

Mechanisms of selenium removal by partially oxidized magnetite nanoparticles for waste water remediation

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1 **MANUSCRIPT**

2 **Selenite and selenate adsorption mechanisms on**
3 **partially oxidized magnetite nanoparticles**

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15 **Keywords:** selenium, oxyanions, Se(IV), Se(VI), iron oxides, maghemite, immobilization,
16 retention, remediation, XPS, XAFS, XANES, EXAFS

17 **Environmental Significance Statement** (max. 120 words)

18 Affordable and easy-to-produce nanoparticles are widely used in wastewater treatment
19 applications. The mixed-valence iron oxide mineral magnetite has emerged as suitable material
20 for the remediation of contaminated wastewaters due to its magnetic properties and high
21 reactivity. Since the physicochemical properties of magnetite are strongly influenced by
22 oxidation, however, the retention behavior of nanoparticulate magnetite can change
23 substantially in natural environments. In this study, we explore the retention efficiency and
24 capacity of partially oxidized magnetite nanoparticles with respect to dissolved selenium
25 oxyanions and illustrate the effective adsorption mechanisms. The obtained results significantly
26 contribute to the understanding of the retention behavior of selenium oxyanions in contact with
27 nanoparticulate magnetite/maghemite phases in oxic environments typical for waste water
28 treatment.

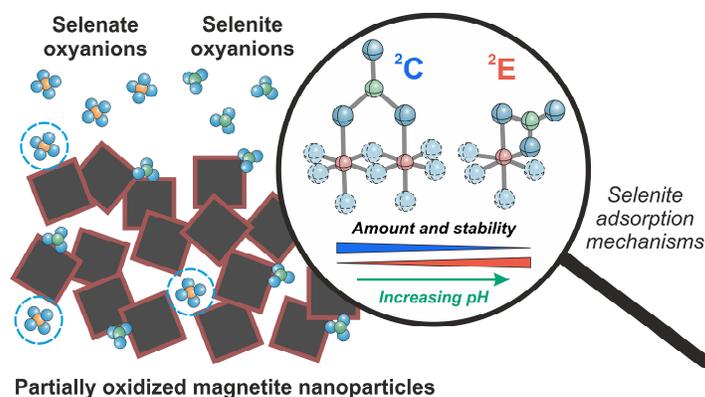
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30 Abstract

31 Magnetite nanoparticles are a promising cost-effective material for the remediation of polluted
32 wastewaters. Due to their magnetic properties and their high adsorption and reduction potential,
33 they are particularly suitable for the decontamination of oxyanion-forming contaminants,
34 including the highly mobile selenium oxyanions selenite and selenate. However, little is known
35 how in field applications the remediation efficiency of magnetite nanoparticles is affected by
36 partial oxidation and the formation of magnetite/maghemite phases. Here we characterize the
37 retention mechanisms and capacity of partially oxidized nanoparticulate magnetite for selenite
38 and selenate at different pH conditions and ionic strengths. Selenate was retained only under
39 acidic conditions and strongly influenced by competing chloride anions, indicative of outer-
40 sphere adsorption. Although the adsorption of selenite was also adversely affected by increasing
41 pH, substantial quantities were retained even at alkaline conditions. Using spectroscopic
42 analyses (XPS, XAFS), both mononuclear edge-sharing (${}^2\text{E}$) and binuclear corner-sharing (${}^2\text{C}$)
43 inner-sphere selenite surface complexes could be identified, while reduction to Se(0) or Se(-II)
44 species could be excluded. Under favorable adsorption conditions up to pH ~ 8 , the affinity of
45 selenite to form ${}^2\text{C}$ surface complexes is higher, whereas at alkaline pH values and less
46 favorable adsorption conditions ${}^2\text{E}$ complexes prevail. Our results demonstrate that magnetite
47 can be used as a suitable reactant for the immobilization of selenium as selenite in remedial
48 applications, even under oxic conditions and without the involvement of reduction processes.

49 Graphical abstract

50 This article provides new insights into the retention behavior of partially oxidized magnetite
51 nanoparticles in contact with selenium oxyanions under oxic conditions



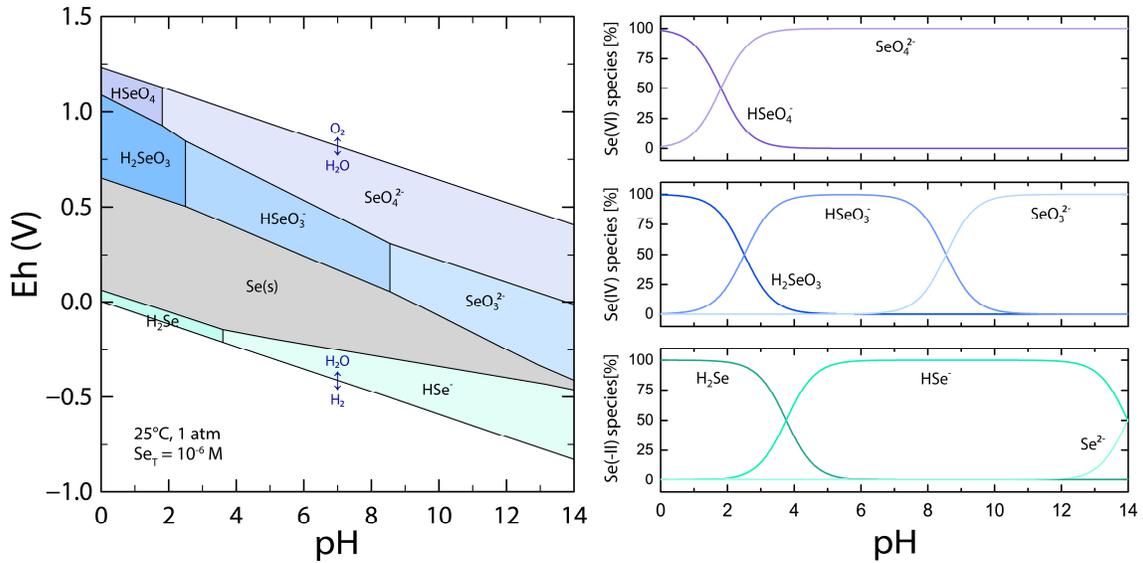
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53 1 Introduction

54 Selenium (Se) pollution of soils, sediments and waters is a global phenomenon. Although Se is
55 a naturally occurring trace element, the major cause of Se release and contamination are human
56 activities such as coal production and combustion, phosphate and sulfide-ore mining, metal
57 processing, oil refining, waste disposal or agricultural irrigation (Dhillon and Dhillon, 2003;
58 Lemly, 2004; Tan et al., 2016). Additionally, Se occurs in vitrified high-level nuclear waste
59 (HLW) in the form of the long-lived, harmful radionuclide ^{79}Se and plays a major role in the
60 long-term safety assessment of HLW repositories (Frechou et al., 2007; De Cannière et al.,
61 2010; Bingham et al., 2011).

62 In aquatic systems, Se levels can rapidly become toxic endangering not only the health of
63 aquatic organisms but also of other beings, including humans, due to bioaccumulation in the
64 food chain (Munier-Lamy et al., 2007; Lenz and Lens, 2009). Mobility and bioavailability of
65 Se in water is mainly controlled by its solubility and retention through (bio)chemical processes
66 (Dhillon and Dhillon, 2003; Fernández-Martínez and Charlet, 2009), which are largely
67 determined by the prevailing Se oxidation state and related chemical speciation. Under reducing
68 conditions, Se forms sparingly soluble minerals and compounds, primarily elemental selenium
69 (Se^0) and metal selenides ($\text{Se}(\text{I})$ and $\text{Se}(\text{II})$) (ESI Fig. A.1). Under (sub)oxic conditions,
70 however, inorganic Se occurs in the oxidation state $\text{Se}(\text{IV})$ and $\text{Se}(\text{VI})$ as highly soluble and
71 mobile oxyanions selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}). Both selenite and selenate form
72 protonated and deprotonated species depending on the solution pH (Fig. 1).

73 A key factor controlling the fate of dissolved Se oxyanions in aquatic environments is sorption
74 on geological materials. Of special relevance in this context are metal (hydr)oxides and
75 particularly iron (hydr)oxides due to their high affinity towards oxyanion-forming pollutants
76 such as Se, As, Sb, V, Mo or Cr (Chan et al., 2009; Nakamaru and Altansuvd, 2014; Börsig et
77 al., 2017; Weidner and Ciesielczyk, 2019). Besides adsorption, reduction of oxyanions to less
78 soluble compounds is an important abiotic immobilization process (Wilkin et al., 2005; Kirsch
79 et al., 2008; Scheinost et al., 2008), driven by Fe^0 or by $\text{Fe}(\text{II})$ -bearing iron (hydr)oxides, yet
80 depends strongly on the prevailing redox conditions.

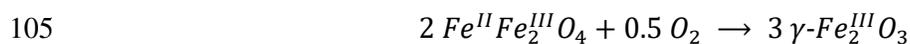


81

82 **Fig. 1:** (Left) Eh-pH diagram for the system Se-H₂O at 25°C and 1 atm; Se_{total} : 10⁻⁶ mol/L. (Right) Stability and
 83 distribution of dissolved Se(-II), Se(IV), and Se(VI) species as a function of pH. Diagrams were calculated
 84 with PHREEQC (USGS) using an adapted *wateq4f* database; thermodynamic Se data: aquatic species [Séby
 85 et al., 2001], solid phases [Salah and Wang, 2014].

86 Magnetite [Fe₃O₄] is one of the most widespread iron (hydr)oxide minerals in nature and is also
 87 known as a sink for dissolved oxyanions due to its high adsorption and reduction potential. Due
 88 to these properties and its magnetic character, which permits an easy separation of magnetite
 89 and associated contaminants from the waste water stream, the use of magnetite is considered in
 90 various in-situ and ex-situ environmental remediation approaches, including wastewater
 91 treatment or soil remediation [Kuppusamy et al., 2016; Usman et al., 2018]. Particularly for
 92 decontamination of wastewaters based on the removal of hazardous oxyanions by nano-
 93 remediation, nanoparticulate magnetite is a promising cost-effective material [Chowdhury and
 94 Yanful, 2010; Horst et al., 2015; Li et al., 2017], as shown by several previous studies [Martínez
 95 et al., 2006; Scheinost and Charlet, 2008; Loyo et al., 2008; Jordan et al., 2009; Missana et al.,
 96 2009; Usman et al., 2018].

97 For field applications, however, it must be taken into account that reactivity and capacity of a
 98 remediation material is highly dependent on its stability under various environmental
 99 conditions. This applies in particular for redox- and pH-sensitive minerals such as magnetite
 100 and other reduced or mixed-valent iron minerals like zerovalent iron (ZVI) and green rust
 101 [Génin et al., 2006; Liu et al., 2014; Mu et al., 2017; Börsig et al., 2018]. A common
 102 phenomenon for magnetite is thereby the transformation into maghemite [γ -Fe₂O₃] under oxic
 103 conditions [ESI Fig. A.1] due to surface oxidation [Rebodos and Vikesland, 2010;
 104 Schwaminger et al., 2017].



106 Maghemite is the Fe(II)-free oxidation product of magnetite and both minerals represent the
107 end members of a solid solution series (Iwatsuki and Fukasawa, 1993; Gorski and Scherer,
108 2010). In case of larger magnetite crystals, oxidation of the mineral surface can result in the
109 formation of a passivating layer of maghemite that protects the underlying magnetite from
110 further oxidation (He and Traina, 2005; Rebodos and Vikesland, 2010; Khan et al., 2015). By
111 contrast, magnetite nanoparticles produced by chemical synthesis usually consist of both
112 magnetite and maghemite with a higher proportion of maghemite in the near-surface region
113 (Kuhn et al., 2002; Signorini et al., 2003; Sharifi Dehsari et al., 2018).

114 In order to assess the efficiency of magnetite for remediation measures, it is therefore important
115 to know to what extent oxidation and formation of a mixed magnetite/maghemite phase affects
116 the retention of pollutants, particularly in terms of the specific mechanisms. The aim of this
117 paper was therefore to characterize the retention efficiency of partially oxidized magnetite with
118 respect to dissolved Se oxyanions. For this, we examined the interaction of selenite and selenate
119 with pre-oxidized magnetite in adsorption experiments at various hydrochemical conditions,
120 including pH and ionic strength. By using hydrochemical data and a combination of solids
121 analysis, we were able to determine the Se retention capacity and stability as well as the
122 involved immobilization mechanisms.

123 2 Materials and Methods

124 2.1 Synthesis of magnetite

125 Magnetite (Mt) was synthesized in the laboratory by progressively oxidizing an aquatic Fe^{2+}
126 solution under alkaline pH conditions (ESI Fig. A.2). A detailed description of the synthesis
127 procedure, the sample preparation as well as of the characterization of the final product can be
128 found in Börsig et al. (2018). In short, 5 g $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$ were dissolved in 500 ml N_2 -degassed
129 Milli-Q water. After adding 55 mL 1 M KOH and 25 mL 1 M NaHCO_3 solution, blueish green
130 colored iron(II) hydroxide precipitated. Continuous stirring resulted in the progressive
131 oxidation of the initial anoxic system by atmospheric oxygen, causing the transformation of
132 iron(II) hydroxide into black magnetite within 48 hours. With approximately 2 g of magnetite
133 formed, the mass to volume ratio (m/V) during synthesis was about 3.4 g/L and the final pH
134 was around 9.2. After synthesis, the magnetite phase was decanted, centrifuged and washed
135 three times with Milli-Q water. After drying at 40°C , the synthesized particles were ground
136 with an agate mortar and stored for analysis and adsorption experiments.

137 XRD analysis of the synthesis product proved the formation of magnetite [Fe₃O₄] without any
138 indication of additional iron (hydr)oxide phases. According to SEM characterization, the
139 magnetite consisted of aggregated particles with a single-particle size of about 50 nm. A
140 specific surface area of 32 m²/g was determined by BET analysis, consistent with literature
141 values (Cornell and Schwertmann, 2003; Salazar Camacho and Villalobos Peñalosa, 2017).
142 XPS analysis and the evaluation of the Fe 2p_{3/2} spectra, however, showed that the Fe(II) to
143 Fe_{total} ratio was only 0.14 (±5%) at the surface and therefore lower than the expected ratio of
144 0.33 for stoichiometric Fe₃O₄. Note that the information depth of the Fe 2p_{3/2} elemental line of
145 magnetite was calculated with 2.2 nm (see ESI). This indicated that the synthesized magnetite
146 was partially oxidized and that the near-surface region of these particles may consist of both
147 magnetite and maghemite.

148 2.2 Adsorption experiments

149 Adsorption of selenite and selenate with this pre-oxidized magnetite was studied in batch
150 experiments under oxic conditions. The experimental setup was almost identical to the
151 conditions at the end of the magnetite synthesis. To investigate selenite and selenate adsorption
152 as a function of the Se concentrations, 50 ml 0.01 M KCl solution that contained distinct
153 volumes of Se stock solution was added to 170.0 mg of washed magnetite powder (m/V ratio
154 = 3.4 g/L). The Se stock solutions were prepared by dissolving defined quantities of Na₂SeO₃
155 or Na₂SeO₄ · 10 H₂O in N₂-degassed Milli-Q water. The added volumes were calculated to
156 obtain initial selenite or selenate concentrations of 10⁻⁵ - 10⁻² mol/L. KCl was used as
157 background electrolyte since also the original synthesis took place in such conditions and to
158 simulate solutions with higher ionic strengths. After mixing, the pH was adjusted to 9.2 by
159 dropwise addition of KOH solution. The 50 mL flasks were sealed and shaken for 48 hours to
160 ensure that adsorption equilibrium was achieved. Due to the strong buffer capacity of magnetite,
161 pH was checked after 24 and 45 hours and if necessary readjusted to pH 9.2. Afterwards, the
162 residual Se concentration in solution was analyzed and the solids were dried at 40°C both with
163 and without prior washing.

164 In addition, similar batch experiments were carried out to study the influence of pH and ionic
165 strength. While selenite or selenate concentration was kept constant (10⁻⁴ mol/L), different ionic
166 strengths of 0.01 M KCl or 0.14 M KCl were tested and pH values were adjusted in the range
167 of 2 to 14 using either HCl or KOH solution.

168 2.3 Analytical techniques

169 Dissolved Se and Fe concentrations were determined by Inductively-Coupled Plasma Optical
170 Emission Spectrometry (ICP-OES; Varian 715ES) or Inductively-Coupled Plasma Mass
171 Spectrometry (ICP-MS; X-Series 2, Thermo Fisher Scientific Inc.) depending on the solution
172 concentrations. X-Ray Diffraction (XRD) for analysis of the mineral composition was
173 performed on a Bruker D8 Advance X-ray diffractometer (Cu K α). The total Se content of the
174 solid phases was determined by polarized Energy Dispersive X-ray Fluorescence Spectroscopy
175 (pEDXRF) with an Epsilon 5 (PANalytical). Electron microscopy with Energy Dispersive X-
176 ray Spectroscopy (EDX) was used to characterize the solid phases. Images were recorded using
177 a LEO 1530 (Zeiss Inc.) Scanning Electron Microscope (SEM) with a NORAN System SIX
178 (Thermo Electron Corp.) EDX-System. To examine oxidation states and to identify elemental
179 composition of the surface area, X-ray Photoelectron Spectroscopy (XPS) measurements were
180 performed using a PHI 5000 VersaProbe II (ULVAC-PHI, Inc.). Detailed information about
181 measurement parameters, sample preparation and data evaluation are described in the [ESI](#).

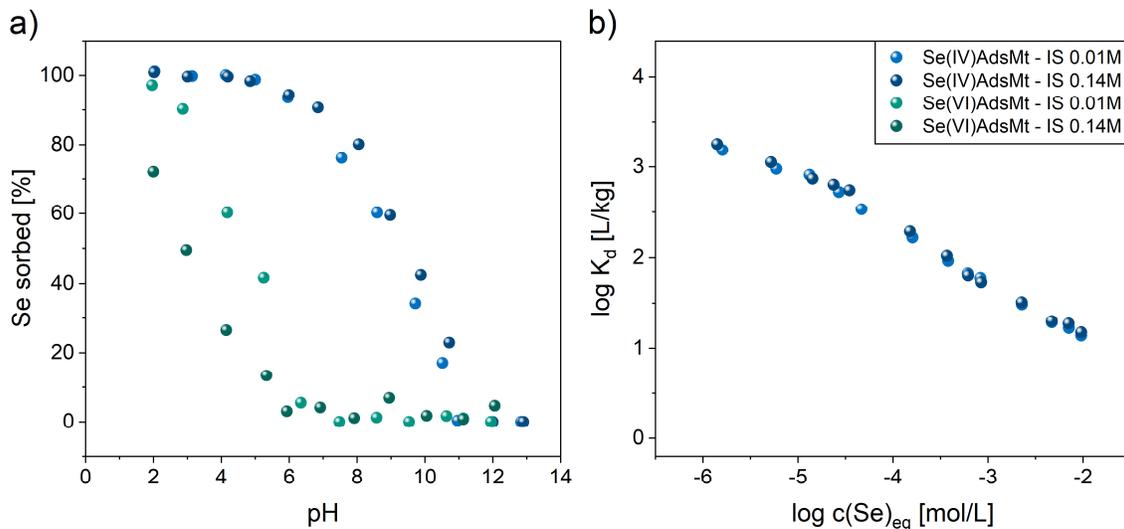
182 X-ray absorption spectroscopy was carried out on selected samples to identify the Se oxidation
183 state, coordination as well as the molecular short-range structure. Se K-edge X-ray Absorption
184 Fine Structure (XAFS) spectra were collected at The Rossendorf Beamline (ROBL) at ESRF
185 (Grenoble, France). Measurement parameters and sample preparation are described in detail in
186 the [ESI](#). Fluorescence deadtime correction, energy calibration and averaging of scans was
187 performed with the software package SixPack {Webb, 2005 #609}([www.sams-
188 xrays.com/sixpack](http://www.sams-xrays.com/sixpack)), while normalization and extraction of the EXAFS chi function was
189 performed with the software WinXAS according to standard procedures [\(Ressler, 1998\)](#). The
190 k^3 -weighted EXAFS data were fit using theoretical back-scattering amplitudes and phase shifts
191 calculated with FEFF 8.2 [\(Ankudinov and Rehr, 1997\)](#). Statistical analysis of spectra was
192 performed with the ITFA program package [\(Rossberg et al., 2003\)](#). Spectra of Se reference
193 samples were taken from [Scheinost and Charlet \(2008\)](#).

194 3 Results and Discussion

195 3.1 Adsorption capacity of oxidized magnetite for selenite and selenate

196 [Fig. 2a](#) shows the adsorption capacity of magnetite for selenite and selenate under oxic
197 conditions as a function of pH and ionic strength. The results demonstrate that the adsorption
198 behavior is primarily affected by the Se species. Selenate is only immobilized under extreme
199 acidic conditions, with about 50% of selenite adsorbed at pH 3. Contrary to selenate, the entire

200 initial selenite amount is immobilized at low pH ($< \text{pH } 5$) and the adsorption edge extends over
 201 a wide pH range from weakly acidic to alkaline (pH 6–11) conditions. Furthermore, while the
 202 adsorption edge of selenate shifts towards lower pH values (~ 1.5 pH unit) in the presence of
 203 higher KCl concentrations, retention of selenite is not affected by higher ionic strengths. Further
 204 confirmation for this observation can also be seen in Fig. 2b, which shows the distribution
 205 coefficient (K_d) as a function of the selenite equilibrium concentration at pH 9.2. With
 206 increasing concentrations of dissolved Se, $\log K_d$ values decrease steadily but are identical for
 207 both ionic strengths. The absolute K_d values are furthermore quite high ($\log K_d$: 3.2–1.2 L/kg)
 208 and correspond to Se surface coverages in the range of 0.05 to 2.5 at/nm^2 . Unlike selenite, the
 209 adsorption of selenate was too low to obtain reliable K_d data at pH 9.2.



210

211 **Fig. 2:** (Left) Selenite and selenate adsorption on magnetite (Mt) depending on pH and ionic strength (IS) at
 212 initial Se concentrations of 10^{-4} mol/L. (Right) Uptake of selenite by magnetite at pH 9.2 as a function of the
 213 Se equilibrium concentration.

214 The observed adsorption behavior is consistent with the literature. Adsorption capacities of iron
 215 (hydr)oxides for anions such as selenite and selenate decrease with increasing pH as the amount
 216 of positively charged surface groups declines by deprotonation. Since in particular the single-
 217 protonated Se species (HSeO_3^- and HSeO_4^-) interact with the hydroxyl groups on the magnetite
 218 surface (Martínez et al., 2006; Kim et al., 2012), the position of the adsorption edges also
 219 correlates with the pH-dependent distribution of those species in solution (Fig. 1). However,
 220 even at alkaline conditions of $\text{pH} > 10$, where the point of zero charge of magnetite (reported
 221 PZC values ranging from 6.5 to 8.1) is already exceeded and the surface is negatively charged
 222 (Milonjić et al., 1983; Hu et al., 2010), significant amounts of selenite are adsorbed.
 223 Responsible for this immobilization is the specific adsorption of selenite resulting in the

224 formation of inner-sphere surface complexes (Martínez et al., 2006; Loyo et al., 2008; Jordan
225 et al., 2009; Kim et al., 2012). Due to this inner-sphere selenite adsorption, large distribution
226 coefficients as well as high Se surface coverages of up to 2.5 at/nm² can be observed even at
227 pH 9.2. Such values were found not only for magnetite (Kim et al., 2012) but also for hematite
228 and goethite (Su and Suarez, 2000; Duc et al., 2003; Rovira et al., 2008; Börsig et al., 2017). In
229 addition, formation of inner-sphere complexes explains why selenite adsorption is not
230 dependent on the ionic strength. By contrast, selenate primarily forms outer-sphere adsorption
231 complexes in contact with iron (hydr)oxides (Hayes et al., 1987; Rietra et al., 2001; Jordan et
232 al., 2013). This would explain the almost non-existent adsorption at higher pH values as well
233 as the negative impact of higher ionic strengths as both parameters cause unfavorable
234 adsorption conditions due to decreasing positive surface charges and competition effects.

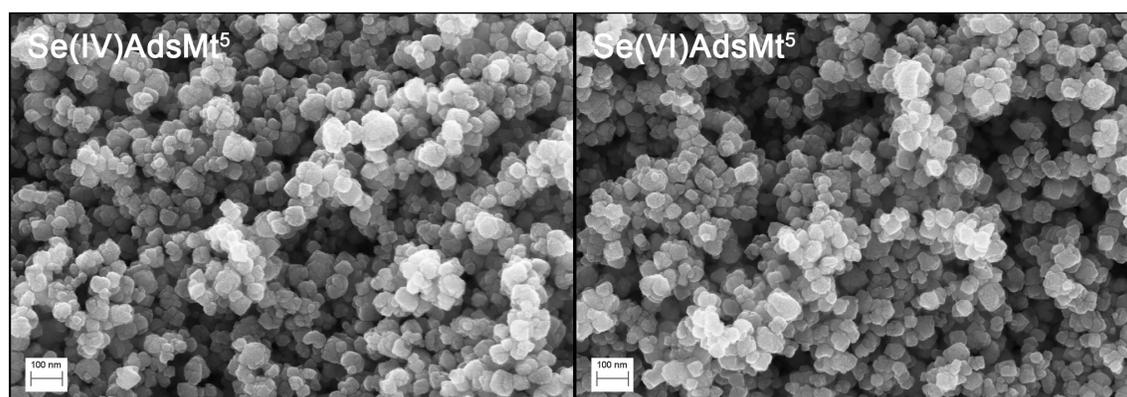
235 When interpreting these adsorption data, it must be taken into account that the used magnetite
236 phase was partly oxidized to maghemite in its near-surface region under the prevailing oxic
237 conditions. However, comparison of Se adsorption studies on magnetite and maghemite reveals
238 that both minerals behave very much alike. The adsorption capacity of both maghemite and
239 magnetite is similar in terms of its dependence on Se speciation, pH or ionic strength (Jordan
240 et al., 2013; Jordan et al., 2014). Interesting is also that several previous Se adsorption studies
241 on magnetite led to similar results regardless of whether the experiments were performed under
242 oxic (Martínez et al., 2006) or anoxic conditions (Loyo et al., 2008; Jordan et al., 2009; Kim et
243 al., 2012). In comparative studies Missana et al. (2009) proved that no differences in terms of
244 selenite sorption occurred under oxic and anoxic conditions. Furthermore, it is not always
245 documented to what extent the synthesized, industrially-produced or natural magnetite tested
246 in the above mentioned sorption studies might also have been affected by a partial oxidation
247 into maghemite. In contrast, magnetite synthesized under well controlled, anoxic conditions
248 proved to be a very effective reducer for selenite {Scheinost, 2008 #139; Scheinost, 2008 #266}.

249 3.2 Effects of selenium adsorption on the properties of the solid phase

250 To assess the impact of selenite or selenate adsorption on the properties of the magnetite phase,
251 selected samples from adsorption experiments were characterized by various solids analysis
252 methods. A detailed description and evaluation of these analyses can be found in the ESI
253 chapter 3.1. In short, XRD and SEM/EDX analyses demonstrated that neither the mineralogical
254 composition (ESI Fig. A.3) nor the morphology (Fig. 3) of the initial magnetite nanoparticles
255 was affected by the adsorption of selenite or selenate respectively. EDXRF data (ESI Table
256 A.1) and SEM/EDX analysis (ESI Fig. A.4), however, proved that the examined solid samples

257 contained significant Se quantities after adsorption, whose proportions depend on the initial Se
258 speciation and concentration. For a solid sample from the selenite system, with a relatively high
259 total Se amount of 4,200 ppm, the oxidation state of this Se proportion was identified by XPS
260 as Se(IV) (ESI Table A.2), demonstrating that the retention of selenite is not accompanied by a
261 change of the Se oxidation state.

262 Furthermore, XPS analysis and the comparison of the Fe(II)/Fe_{total} ratio of the solids before and
263 after the adsorption of selenite or selenate yielded to comparable results (ESI Table A.2). This
264 observation that the oxidation of magnetite to maghemite is not progressing significantly during
265 the oxidic adsorption experiments, can be explained by the formation of an initial maghemite
266 oxidation layer that prevents the underlying magnetite core from further aerial oxidation (He
267 and Traina, 2005; Rebodos and Vikesland, 2010; Khan et al., 2015).



268

269 **Fig. 3:** SEM results of magnetite samples from selenite and selenate adsorption studies; $c(\text{Se})_0 = 5 \times 10^{-3}$
270 mol/L.

271

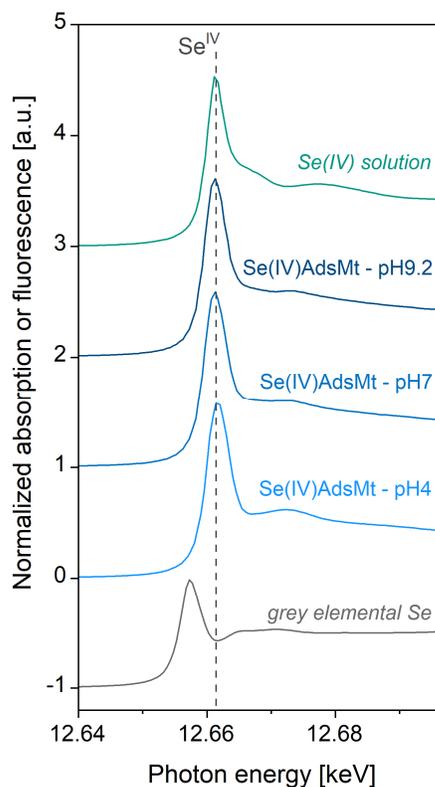
272 3.3 Characterization of the adsorption complexes

273 Se K-edge XAFS analysis was used to characterize the oxidation state (XANES) as well as the
274 local structure (EXAFS) of the immobilized Se. For this purpose, magnetite samples from
275 selenite or selenate adsorption experiments conducted at pH 4, 7 and 9.2 were analyzed in order
276 to investigate the influence of pH on the sorption mechanism.

277 Unfortunately, even at pH 4, selenate sorption on magnetite was too low to be analyzed by
278 XAFS spectroscopy. A determination of the specific adsorption mechanisms was therefore not
279 possible in case of the selenate system. However, the low retention capacity in combination
280 with the negative impact of higher ionic strengths and pH values generally points to the
281 formation of outer-sphere adsorption complexes. That selenate oxyanions form primarily outer-
282 sphere complexes in contact to iron (hydr)oxides was previously shown for maghemite (Jordan

283 et al., 2013) and hematite (Börsig et al., 2017) by XAFS, as well as by SCM for magnetite
284 (Martínez et al., 2006). It should be noted, however, that the observed dependency on ionic
285 strength and pH alone is not an unambiguous characteristic in favor of an outer-sphere selenate
286 adsorption (Su and Suarez, 2000).

287 Unlike the samples from the selenate systems, the selenite samples had taken up enough Se to
288 be analyzed by XAFS analysis. Fig. 4 shows the Se K-edge XANES spectra of the analyzed
289 samples from the selenite system together with reference spectra of Se(IV) (Na_2SeO_4 solution)
290 and Se(0) (grey elemental Se) compounds. For all three samples, the adsorption edge exactly
291 matches that of the Se(IV) reference spectra (12.660 KeV), indicating that the initial tetravalent
292 oxidation state remained unchanged. XANES data are thus in line with the XPS results which
293 showed that the adsorption processes caused neither selenite reduction nor oxidation. An
294 immobilization due to selenite reduction and formation of sparingly soluble reduced Se
295 compounds such as elemental Se^0 or selenide minerals can therefore be excluded not only at
296 alkaline but also at acidic pH conditions. It is known that in anoxic systems reduction of selenite
297 oxyanions by Fe(II)-bearing minerals like magnetite is generally possible (Scheinost et al.,
298 2008; Scheinost and Charlet, 2008; Börsig et al., 2018). However, even in an anoxic
299 environment, selenite reduction does not inevitably take place, as other selenite-magnetite
300 adsorption studies have proven (Loyo et al., 2008; Jordan et al., 2009; Missana et al., 2009).
301 The exact reasons for this are unclear, but several possible explanations have been discussed in
302 previous studies. According to Loyo et al. (2008), one reason could be the slow reaction time
303 of the selenite reduction process. However, a direct comparison of the reaction times used in
304 the above mentioned studies, ranging from a few hours to 30 days, is difficult because of the
305 partially very different experimental setups (i.e. initial Se concentrations, magnetite amounts,
306 pH, presence of secondary ions, etc.). For this reason, the reaction time must rather be seen in
307 relation to the respective mineral surface coverage and reduction kinetics. According to
308 Missana et al. (2009), reduction of selenite oxyanions is only possible if the selenite surface
309 coverage of the corresponding Fe(II)-bearing mineral phase is relatively low, as high coverages
310 slow down electron transfer processes. This theory, however, has not yet been experimentally
311 proven. Furthermore, the presence or absence of Se reduction processes could be affected by
312 the specific Fe(II)/Fe(III) ratio of the magnetite phase, since the magnetite stoichiometry
313 strongly influences its physicochemical properties, including the sorption capacity and the
314 reduction potential (Gorski and Scherer, 2010). Higher Fe(II) fractions have a positive impact
315 on the reduction potential of magnetite, which was proven in sorption studies with uranium
316 (Latta et al., 2012) and neptunium (Wylie et al., 2016), among others.



317

318

319 **Fig. 4:** Se K-edge XANES spectra of Se references and magnetite samples from selenite adsorption studies
 320 performed at different pH values; $c(\text{Se})_0 = 10^{-3}$ mol/L.

321 To identify the specific adsorption type, the samples were analyzed by Se K-edge EXAFS
 322 spectroscopy (Fig. 4). The k^3 -weighted spectra were fit with a FEFF 8.2 file generated with the
 323 crystallographic structure of mandarinoite ($\text{Fe}_2(\text{SeO}_3)_3 \cdot 6\text{H}_2\text{O}$, CIF 0005198, Hawthorne,
 324 1984). For all three selenite sorption samples, the EXAFS Fourier transforms (FT) are
 325 dominated by a strong peak at 1.35 \AA (uncorrected for phase shift). Responsible for this peak
 326 is the oxygen coordination shell. The fit of this shell using a single scattering Se-O path resulted
 327 in coordination number (CN) of 2.8 and atomic distances of $1.70\text{--}1.71 \text{ \AA}$ (Table 1), confirming
 328 the tetravalent oxidation state and the unchanged pyramidal-shaped molecular structure of the
 329 selenite oxyanion. Beyond the oxygen coordination shell, a small double peak arises in the
 330 range $2.3\text{--}3.5 \text{ \AA}$ (uncorrected for phase shift), with the relative ratio of the two peaks changing
 331 with pH: For the sample representing acidic conditions [Se(IV)AdsMt-pH4], the right-side peak
 332 at 2.9 \AA dominates, whereas under alkaline conditions [Se(IV)AdsMt-pH9.2] the left-side peak
 333 at 2.6 \AA becomes more pronounced. In addition, the peak intensities at alkaline pH are generally
 334 lower than for acidic conditions. The peaks could be fitted with two individual single scattering
 335 Se-Fe paths, providing between 0.3–0.9 Fe atoms at an atomic distance of $2.90\text{--}2.93 \text{ \AA}$, and

336 0.4–0.9 Fe atoms at an atomic distance of 3.37–3.40 Å (Table 1). Note that the Debye-Waller
 337 factors of both Se-Fe paths were kept correlated, to achieve a satisfying fitting of those peaks.
 338 The graphical representation of the fit results can be found in ESI Fig. A.5.

339 **Table 1: Se-K XANES edge energies and EXAFS fit results of selenite-magnetite adsorption samples**
 340 **($S_0^2 = 0.9$).**

| Sample | E_0 [keV] | Oxygen shell | | | Iron shells | | | ΔE_0 [eV] | χ_{res} [%] | |
|-----------------|-------------|-----------------|--------------------|---|-------------|--------|------------------------------|---------------------|------------------|------|
| | | CN ^a | R [Å] ^b | σ^2 [Å ²] ^c | CN | R [Å] | σ^2 [Å ²] | | | |
| Se(IV)AdsMt-pH4 | 12.6600 | 0.9 | O | 2.8 | 1.70 | 0.9 Fe | 2.93 | 0.0093 ^d | 14.8 | 12.5 |
| | | | | | | 1.7 Fe | 3.40 | 0.0093 ^d | | |
| Se(IV)AdsMt-pH7 | 12.6595 | 0.9 | O | 2.8 | 1.70 | 0.5 Fe | 2.93 | 0.0048 ^d | 15.4 | 13.4 |
| | | | | | | 0.6 Fe | 3.39 | 0.0048 ^d | | |
| Se(IV)AdsMt-pH9 | 12.6596 | 0.9 | O | 2.8 | 1.71 | 0.3 Fe | 2.90 | 0.0030 ^d | 15.7 | 14.6 |
| | | | | | | 0.4 Fe | 3.37 | 0.0030 ^d | | |

^a CN: coordination number, error $\pm 25\%$. ^b R: radial distance, error ± 0.01 Å. ^c σ^2 : Debye-Waller factor, error ± 0.0005 Å².

^d correlated σ^2 .

341 Although the necessity for such relatively small coordination numbers may be questioned at
 342 first due to their inevitably larger error, the use of two scattering paths was required to achieve
 343 stable fitting results. Contrary to this, the use of only one Se-Fe path or a mixture of Se-Fe and
 344 Se-O paths led to poor fitting results. Furthermore, data of other studies (Missana et al., 2009;
 345 Jordan et al., 2014) as well as the results of principal component analysis (see chapter 3.4)
 346 support this assumption.

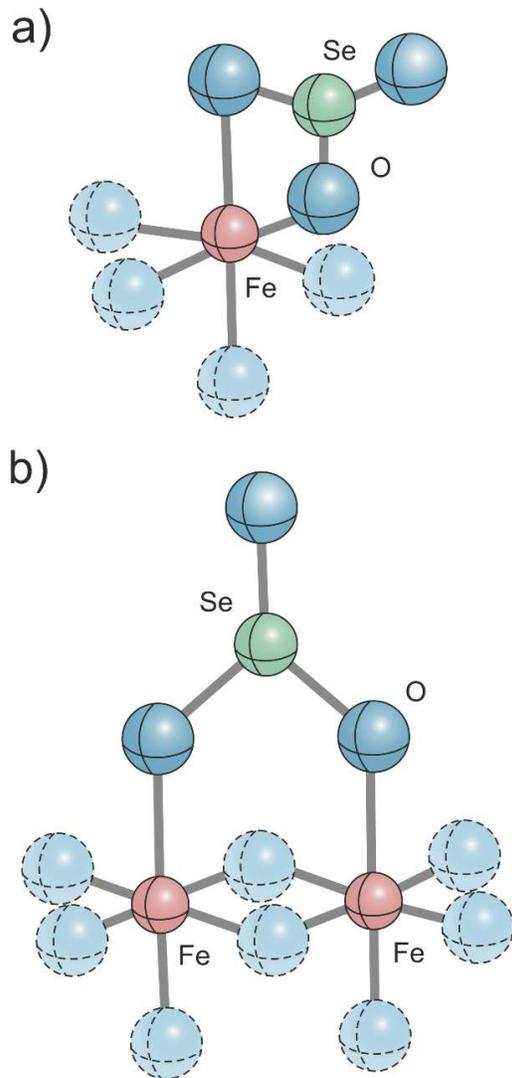


Fig. 5: Model showing the structure of (a) ²E and (b) ²C adsorption complexes between selenite molecules and FeO₆ octahedra.

The occurrence of Fe atoms in the second shell indicate an inner-sphere bonding between the selenite oxyanion and the mineral surface. The shorter Fe shell with a distance of 2.90–2.93 Å points to the formation of a bidentate mononuclear edge-sharing ²E arrangement. As shown in Fig. 5a, ²E adsorption complexes are characterized by two oxygen atoms of the selenite molecule simultaneously forming the edge of an FeO₆ octahedron on the iron (hydr)oxide surface. The longer Fe shell, on the other hand, represents bidentate binuclear corner-sharing ²C adsorption complexes, where one adsorbed selenite molecule is attached to two FeO₆ octahedra (Fig. 5b). That the interaction of selenite oxyanions with iron (hydr)oxides can cause the (simultaneous) formation of these types of inner-sphere adsorption complexes, was also demonstrated by several previous studies (Hayes et al., 1987; Manceau and Charlet, 1994; Hiemstra et al., 2007; Missana et al., 2009; Jordan et al., 2014; Börsig et al., 2017).

370 According to the EXAFS results, other types of sorption or retention mechanisms can be
 371 excluded. For instance, Missana et al. (2009) reported formation of a discrete ferric selenite
 372 phase like Fe₂(SeO₃)₃ · 6H₂O at pH 4. This would result in higher Fe coordination numbers as
 373 well as in the presence of additional Se backscatter atoms, which are both missing in our
 374 EXAFS data. Also the formation of monodentate mononuclear corner-sharing ¹V complexes,
 375 which can arise for instance during the adsorption of As-oxyanions (arsenate or arsenite) on
 376 magnetite or maghemite can be ruled out (Morin et al., 2008; Zhang et al., 2011; Navarathna et
 377 al., 2019), since structural features in the EXAFS FT range beyond 3.5 Å are absent.
 378 Furthermore, we could exclude the presence of tridentate hexanuclear corner-sharing ³C
 379 complexes, that have been shown to form with the oxyanions arsenite (Wang et al., 2008; Liu
 380 et al., 2015) and antimonite (Kirsch et al., 2008) at the {111} faces of magnetite, since

381 backscatterer atoms at higher atomic distances are absent. This assumption is supported by
382 results of previous studies, in which also no hints for selenite ^{1}V or ^{3}C adsorption complexes
383 on magnetite or maghemite have been found (Missana et al., 2009; Jordan et al., 2014). Jordan
384 et al. (2014) explain this different behavior of selenite compared to arsenite or antimonite by
385 the different sizes of these trigonal pyramidal oxyanion molecules.

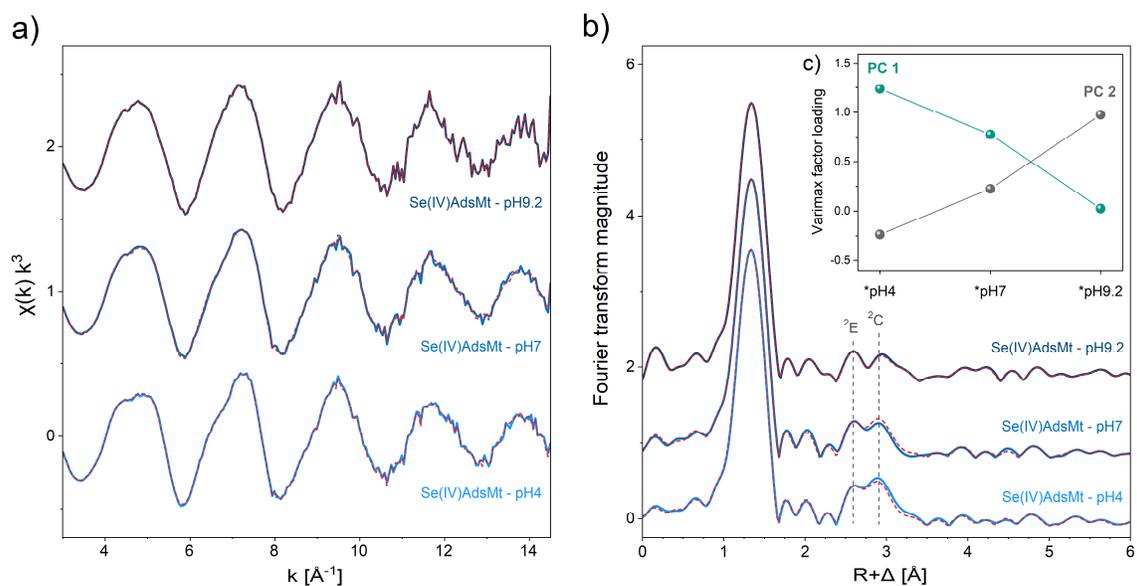
386 3.4 Properties and stability of the selenite surface complexes

387 Based on XAFS data, interaction of dissolved selenite with magnetite under oxic conditions
388 leads to the simultaneous formation of ^{2}E and ^{2}C adsorption complexes. Which types of
389 adsorption complexes develop on a particular material generally depends on the prevailing
390 hydrochemical conditions and the structural and morphological properties of the adsorbent
391 phase. This can be explained by the atomic structure and features of specific crystal surfaces.
392 Due to the distinct arrangement of functional surface groups or, respectively, adsorption sites,
393 certain types of adsorption complexes occur mainly on certain crystal surfaces. Since the
394 affinity of an adsorbate for certain adsorption sites is determined among other things by its
395 general surface coverage (Peak and Sparks, 2002; Fukushi and Sverjensky, 2007), which in turn
396 is influenced by the pH value, different crystal surfaces show different reactivities depending
397 on the degree of coverage or pH. In case of oxyanion adsorption on magnetite, formation of ^{2}C
398 adsorption complexes is mainly associated with the {100} crystal surface, while the ^{2}E
399 complexes are related to the {110} or {111} facets (Jönsson and Sherman, 2008; Wang et al.,
400 2008; Wang et al., 2011; Liu et al., 2015; Navarathna et al., 2019).

401 Changing selenite adsorption types depending on the solution pH were determined by EXAFS
402 analysis for both magnetite (Missana et al., 2009) and maghemite (Jordan et al., 2014). The
403 respective results indicate that ^{2}E and ^{2}C selenite adsorption complexes appear simultaneously
404 at acidic conditions or at high surface coverages, respectively, with the corner-sharing ^{2}C
405 complexes being dominant. With increasing pH values or decreasing surface coverages, the
406 share of ^{2}C complexes tends to decrease and at alkaline conditions (>pH 8) only edge-sharing
407 ^{2}E adsorption complexes occur. However, the authors of both studies noted that the evaluation
408 of EXAFS data for such samples is quite difficult. Due to the small coordination numbers,
409 especially at neutral or alkaline conditions, identification of the adsorption complexes as well
410 as determination of their relative shares becomes more and more challenging. This challenge
411 also arises for the EXAFS data of this work. Particularly the samples at pH 7 and pH 9.2 are
412 characterized by small Fe coordination numbers, which makes it difficult to estimate their
413 relative fractions.

414 We therefore performed a statistical analysis of the EXAFS spectra with Iterative
 415 Transformation Factor Analysis (ITFA) (Rossberg et al., 2003). ITFA allows determining the
 416 number of principal components (PC) and their respective factor loadings. Fig. 6a illustrates
 417 the good match between the experimental spectra (black) and their reconstructions (red lines)
 418 by two PC. The ITFA thus confirms that two individual spectral components are needed to
 419 characterize the EXAFS spectra of all three adsorption samples.

420 Moreover, the corresponding Varimax factor loadings (Fig. 6b) show that the sample at pH 4
 421 is solely dominated by PC 1, whereas PC 2 primarily represents selenite adsorption under
 422 alkaline conditions. Based on the previous observations and the findings of Missana et al.
 423 (2009) and Jordan et al. (2014), these results can be interpreted in a way that the different factor
 424 loadings are associated with a varying distribution of ${}^2\text{E}$ and ${}^2\text{C}$ surface adsorption complexes.
 425 Accordingly, PC 1 reflects a combination of ${}^2\text{E}$ and ${}^2\text{C}$ adsorption complexes with a higher
 426 proportion of corner-sharing ${}^2\text{C}$ complexes, while PC 2 represents a mixture of both
 427 complexation types with a higher share of ${}^2\text{E}$ complexes. Under neutral or slightly alkaline
 428 conditions, both adsorption types would thus occur in approximately equal proportions, which
 429 is consistent with the factor loading of sample Se(IV)AdsMt-pH7.



430

431

432 **Fig. 6:** (a & b) Se K-edge EXAFS spectra of magnetite samples from selenite adsorption studies performed
 433 at different pH values (blue lines) and their reconstruction by two factors (red lines). (c) Varimax loadings
 434 of the two factors.

435 The dependency of the complexation type from the pH value can basically be interpreted that
 436 increasing pH values and a higher negative surface charge cause a change in the stability and

437 thus in the prevailing dominance of the selenite adsorption complexes. Under favorable
438 adsorption conditions, the affinity of selenite oxyanions to form corner-sharing ²C complexes
439 is generally higher than for the edge-sharing ²E complexes, leading to a quantitatively
440 predominant of the ²C complexes over a wide pH range. However, at more alkaline conditions,
441 which are generally unfavorable for selenite adsorption, the ²E complexes become more stable.
442 This effect leads to a significant increase in the proportion of ²E over ²C complexes, although
443 the absolute amount of adsorbed selenite decreases with increasing pH.

444 4 Conclusion

445 When redox-sensitive materials are considered to prevent the migration of pollutants, it must
446 be taken into account that the retention properties of these materials can change considerably
447 in natural environments. This study demonstrates that magnetite nanoparticles can effectively
448 remediate selenite and selenate contaminated wastewaters even if they are oxidized. However,
449 the retention requires suitable hydrochemical conditions, which mainly concern the prevailing
450 pH and the corresponding selenium speciation. While retention of selenate only takes place at
451 acidic conditions, selenite is immobilized over a large pH range. No reduction processes were
452 involved in the selenium immobilization. The specific retention mechanism are attributable to
453 the formation of surface adsorption complexes. A mixture of mononuclear edge-sharing (²E)
454 and binuclear corner-sharing (²C) inner-sphere complexes in case of selenite and most likely
455 outer-sphere surface complexes in case of selenate. It was found that both types of inner-sphere
456 selenite complexes have different affinities and stabilities depending on the solution pH.

457 Regarding the assessment of the remediation efficiencies of oxidized magnetite, the results
458 show that the mechanisms of selenite and selenate adsorption are comparable to the findings
459 from previous adsorption studies on pure maghemite. Accordingly, in systems where no
460 reduction takes place, partially oxidized magnetite nanoparticles can approximately be
461 considered as a maghemite-like adsorbent phase. These findings help to better understand the
462 retention behavior of selenium oxyanions in contact with nanoparticulate magnetite/maghemite
463 phases under oxic conditions and could be used in modeling the migration of selenium
464 oxyanions in subsurface environments.

465 Conflicts of interest

466 There are no conflicts of interest to declare.

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