower $Q_{10}$ value (0.7 mg Se(IV)/g) recorded for GEH in RSSCTs compared to batch experiments (1.35 mg Se(IV)/g) where a particle size <63 μm was used, is related to the high bulk density of GEH (Table 5). This results in low intraparticle porosity and hinders the approximation of SeO$_3^{2-}$ anions to adsorption sites due to the lower diffusion rate.

FeOOHs with low bulk densities (0.5 ± 0.1 g/mL) presented a different correlation to PSCD, as shown by the slope of correlation lines (Fig. 6). This observation is possibly related to molecular structure. The structural sulfates of FeOOH/2, FeOOH/2.5, FeOOH/3 and FeOOH/4 (Table 1) somehow prevent the SeO$_3^{2-}$ anion from accessing adsorption sites, thus resulting in lower correlation between $Q_{10}$ value and PSCD ($Q_{10} = 2.1\cdot\text{PSCD} - 2.4$) compared to that of FeOOH/5.7, FeOOH/5 and Bayoxide, which do not incorporate structural sulfates ($Q_{10} = 3\cdot\text{PSCD} - 0.6$). FeOOH/5.7 presented the highest ratio:

$$Q_{10 \over \text{PSCD}} = \frac{3.6}{1.42} = 2.53$$  \hspace{1cm} (Equation 5)

This high ratio is attributed to the significant percentage of chemically sorbed sulfates (3.7 wt. %, Table 1) and absence of structural ones, which favors the exploitation of a higher percentage of adsorption sites.

<table>
<thead>
<tr>
<th>Material</th>
<th>$Q_{10}$</th>
<th>PSCD</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bayoxide</td>
<td>0.41</td>
<td>0.0</td>
<td>3.1</td>
</tr>
<tr>
<td>GEH</td>
<td>1.28</td>
<td>4.0</td>
<td>0.7</td>
</tr>
</tbody>
</table>

![Graph showing correlation between $Q_{10}$ and PSCD](image)
Fig. 6. Correlation of positive surface charge density of FeOOHs with adsorption capacities for Se(IV) ($Q_{10}$ values) in RSSCTs. (Solid circles (●) indicate FeOOHs with structural sulfates and solid squares (●) indicate FeOOHs without structural sulfates).

At the end of the RSSCT experiments the spent adsorbents were subjected to leaching tests according to TCLP and EN 12457 protocols. The results indicated that all spent adsorbents could be treated as non-hazardous wastes according to the TCLP protocol, while according to the EN 12457 protocol they could be treated as either non-hazardous wastes (FeOOH/2.5, FeOOH/5.7, FeOOH/8) or inert wastes (FeOOH/2, FeOOH/3, FeOOH/4, Bayoxide, GEH) (Table 6).

Table 6. Leaching characteristics of spent adsorbents in RSSCT experiments.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity, mg Se(IV)/g</th>
<th>EN12457-01 $Q_{10}$</th>
<th>End of RSSCTs</th>
<th>TCLP $^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mg Se(IV)/kg</td>
<td>mg Se(IV)/L</td>
<td></td>
</tr>
<tr>
<td>FeOOH/2</td>
<td>3.5</td>
<td>4.9</td>
<td>0.4</td>
<td>0.042</td>
</tr>
<tr>
<td>FeOOH/2.5</td>
<td>4.3</td>
<td>8.1</td>
<td>1.9</td>
<td>0.055</td>
</tr>
<tr>
<td>FeOOH/3</td>
<td>2.5</td>
<td>4.4</td>
<td>0.4</td>
<td>0.090</td>
</tr>
<tr>
<td>FeOOH/4</td>
<td>2.3</td>
<td>3.9</td>
<td>0.3</td>
<td>0.033</td>
</tr>
<tr>
<td>FeOOH/5.7</td>
<td>3.6</td>
<td>4.4</td>
<td>1.8</td>
<td>0.089</td>
</tr>
<tr>
<td>FeOOH/8</td>
<td>2.7</td>
<td>3.7</td>
<td>1.1</td>
<td>0.047</td>
</tr>
<tr>
<td>Bayoxide</td>
<td>1.7</td>
<td>3.9</td>
<td>0.5</td>
<td>0.033</td>
</tr>
<tr>
<td>GEH</td>
<td>0.7</td>
<td>1.5</td>
<td>0.1</td>
<td>0.022</td>
</tr>
</tbody>
</table>

$^1$ Limit for inert wastes = 0.5 mg/kg, Limit for non-hazardous wastes = 2 mg/kg.

$^2$ Limit for non-hazardous wastes = 5 mg/L.
3.8 Mechanism of selenite adsorption

To identify the oxidation state of selenium, XANES spectroscopy at the Se-K-edge was implemented, since the white line that accounts for the 1s→4p transition is well-known to vary as a function of valence (Qin et al., 2017; Schwartz et al., 2016). The Se-K-XANES spectra of saturated FeOOH/2.5 (19 mg Se(IV)/g FeOOH/2.5) and FeOOH/8 (25 mg Se(IV)/g FeOOH/8) samples and the Na₂SeO₃ reference are shown in Fig. 7. To identify the oxidation state of Se, the typical analysis based on the edge position is followed, using the maximum of the first derivative. It was found that in the studied samples the absorption edge position lies at 12647.6 – 12647.8 ± 0.5 eV, i.e., in the same position as the reference Na₂SeO₃ (12647.9 ± 0.5 eV). Thus, independent of the amount of Se adsorbed and the pH synthesis of the adsorbent, only Se(IV) was detected.

The influence of the synthesis parameters on selenite-adsorption capacity was investigated using EXAFS measurements at the Se-K-edge. The Fourier Transforms (FTs) of the $k^3 \chi(k)$ EXAFS spectra of the studied samples are shown in Fig. 7b. The fitting was performed assuming that in the 1\textsuperscript{st} nn shell, Se(IV) forms a trigonal pyramid and bonds to three oxygen atoms. In the Fe-comprised shell, it was assumed that the selenite oxyanions are involved in bidentate mononuclear (1\textsuperscript{E}) and two types of binuclear inner-sphere complexation (2\textsuperscript{C}) with surface Fe(O, OH)₆ octahedra. In particular, chemisorption by the formation of 2\textsuperscript{C} geometries is realized by either Se(IV) bonding to double oxygen sites of edge sharing Fe-octahedra (1\textsuperscript{st} type, inset of Fig. 7b) or Se(IV) linkage to two oxygen atoms (2\textsuperscript{nd} type) that belong to corner-sharing Fe surface octahedra (2\textsuperscript{nd} type, inset of Fig. 7b). Results of the EXAFS analysis are presented in Table S3 (Supplementary Material).
Fig. 7. (a) Se-K-edge XANES spectra of the studied samples and reference Na$_2$SeO$_3$. (b) Fourier Transforms (FT) of the $k^3 \chi(k)$ Se-K-edge EXAFS spectra of the studied samples. The fitting and the experimental curves are shown in colored and black solid lines, respectively.

According to the EXAFS analysis results, Se(IV) is involved in three types of surface complexes. In particular, bidentate mononuclear edge-sharing ($^1E$) linkage exists between the SeO$_3^{2-}$ pyramids and the Fe(O,OH)$_6$ octahedra, while SeO$_3^{2-}$ also adsorbs to two corner oxygen sites that belong to either edge- or corner-sharing Fe-octahedra. In both samples, the Se-O bond length was found equal to 0.169 - 0.170 (± 0.001) nm, consistent with the trigonal pyramidal coordination of Se(IV) (Eklund and Persson, 2014). In the bidentate mononuclear ($^1E$) complexes, Fe is located at 0.219 - 0.220 (± 0.002) nm from the sorbed Se(IV), while for the two different types of bidentate binuclear ($^2C$) geometries, the respective Se-Fe distances are found equal to 0.286 - 0.292 (± 0.003) nm and 0.330 - 0.331 (± 0.004) nm, respectively (Missana et al., 2009). Nevertheless, the type of Se(IV) adsorption geometries and sorption mode onto the FeOOH are strongly affected by the synthesis pH. More specifically, as Table S3 (Supplementary Material) shows, although in both samples approximately half of the Se(IV) oxyanions form both $^1E$ and $^2C$
inner sphere complexes, major differences are detected in the number of Se(IV) that belong to the two types of bidentate binuclear sphere configuration. Indeed, at FeOOH/2.5, only 12.8 (± 3.0) at% of the SeO$_4^{2-}$ pyramids link to oxygen atoms that belong to corner sharing Fe-octahedra, while for FeOOH/8 this type of geometry accounts for 37.2 (± 7.0) at% of the SeO$_4^{2-}$. The preferential sorption of SeO$_4^{2-}$ by forming 2C inner sphere complexes with corner-rather than edge-sharing Fe-centered polyhedra of the surface upon increasing pH, can be related to the different nanostructure of the adsorbent. More specifically, the presence of structural sulfates in FeOOH/2.5 could possibly inhibit SeO$_4^{2-}$ anion to approach the oxygen sites of corner-sharing Fe-octahedra. On the other hand, in the FeOOH/8 sample, the dominant phase detected is lepidocrocite, a layer structure that permits the linkage of SeO$_4^{2-}$ with oxygen sites of both corner- and edge-sharing Fe-octahedra. The observation that structural sulfates may interfere in the mechanism of Se(IV) adsorption as shown by the EXAFS study, confirms the aforementioned results derived from the correlation of PSCD to Se(IV) adsorption onto FeOOHs.

3.9 Regeneration of FeOOH/5.7

On-site regeneration of adsorbents is crucial for economic reasons. The study of pH influence on Se(IV) adsorption showed adsorption capacity nears zero when pH values exceed 10 (Fig. 2). Based on this information the regeneration of FeOOH/5.7 was achieved by pumping an up-flow of 600 mL/h of 0.02 N NaOH solution (pH = 12 ± 0.5). The regeneration results are shown in (Fig. S10, Supplementary Material) and indicated that at 3.5 h (Fig. S10a, Supplementary Material) the regeneration process was completed by spending approximately 110 bed volumes of NaOH solution (Fig. S10b, Supplementary Material). The leachate was treated following the method of Geoffroy and Demopoulos 2009 and >99% Se(IV) was separated as elemental selenium.

The regenerated FeOOH/5.7 column was re-used for Se(IV) removal under the same RSSCT conditions described in section 2.5. Use of the regenerated FeOOH/5.7 also produced residual concentrations significantly lower than the DWRL of 10 μg/L (Fig. 8), however the Q$_{10}$ value was lower (2.6 mg Se(IV)/g) than that of the fresh adsorbent (3.6 mg Se(IV)/g). The mass balance of Se(IV) in the
regeneration process, along with the determination of residual Se(IV) in the regenerated FeOOH/5.7 sample, revealed that $1.1 \pm 0.1$ mg Se(IV)/g remained in the FeOOH/5.7 sample, which explains the efficiency loss. These results are in accordance with those of arsenic regeneration (Tresintsi et al., 2014c). However, taking into account the installation and operational expenses for the regeneration process and the 25% decreased efficiency of regenerated FeOOH ($Q_{10}$-value), the cost of Se(IV) removal decreases by at least 50% when the regeneration process is applied.

4. Conclusions

The present study focused on selenium removal from natural waters at residual concentration below the EU drinking water regulation limit (DWRL) of 10 μg/L using FeOOHs synthesized at various conditions. The experimental results revealed that the positive charge surface density (PSCD) of the FeOOHs was increased by lowering synthesis pH to a value up to 2.5, due to the increasing of sulfate adsorption onto the Stern layer (synthesis pH < 8), which are ion-exchangeable and contribute to increased PSCD.

The batch experiments showed that FeOOHs are not effective for Se(VI) adsorption at concentrations lower than 100 μg/L. FeOOHs adsorption capacity ($Q_{10}$ value) for Se(IV) is strongly
correlated with PSCD, while declines exponentially when pH values exceed 7. The positive ΔH° value of 21.4 kJ/mol indicates an endothermic chemisorption of Se(IV) by FeOOH/2.5, a result that was also verified by the EXAFS data.

The RSSCTs showed that Q_{10} values for Se(IV) were almost three orders of magnitude greater than those of Se(VI) and higher than those of batch reactor experiments for Se(IV), which is attributed to better exploitation of intraparticle adsorption sites since the RSSCTs ran for more than two months. The correlation observed between Q_{10} value and PSCD is reversely influenced by FeOOHs bulk density and structural sulfates that hinder the exploitability of adsorption sites. The Q_{10} value of the qualified FeOOH/2.5 for Se(IV) recorded in these experiments is 2.5 times higher than that of the commercial FeOOH Bayoxide, and six times higher than that of the commercial FeOOH GEH, while the effective regeneration of FeOOHs significantly decreases operational costs for Se(IV) removal.

Conclusively, the Q_{10} values of FeOOH/2 (3.5 mg Se(IV)/g), FeOOH/2.5 (4.3 mg Se(IV)/g) and FeOOH/5.7 (3.5 mg Se(IV)/g) deem these three iron oxy-hydroxides suitable for commercial exploitation.

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References


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Graphical abstract
**Highlights**

- Strong correlation between the PSCD of FeOOHs and $Q_{10}$ value for Se(IV).
- Three orders of magnitude greater $Q_{10}$ values for Se(IV) in comparison to Se(VI).
- Sulfates adsorbed on Stern layer contribute to PSCD and increase $Q_{10}$ value for Se(IV).
- Structural sulfates of FeOOHs hinder Se(IV) adsorption.
- Se(IV) is chemisorbed involving $^1E$ and $^2C$ linkage between the SeO$_3^{2-}$ and FeOOH.
Figure 1
Figure 2

Graph showing the relationship between $C_{e,\text{Se(IV)}}$ (µg/L) and equilibrium pH.
Figure 3

The graph shows a linear relationship between the quantity of Se(IV) adsorbed, $Q_{10, \text{mg Se(IV)}}/g_{\text{ads}}$, and the PSCD, mmol[OH$^{-}$]/g. The equation of the line is given by:

$$y = 0.739x + 0.56$$

with a correlation coefficient of $R^2 = 0.941$.
Figure 4

\[
Q = \frac{0.1026t}{1 + 0.0174t}
\]

\[
Q = 0.6499t^{1/2} - 2.7878
\]
Figure 5
Figure 6

- Teal line: $y = 2.1x - 2.4$, $R^2 = 0.982$
- Orange line: $y = 3x - 0.6$, $R^2 = 0.975$

$Q_{10}^*$, mg Se(IV)/g$_{ads}$ vs. PSCD, mmol [OH$^-$]/g
Figure 7