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## Aging and reactivity assessment of nanoscale zerovalent iron in groundwater systems

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26 **Abstract**

27 In this study, changes in the reactivity of nanoscale zerovalent iron (NZVI) in five  
28 different groundwater (GW) systems under anoxic and oxic conditions were examined  
29 over a wide range of aging time (0–60 d). *p*-nitrophenol (*p*-NP) was used as a redox-  
30 sensitive probe, whereas nalidixic acid (NA), a typical antibiotic found in the natural  
31 environment, was used as a sorbing compound. Investigation of the *p*-NP reduction in  
32 pure water systems showed that NZVI lost 41% and 98% of its reductive activity under  
33 anoxic and oxic conditions after 60 d, while enhancement of its reactivity was observed  
34 after short-term aging in GW (1–5 d), followed by a further decline. This behavior has  
35 been ascribed to the formation of secondary Fe(II)-bearing phases, including magnetite  
36 and green rust, resulting from NZVI aging in GW. Adsorption experiments revealed  
37 that GW-anoxic-aged NZVI samples exhibited a good affinity toward NA, and a greater  
38 NA adsorption ( $\sim 27 \mu\text{mol g}^{-1}$ ) than that of pristine NZVI ( $\sim 2 \mu\text{mol g}^{-1}$ ) at alkaline pH  
39 values. Surface complexation modeling showed that the enhanced adsorption of NA  
40 onto secondary minerals can be attributed to the Fe(II)-NA surface complexation. This  
41 considerable change in the reductive ability and the adsorption capacity of NZVI arising  
42 from groundwater corrosion calls for greater attention to be paid in assessment studies,  
43 where NZVI is injected for long-term remediation in groundwater.

44

45 **Keywords:** NZVI; aging effect; groundwater; reactivity; secondary minerals.

46

## 47 1. Introduction

48 Nanoscale zerovalent iron (NZVI) is one of the most extensively studied  
49 nanomaterials of environmental clean-up technologies (Li et al. 2017; Phenrat et al.  
50 2016; Wei et al. 2010; Xia et al. 2017). Because NZVI is an environmentally safe  
51 material with high surface area and great reactivity, it has been widely applied in  
52 treatments of contaminants, including persistent organic compounds (Joo et al. 2004),  
53 toxic inorganic contaminants (Ryu et al. 2011), and even radioactive nuclides (Tsarev  
54 et al. 2017).

55 Despite NZVI having been frequently applied in *in-situ* groundwater remediation  
56 (Libralato et al. 2017; Mueller et al. 2012), the remedial performance of NZVI is  
57 sensitive to many geochemical factors in groundwater such as organic matter  
58 (Giasuddin et al. 2007; Zhou et al. 2022), cations (Chen et al. 2018), and anions (Su et  
59 al. 2012). For instance, inhibition of As(V) and As(III) removal by NZVI was reported  
60 in the presence of humic acid (Giasuddin et al. 2007), while the presence of  $\text{Cl}^-/\text{SO}_4^{2-}$   
61  $/\text{Cu}^{2+}$  enhanced the reduction of hexachlorobenzene (Su et al. 2012). Groundwater  
62 constituents may affect not only the NZVI reactivity but also its fate or mineralogical  
63 transformation over long-term aging in the natural environment. Indeed, NZVI can be  
64 completely or partially oxidized into various Fe(II)/Fe(III) (hydr)oxides depending on  
65 the groundwater conditions (Bae et al. 2018). In the presence of  $\text{HCO}_3^-$ , the formation  
66 of magnetite/carbonate green rust/iron carbonate hydroxide as aging products of NZVI

67 have been observed (Xie and Cwiertny 2012), whereas the presence of  $\text{SO}_4^{2-}$  enabled  
68 the formation of magnetite/schwertmannite (Reinsch et al. 2010). Further investigations  
69 of NZVI aging in synthetic groundwater revealed that magnetite was a major aging  
70 product with traces of goethite/amakinite under anoxic conditions (Schöftner et al.  
71 2015), with lepidocrocite being the only iron phase found after 60 d aging under oxic  
72 conditions (Dong et al. 2012). However, a comprehensive understanding of short- and  
73 long-term aging effects on NZVI behavior in real groundwater is still limited. Despite  
74 very few investigations (Adeleye et al. 2013) on the long-term environmental fate of  
75 commercial NZVI in groundwater, little is known about the reactivity of the generated  
76 secondary iron phases which can further influence interactions with co-existing  
77 contaminants.

78       Herein, a comprehensive kinetic assessment of reductive and adsorptive capacities  
79 of NZVI and aged NZVI in various real groundwater was performed under oxic and  
80 anoxic conditions to determine the NZVI reactivity versus corrosion over a wide range  
81 of aging time (0–60 d). Specifically, the main aim was to assess the interaction  
82 mechanisms of “aged” NZVI particles with *p*-nitrophenol (*p*-NP), a redox-sensitive  
83 probe, and nalidixic acid (NA), a sorbing antibiotic contaminant in natural systems.  
84 Five different groundwater samples from different places in France were used in this  
85 study. The reduction of *p*-NP by fresh NZVI in pure water (PW) and the five  
86 groundwater samples was first evaluated, and the mineral transformation of NZVI  
87 particles after the reaction was analyzed by X-ray diffraction (XRD) and high-

88 resolution transmission electron microscopy (HR-TEM). Structural and compositional  
89 analyses were performed for aging products at the desired aging time under anoxic and  
90 oxic conditions, and additional reduction experiments were performed to investigate  
91 the changes in the reductive activity of NZVI aging products. NA adsorption on the  
92 NZVI aging products was also evaluated as a function of pH, and a surface  
93 complexation model was developed to describe the impact of surface-bound Fe(II) of  
94 aged NZVI samples on NA adsorption.

95

## 96 **2. Materials and methods**

### 97 *2.1. Chemicals and materials*

98 Complete information on chemicals used in this study is presented in the  
99 Supporting Information (SI). NZVI (50–100 nm) was synthesized by following our  
100 previous method (Deng et al. 2020). It exhibited a typical chain-like core-shell structure  
101 as per high-resolution transmission electron microscopy (HR-TEM) analysis (Fig. S1).  
102 Maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, >99.0%) was purchased from Alfa Aesar (Ward Hill, MA, USA).  
103 Magnetite (Fe<sub>3</sub>O<sub>4</sub>) (Cheng et al. 2018), lepidocrocites ( $\gamma$ -FeOOH) (Paterson 2000),  
104 carbonate green rust ( $[\text{Fe}^{2+}_4\text{Fe}^{3+}_2(\text{HO})_{12}]^{2+} \cdot [\text{CO}_3^{2-} \cdot m\text{H}_2\text{O}]^{2-}$ ) (Williams and Scherer  
105 2001) and goethite ( $\alpha$ -FeOOH) (Xu et al. 2017a), were synthesized following the  
106 published methods. Five groundwater samples were collected in France at sites with

107 the following GPS locations: GW1 (48.02881, -1.47230), GW2 (48.02944, -1.47215),  
108 GW3 (45.71039, -0.00009), GW4 (45.70212, -0.00808), and GW5 (45.70209, -  
109 0.00895). Raw groundwater samples were filtered using 0.2  $\mu\text{m}$  membranes (Whatman;  
110 Maidstone, Kent, UK) to remove solids and microbes.

111 The glasswares used for the reaction were soaked in 5% (v/v) HCl for at least 48 h  
112 and rinsed before use. Unless specifically stated, all solutions were prepared with  
113 deoxygenated deionized water (DDIW, 18.2  $\text{M}\Omega\cdot\text{cm}$ ) prepared by purging with  
114 nitrogen ( $\text{N}_2$ , 99.99%) for 4 h and stored in an anaerobic chamber (Jacomex, Dagneux,  
115 France).

116

## 117 2.2. *Groundwater characterization*

118 Physicochemical characteristics including pH, electrical conductivity (EC), total  
119 dissolved solids (TDS), total organic carbon (TOC), total hardness (TH), total  
120 phosphate (TP), common anions, and cations (Table S1) of the groundwater samples  
121 were measured following the guidelines of “Standard Methods For The Examination of  
122 Water and Wastewater American Public Health Association” (Eaton et al. 1966).  
123 Particularly, anions in groundwater were determined using ion chromatography (IC;  
124 Dionex Corp., Sunnyvale, CA, USA), while cations were measured by inductively  
125 coupled plasma mass spectrometry (ICP-MS, Agilent 7700x; Agilent Technologies,  
126 Santa Clara, CA, USA). The pH and EC were determined using a pH meter (HANNA,

127 HI991003; Hanna Instruments, Smithfield, RI, USA) and a conductivity meter LF 340  
128 (WTW, Weilheim, Germany), respectively. Total hardness was determined by the  
129 EDTA titration method, and TDS was measured gravimetrically (Patnaik 2017). Silicate  
130 and phosphate analyses were performed according to the molybdenum blue method  
131 (Grasshoff et al. 2009), and the ammonium molybdate spectrometric methods (Standard  
132 and ISO 2004), respectively. The concentration of carbonate species was measured by  
133 the acid titration method (Eaton et al. 1966).

134

### 135 2.3. *Characterizations of NZVI and aged NZVI particles*

136 The aged NZVI was prepared by using NZVI ( $10 \text{ g L}^{-1}$ ) suspensions in 15-mL vials  
137 containing DDIW or deoxygenated GW1. Subsequently, the NZVI suspension was  
138 placed under ambient air condition (oxic aging) or in an anaerobic chamber (anoxic  
139 aging) and allowed to age for 1, 5, 15, 30, and 60 d. Given that the particles settle in the  
140 vial with increasing aging time, thus potentially reducing the contact time with water,  
141 the suspensions were vigorously mixed by hand shaking once a day (Dong et al. 2018).  
142 The pH variation during aging was monitored using a portable pH meter. Aged NZVI  
143 particles were separated by centrifugation at the desired aging time and dried in a  
144 vacuum freeze drier ( $-52 \text{ }^{\circ}\text{C}$ , 24 h) for further characterization and experiments.

145 XRD (Bruker D8 Advance, Cu  $K\alpha 1$  radiation,  $\lambda = 1.5406 \text{ \AA}$ ) was used to identify  
146 the aging products of NZVI. The samples were transferred to sample holders and treated



147 with 1: 1 (v/ v) glycerol solution to avoid surface oxidation during the XRD analysis  
148 (Bae and Lee 2014). The morphological information of aged NZVI particles was  
149 obtained by HR-TEM (JEM-2100; JEOL, Tokyo, Japan) with selected area electron  
150 diffraction (SAED). The dried NZVI aging products were transferred to ethanol  
151 solution and sonicated for 30 min. Finally, a drop of the diluted suspension was placed  
152 on the copper TEM grid and analyzed at an acceleration voltage of 200 kV.

153

#### 154 2.4. Reduction and adsorption experiments

155 Experiments to measure the reactivity of fresh NZVI in different waters were  
156 carried out in 200-mL flasks in an anaerobic chamber to avoid the effect of dissolved  
157 oxygen during the reaction. An exact amount (1 mL) of 20 mM *p*-NP stock solution  
158 was transferred to the flask containing 200 mL of filtered groundwater or DDIW,  
159 followed by stirring at 500 rpm to prepare an initial *p*-NP concentration of 0.1 mM.  
160 Then, 10 mg of NZVI was introduced into the solution to initiate the reduction of *p*-NP  
161 by NZVI. At each sampling time, 1 mL of the sample was taken from the suspension  
162 and filtered through a 0.2- $\mu$ m filter (Whatman) for high-performance liquid  
163 chromatography (HPLC) analysis.

164 Similar procedures were conducted to investigate the reductive activity of aged  
165 NZVI particles. Briefly, aged NZVI suspension (10 g L<sup>-1</sup>) was firstly bath-sonicated for  
166 1 h. The aged NZVI suspension (1 mL) was added to 200 mL of *p*-NP solution (0.1

167 mM). Then, samples were taken at the desired time intervals and analyzed by HPLC.  
168 In contrast to the reduction experiments, adsorption batch experiments of NZVI aging  
169 products were initiated by transferring 10 mg of aged NZVI particles into 200 mL of  
170 NaCl solution (10 mM). The pH was then adjusted to the required value using 0.1 M  
171 and/or 1 M NaOH/HCl solutions. After 2 h of adsorption, an aliquot was taken and  
172 filtered (0.2- $\mu\text{m}$ , Whatman) to measure NA and dissolved Fe(II). To investigate the role  
173 of each mineral phase on the reactivity of aged NZVI, additional reduction and  
174 adsorption assessments of iron-containing minerals (*i.e.*, magnetite, maghemite,  
175 carbonate green rust, lepidocrocite, and goethite, 50 mg L<sup>-1</sup>) were carried out following  
176 the same procedures described above. All experiments in this study were performed in  
177 triplicate, and the data reported here were the average of the three replicated  
178 experiments, and error bars represent the relative standard deviation.

179

## 180 2.5. Analytical Methods

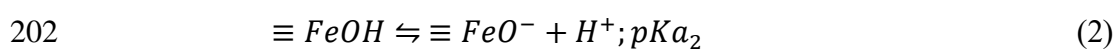
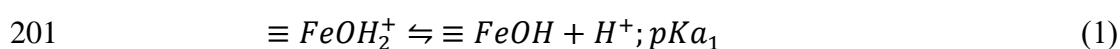
181 The aqueous concentration of *p*-NP, *p*-AP, and NA were determined using an HPLC  
182 (Waters 600 controller; Waters Corporation, Milford, MA, USA) equipped with a  
183 photodiode array detector (Waters 996; Waters Corporation) and a reversed-phase C18  
184 column (250 mm  $\times$  4.6 mm; *i.d.*, 5  $\mu\text{m}$ ). The UV detector was set to 273, 317, and  
185 258 nm for *p*-NP, *p*-AP, and NA analyses, respectively (Bae et al. 2016, Xu et al. 2017c).  
186 The mobile phase (mixture of acetonitrile/water (50/50, v/v) containing 0.1% formic

187 acid) was prepared and used at the flow rate of 1 mL min<sup>-1</sup> in the isocratic mode for the  
188 measurement of *p*-NP, *p*-AP, or NA. The dissolved Fe(II) concentration was measured  
189 using the 1,10-phenanthroline method at a wavelength of 510 nm with a UV-vis  
190 spectrophotometer (U-3310, Hitachi; Hitachi Ltd., Tokyo, Japan) (Fadrus and Malý  
191 1975).

192

### 193 2.6. *Surface complexation modeling*

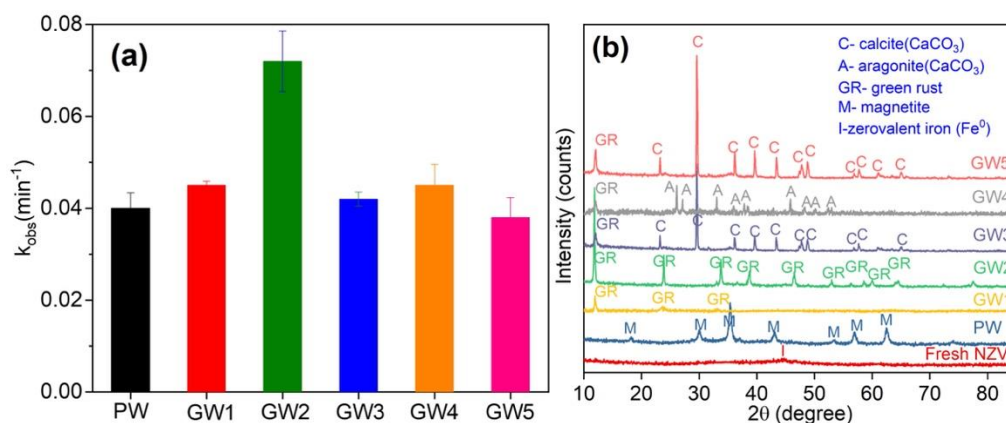
194 The NA adsorption by NZVI aging products at different pH values was described  
195 using surface complexation modeling. The geochemical speciation code PHREEQC  
196 and the “Minteq” database were used (D. L. Parkhurst and C. A. J. Appelo 1999). The  
197 pK<sub>a</sub> of NA is 6.19, and the logarithm of the formation constant of NA–Fe<sup>+</sup> (aq) is 3.99  
198 (Vincent et al. 1981). The surface complexation model for iron oxides was used, as  
199 previously reported, and the protonation of Fe surface sites was formulated following a  
200 2-pK<sub>a</sub> approach (Eq. 1 and 2) (Cheng et al. 2018, Hanna, 2007).



203 The charge-potential relationship was described according to the constant  
204 capacitance model (CCM), and the modeling parameters are presented in Table S2. We  
205 adapted the parameters of the three plane model (TPM) to use the CCM in PHREEQC  
206 (version 2) (Cheng et al. 2018).

207 **3. Results and discussion**

208 **3.1. Reduction of *p*-NP by NZVI suspensions in various groundwater systems**



209

210 Figure 1. (a) Pseudo-first-order kinetic rate constants ( $k_{obs}$ ,  $\text{min}^{-1}$ ) of *p*-NP reduction by

211 fresh NZVI in various water matrices, and (b) XRD data of corresponding solids.

212 Experimental conditions:  $[p\text{-NP}]_{\text{initial}} = 0.1 \text{ mM}$ ,  $[\text{NZVI}] = 50 \text{ mg L}^{-1}$ ,  $\text{pH} = 9.0 \pm 0.2$ .

213 Correlation coefficient ( $r^2$ ) ranges from 0.95 to 0.99.

214

215 The removal kinetics of *p*-NP in various water matrices showed that *p*-NP was

216 completely removed by NZVI within a 2 h-reaction in all experiments under anoxic

217 conditions (Fig. S2). The aqueous concentrations of *p*-AP after the reaction revealed a

218 complete mass balance of the conversion reaction of *p*-NP into *p*-AP (Table S3),

219 indicating the negligible adsorption of *p*-NP or *p*-AP on NZVI surfaces in this study.

220 The pseudo-first-order kinetic rate constants ( $k_{obs}$ ,  $\text{min}^{-1}$ ) were determined by

221 considering the early stage of kinetics data over 30 min of reaction time (Fig. 1a). The

222 highest rate constant was observed in GW2 ( $0.07 \text{ min}^{-1}$ ), compared to PW and other  
223 groundwater systems.

224 In contrast to the black color of NZVI in the PW system, a change of suspension  
225 color to bluish-green was observed in the groundwater samples. The XRD analysis  
226 revealed various corrosion products of NZVI depending on the water matrix (Fig. 1b).  
227 In PW, diffraction peaks were observed at  $18.4^\circ$ ,  $30.2^\circ$ ,  $35.5^\circ$ ,  $43.2^\circ$ ,  $53.6^\circ$ ,  $57.2^\circ$ , and  
228  $62.8^\circ$ ; these peaks can be assigned to maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ )/magnetite ( $\text{Fe}_3\text{O}_4$ ).  
229 Carbonate green rust was detected in all groundwater systems, together with calcite in  
230 GW3 and GW5 and aragonite in GW4 (Fig. 1b) (Dong et al. 2020, Kontoyannis and  
231 Vagenas 2000).

232 The pH and concentration of the main dissolved species including anions and TOC  
233 in the five groundwater matrices were determined after the reaction (Table S4). The  
234 suspension pH in groundwater systems increased to approximately 9, owing to the  
235 anaerobic corrosion of NZVI ( $\text{Fe}(0) + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{OH}^- + \text{H}_2$ ) (Deng et al. 2020).  
236 As the distribution of carbonate species is strongly dependent on the pH value (Fig. S3),  
237 an increase in  $\text{CO}_3^{2-}$  species is expected, which can result in the formation of carbonate-  
238 bearing minerals (e.g.,  $\text{CaCO}_3$  and carbonate green rust). The precipitation of  $\text{CaCO}_3$   
239 occurred mainly in GW3, GW4, and GW5 systems because of the relatively higher  
240 initial concentration of calcium (2.44–2.61 mM) and bicarbonate (4.2–4.3 mM) (Table  
241 S1). Indeed, a drop in the aqueous concentration of dissolved carbonates was observed,  
242 especially in GW3, GW4, and GW5, which was comparable to the  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$

243 concentrations after the reaction (Table S4). Up to 88% of the initial  $\text{NO}_3^-$  concentration  
244 was eliminated in groundwater samples after the reaction, likely because of the  
245 reductive removal of  $\text{NO}_3^-$  by NZVI (Hwang et al. 2011; Su et al. 2014). For silicate  
246 concentration, up to 90% loss was detected after the reaction, probably due to its strong  
247 binding affinity toward iron minerals (Kanematsu et al. 2018). However, no significant  
248 change in Total Organic Carbon (TOC) was observed before and after reaction with  
249 NZVI (Table S4).

250 In contrast, the NZVI corrosion products, particularly Fe(II)-containing minerals,  
251 could further contribute to the reduction of *p*-NP. Indeed, previous studies have reported  
252 the greater reductive ability of green rust than that of magnetite (Digiacomio et al. 2020,  
253 Usman et al. 2018). An independent set of experiments using synthetic Fe-minerals  
254 confirmed that carbonate green rust led to 43% of *p*-NP removal in 5 h, whereas only  
255 8% of *p*-NP was removed by magnetite, and almost no removal of *p*-NP by Fe(III)-  
256 oxyhydroxides was observed (Fig. S4). Therefore, the carbonate green rust generated  
257 in NZVI-groundwater suspensions could additionally reduce *p*-NP. Other groundwater  
258 constituents, such as nitrate and silicate, may decrease the *p*-NP reduction efficiency  
259 owing to the inhibitory effects caused by the competitive reduction reaction of nitrate  
260 with *p*-NP (Alowitz and Scherer 2002, Westerhoff and James 2003), and the blocking  
261 of the reactive sites by silicate (Meng et al. 2002). This may explain why the highest  
262 rate constant for *p*-NP reduction was observed for GW2, which contained a lower  
263 nitrate concentration. Nevertheless, to avoid the formation of  $\text{CaCO}_3$  phases, which

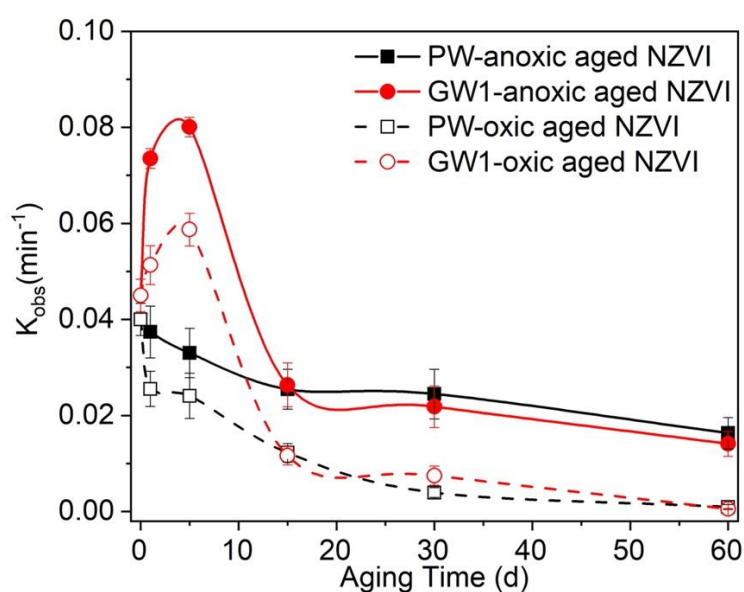
264 could potentially interfere with the NZVI aging process, GW1 was selected and used

265 for the kinetic assessment (reduction and adsorption) of aged samples.

266

267

### 268 3.2. Effects of NZVI aging products on the reduction of *p*-NP



269

270 Figure 2. Variation of pseudo-first-order kinetic rate constants ( $k_{obs}$ ,  $\text{min}^{-1}$ ) of *p*-NP

271 reduction with the aging time of differently aged NZVIs. Experimental conditions: [*p*-

272 NP]<sub>initial</sub> = 0.1 mM, [NZVI] = 50 mg L<sup>-1</sup>, reaction pH = 9.0 ± 0.2. GW: groundwater; PW:

273 pure water. Correlation coefficient ( $r^2$ ) ranges from 0.95 to 0.99.

274

275 Kinetics of removal of *p*-NP by different aged NZVI particles were monitored to

276 check the impact of aging time on the overall reduction ability of NZVI suspension (Fig.

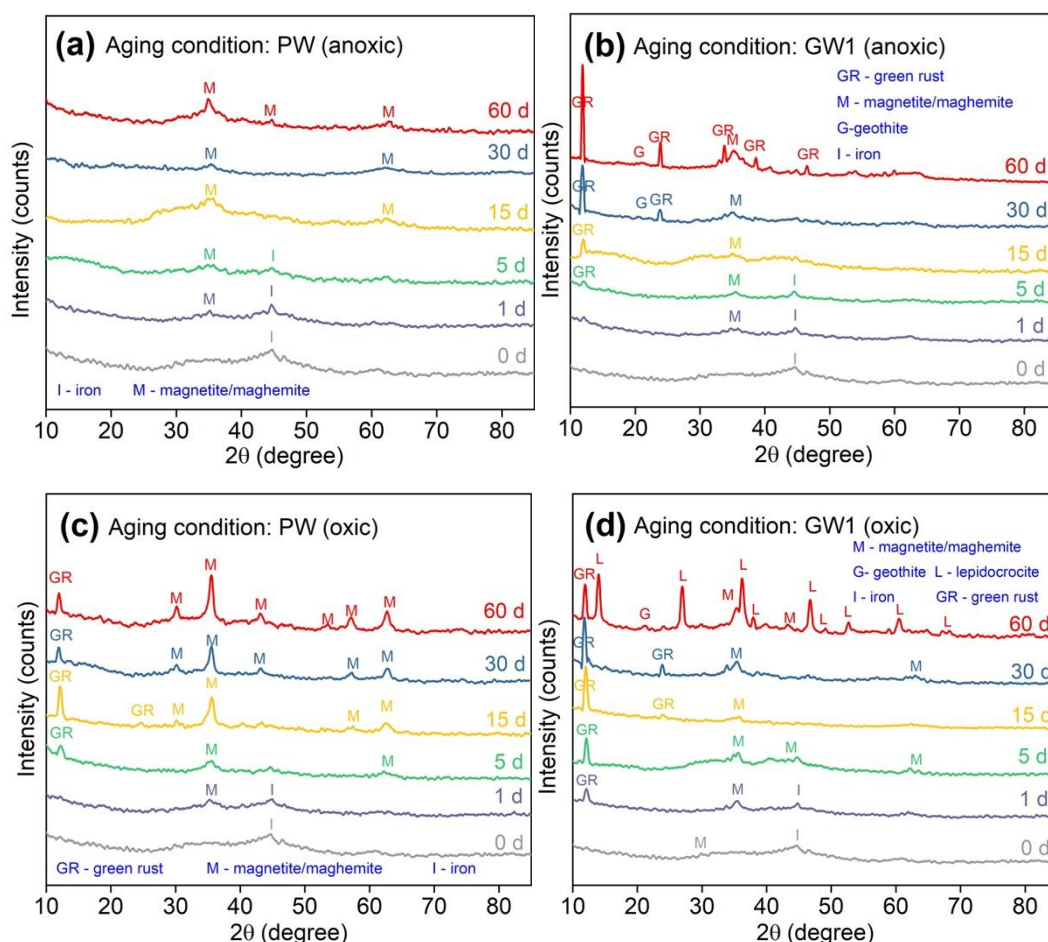
277 S5). For PW systems,  $k_{obs}$  values continuously decreased as the aging time increased

278 under both anoxic and oxic conditions (Fig. 2). Almost 50% of *p*-NP was reduced into  
279 *p*-AP in the 60 d-aging sample under anoxic conditions, while no reduction was  
280 observed for the 60 d-aged samples under oxic conditions (Fig. S5). A bell-shaped curve  
281 was observed for  $k_{\text{obs}}$  variation with aging time for GW1-aged NZVI; *i.e.*,  $k_{\text{obs}}$  values  
282 increased over the early stage of aging (0–5 d) and then decreased with further aging.  
283 In particular, the reductive ability of NZVI in groundwater reached a maximum after 5  
284 d aging, which was much higher (~1.8 times) than that of the fresh materials. In general,  
285 the samples of anoxic-aged NZVI showed better *p*-NP reduction than that of the oxic-  
286 aged NZVI. Similar trend of NZVI reactivity against aging time in simulated  
287 groundwater under anoxic conditions has been previously reported (Xiao et al. 2022).  
288 This behavior could be explained by the preservation of fresh NZVI and/or the  
289 occurrence of more reactive Fe phases under anoxic conditions.

290 In order to assess the phase transformation of NZVI in PW and GW1 systems, XRD  
291 analyses of secondary iron minerals were conducted under oxic and anoxic conditions  
292 (Fig. 3). The abundance of the  $\alpha$ -Fe phase decreased gradually for all the samples. For  
293 PW-anoxic-aged NZVI, the XRD peaks of Fe(0) remained until 5 d, and  
294 magnetite/maghemite was detected as the main aging product (Fig. 3a), while the  
295 disappearance of the Fe(0) peak coupled with the appearance of carbonate green rust  
296 and magnetite/maghemite was observed in the 5 d-aged sample of PW-oxic-aged NZVI  
297 (Fig. 3c). In contrast, peaks of carbonate green rust and magnetite/maghemite were  
298 detected in GW1-anoxic-aged NZVI, with the disappearance of Fe(0) observed at



299 longer aging times (Fig. 3b). In GW1-oxic-aged NZVI, an increase in peaks of  
 300 carbonate green rust and magnetite/maghemite was observed at only 1 d of aging (Fig.  
 301 3d). Then, a significant increase in Fe(III)-oxyhydroxides (lepidocrocite and/or goethite)  
 302 with a decrease in peaks of carbonate green rust at 60 d was observed, suggesting the  
 303 conversion of carbonate green rust into lepidocrocite and/or goethite under oxic  
 304 conditions (Legrand et al. 2004, Schwertmann and Fechter 1994). More details about  
 305 the changes in solution chemistry and pH values of NZVI suspensions along the aging  
 306 process are given in the SI (Fig. S6).



307

308

309 Figure 3. XRD pattern of fresh and NZVI aging products: (a) PW-anoxic-aged NZVI,

310 (b) GW1-anoxic-aged NZVI, (c) PW-oxic-aged NZVI, and (d) GW1-oxic-aged NZVI.

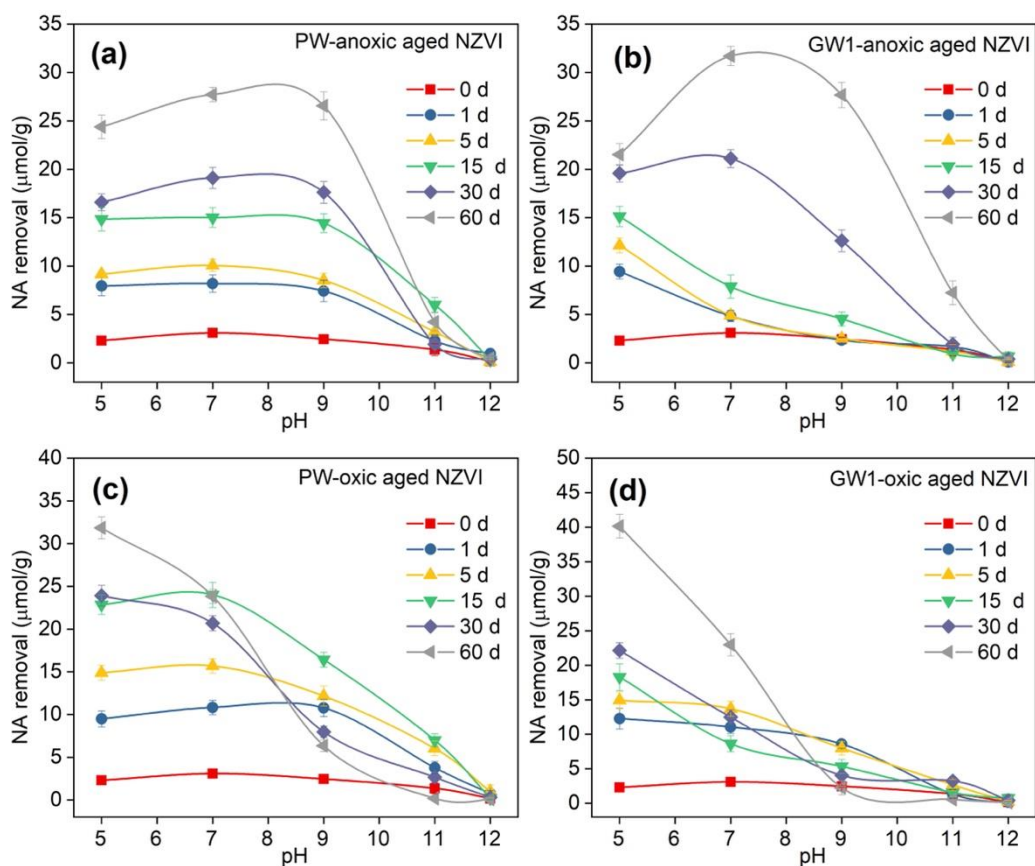
311 Experimental conditions:  $[p\text{-NP}]_{\text{initial}} = 0.1 \text{ mM}$ ,  $[\text{NZVI}] = 50 \text{ mg L}^{-1}$ , reaction  
312  $\text{pH} = 9.0 \pm 0.2$ . GW: groundwater; PW: pure water.

313

314 Collectively, these results showed that NZVI gradually lost its reactivity under both  
315 anoxic and oxic conditions in the PW system, probably due to the consumption of Fe(0)  
316 and accumulation of an oxyhydroxide layer coating the NZVI surface. In groundwater  
317 systems, though an initial enhancement of *p*-NP removal was observed over a short  
318 aging time (1–5 d), a decline was observed at later aging times. The greater reduction  
319 ability of carbonate green rust compared to that of magnetite, maghemite, lepidocrocite,  
320 or goethite (see Fig. S4) may explain the higher  $k_{\text{obs}}$  values observed in groundwater  
321 systems over the initial aging period. Previous work has also shown that the breakdown  
322 of the iron oxide shell coating of the ZVI may occur during the early stage of aging,  
323 thereby allowing better access to the core Fe(0) (Xie and Cwiertny 2012). Furthermore,  
324 as previously reported, the divalent cationic metal contained in groundwater may bind  
325 to surface coatings and induce surface oxide layer dissolution or NZVI depassivation  
326 (Liu et al. 2014).

327

328 3.3. Effects of NZVI aging products on the adsorption of nalidixic acid



329

330

331 Figure 4. Nalidixic acid adsorption versus pH by fresh and different aged NZVI samples:

332 (a) PW-anoxic-aged NZVI, (b) GW1-anoxic-aged NZVI, (c) PW-oxic, and (d) GW1-

333 oxic. Experimental conditions:  $[NA]_{initial} = 10 \mu M$ ,  $[NZVI] = 50 \text{ mg L}^{-1}$ , adsorption

334 duration = 2 h. GW: groundwater; PW: pure water.

335

336 NA adsorption to differently aged NZVI particles was investigated over a wide pH

337 range (5–12) (Fig. 4). The NA adsorption of NZVI aging products generally increased

338 with increasing aging time, especially under acidic/neutral conditions. However, a

339 different scenario of NA adsorption was observed for groundwater-aged NZVI samples.

340 NA adsorption by GW1-anoxic-aged NZVI decreased sharply as the pH increased, but  
341 the adsorption envelope exhibited a bell-shaped curve with increasing aging time. In  
342 contrast, GW1-oxic-aged NZVI exhibited an inversed S-shaped adsorption curve.

343       Considering the different binding affinity of NA to different iron minerals (Cheng  
344 et al. 2018, Xu et al. 2017b), this adsorption behavior by aged NZVI could be attributed  
345 to the change in mineral composition of NZVI aging products. The adsorption capacity  
346 of individual Fe oxyhydroxides, including magnetite, maghemite, carbonate green rust,  
347 lepidocrocite, and goethite, were evaluated over the same pH range (5–12) (Fig. S7). A  
348 negligible amount of NA was adsorbed by fresh NZVI, whereas Fe-(hydro)oxides  
349 exhibited significant NA adsorption capacity, especially in acidic to neutral pH. Under  
350 alkaline conditions, green rust exhibited better NA adsorption performance (when the  
351 adsorbed amount was normalized to mass and not surface area) than magnetite.  
352 However, a quantitative comparison of adsorption capacities must be made with caution  
353 since these synthetic minerals have different properties, including crystallinity, specific  
354 surface area, and surface charge.

355       According to the shape of the NA adsorption envelope (Fig. S7), more adsorption  
356 at circumneutral pH was observed with Fe(II)-Fe(III) mixed valent minerals (*e.g.*,  
357 magnetite and carbonate green rust), while Fe(III) bearing minerals (*e.g.*, lepidocrocite,  
358 goethite, and maghemite) exhibited an S-shaped curve or downward trend. Generally,  
359 organic ligands binding to metal-oxides show maximum adsorption at a pH near the  
360 pKa value (6.19 for NA). Indeed, previous reports showed typical NA adsorption by

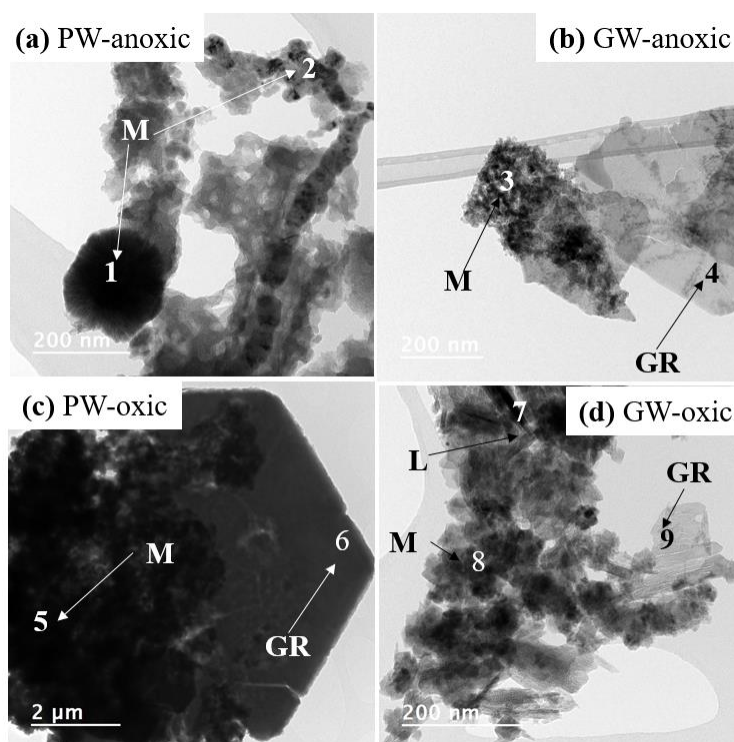
361 Fe-oxides with maximum NA adsorption at pH around 6 (Robberson et al. 2006, Xu et  
362 al. 2017b). However, the pH-adsorption curve of NA shifted to larger pH values in the  
363 case of magnetite and green rust, probably because of the presence of released Fe(II) in  
364 solution. As previously observed for magnetite, the addition of dissolved Fe(II) in  
365 suspension increased the NA adsorption at neutral to alkaline pH values (Cheng et al.  
366 2018). Here, Fe(II) release during NA adsorption was monitored for the 60 d-aged  
367 sample and presented in Fig. S8. Ferrous ion release was detected in all cases at pH 5  
368 and 7 and became negligible at pH above 9. Interestingly, the pH dependence of NA  
369 adsorption is fully consistent with that of dissolved Fe(II) concentration. For instance,  
370 a high dissolved Fe(II) amount was observed for anoxic-aged NZVI samples, which  
371 exhibited greater adsorption performance even at high pH values. PW-oxic-aged NZVI  
372 samples showed more NA adsorption than GW-oxic-aged NZVI under alkaline  
373 conditions. This correlation suggests that the amount of dissolved Fe(II) or the mineral  
374 bound-Fe(II) plays a key role in NA adsorption behavior onto NZVI secondary phases.  
375

#### 376 *3.4. Surface complexation modeling for nalidixic acid binding onto the 60 d-aged* 377 *sample*

378 First, determining the mineral composition of the aged samples is a prerequisite to  
379 describing the NA binding to secondary iron phases. In this study, the most aged sample  
380 (60 d) was selected to determine the proportion of identified secondary minerals (see

381 Table S5). Almost 100% of the magnetite/maghemite phase was present in PW-anoxic-  
382 aged NZVI, while GW1-anoxic-aged NZVI contained approximately 55% of  
383 magnetite/maghemite, 10% of goethite, and 35% of carbonate green rust. For PW-oxic-  
384 aged NZVI, magnetite/maghemite was the main aging product (~86%) with 14% of  
385 carbonate green rust, while GW1-oxic-aged NZVI contained various Fe mineral phases  
386 (magnetite/maghemite, ~55%; goethite, ~8%; carbonate green rust, ~7%; and  
387 lepidocrocite, ~30%).

388



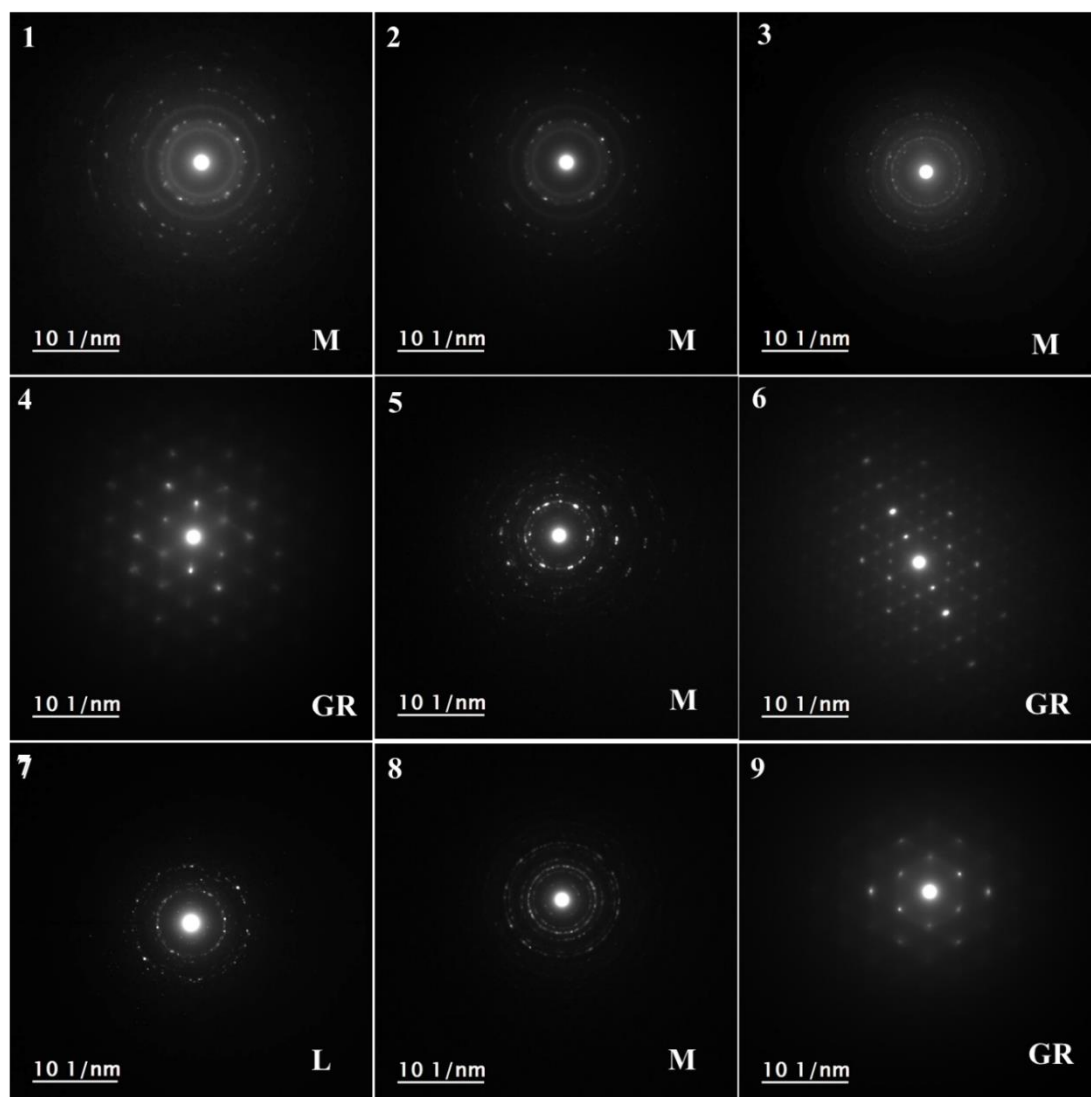
389

390 Figure 5. Transmission electron microscopy images of NZVI aging products at 60 days  
391 under different conditions: (a) PW- anoxic system, (b) GW-anoxic system, (c) PW-oxic  
392 system, and (d) GW-oxic system. Note: M: magnetite/maghemite; GR: green rust; L:  
393 lepidocrocite; GW: groundwater; PW: pure water. (Electron diffraction patterns of the

394 numbered areas are presented in Fig. 6).

395

396 HR-TEM images confirmed that the initial chain-like aggregated structures and  
397 large-sized spherical aggregates (approximately 200 nm) of NZVI (Fig. S1) were  
398 transformed into magnetite/maghemite after 60 d of aging in a PW-anoxic system (Fig.  
399 5a). In GW1-anoxic-aged NZVI samples, the particle size of magnetite/maghemite  
400 decreased significantly (approximately 5 nm), and magnetite/maghemite seemed to be  
401 attached to the surface of the hexagonal shape of carbonate green rust (Fig. 5b). Under  
402 oxic conditions, carbonate green rust was observed in both PW- and GW1-aged  
403 products (Figs. 5c, d). Particularly, the co-existence of magnetite with carbonate green  
404 rust was detected in PW-oxic-aged NZVI samples, while needle-shaped particles of  
405 lepidocrocite were observed in GW1-oxic-aged NZVI. All the SAED patterns of  
406 specific Fe mineral phases in Figure 5 are also provided in Figure 6, which shows the  
407 typical patterns of each mineral (Araújo-Neto et al. 2014, Génin et al. 2005, Krystofiak  
408 et al. 2013, Liao et al. 2020).



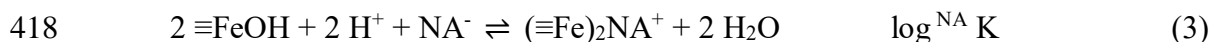
410 Figure 6. Electron diffraction patterns of selected areas from Fig. 5. Note: M,  
 411 magnetite/maghemite; GR, green rust; L, lepidocrocite.

412

413 To describe the mechanism underlying NA adsorption onto the 60 d-aged sample,  
 414 we applied a surface complexation model. We assumed that NA binds to two surface  
 415 hydroxy groups by involving its carboxylate and its keto-group as follows :(Cheng et  
 416 al. 2018)

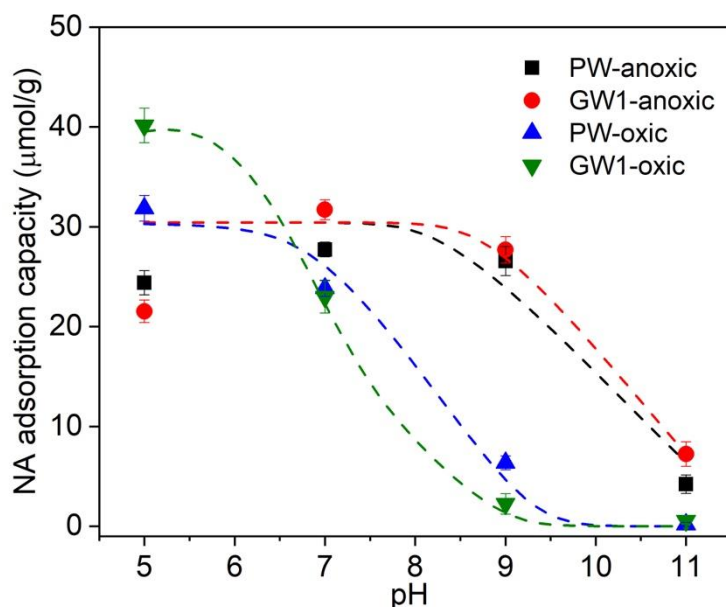


417



419

420 Only the predominant phases were taken into consideration, and the mixed valent  
421 iron minerals (*i.e.*, magnetite and green rust) were supposed to exhibit similar behavior  
422 with respect to NA adsorption. Consequently, the magnetite parameters were used in  
423 the adsorption model in PW-anoxic-aged NZVI, GW1-anoxic-aged NZVI, and PW-  
424 oxic-aged NZVI samples. In the case of GW1-oxic-aged NZVI, the dominant phases  
425 were maghemite and lepidocrocite. NA adsorption to maghemite or lepidocrocite was  
426 first calculated, and all modeling parameters are shown in Table S2. The complexation  
427 of NA-Fe(II) was accounted for by using dissolved Fe(II) concentration as input  
428 parameters in this model.



429

430 Figure 7. Experimental (symbols) and modelled (dashed lines) variation of naldixic  
431 acid adsorption capacity of 60 d-aged NZVI sample with pH.

432

433       The model satisfactorily predicted the pH dependence of NA adsorption to aged  
434 NZVI but overestimated the NA adsorption at pH 5 in the anoxic-aged NZVI system  
435 (Fig. 7). This may be ascribed to the higher amount of dissolved Fe(II) under acidic  
436 conditions (see Fig. S8), which can affect NA-Fe (II) complexation in solution and thus  
437 ternary surface complexation (*i.e.*, surface–metal–ligand complex) (Cheng et al. 2018).  
438 We also simplified the model by considering only the predominant phase of mixed-  
439 valence oxides (magnetite) in anoxic-aged NZVI samples despite the co-existence of  
440 green rust. Nevertheless, the good accuracy of the experimental and modeling data at  
441 neutral and alkaline pH confirms the key role of surface-bound Fe(II) in the adsorption  
442 of NA.

443       In summary, aged NZVI samples showed a good capacity for NA adsorption, which  
444 increased with aging time. The high NA adsorption onto NZVI products at neutral to  
445 alkaline pH can be ascribed to the surface-bound Fe(II) in the secondary phases.

446

#### 447 **4. Conclusions**

448       We investigated the aging and reactivity of NZVI in various groundwater systems.  
449 First, the nature of secondary iron phases resulting from NZVI aging in groundwater is  
450 strongly dependent on the groundwater composition. The final products of NZVI after  
451 reaction were mainly magnetite in pure water system, while green rust was predominant

452 in groundwater systems. With the aging process (up to 60 d), NZVI continuously lost  
453 its reductive activity in the PW system. However, in the groundwater this reductive  
454 ability was first enhanced in the short-term (1-5 d) and then declined at longer aging  
455 times. Adsorption tests revealed higher NA binding to NZVI aging products (~ 30  
456  $\mu\text{mol/g}$  at pH 7), while NA uptake by fresh NZVI was negligible. Notably, the  
457 adsorption capacity of NA generally increased with aging time, with unexpected greater  
458 adsorption at neutral to alkaline pH values. Additional experiments and surface  
459 complexation modeling suggested that this strong adsorption at alkaline conditions can  
460 be attributed to the surface-bound Fe(II). These results shed light on an overlooked  
461 aspect of interactions of environmental compounds with the secondary Fe minerals  
462 resulting from NZVI corrosion in groundwater. Our findings will also help to predict  
463 the fate of NZVI in groundwater, and the impact of the secondary Fe minerals on the  
464 mobility and transformation of contaminants in soil and groundwater.

465

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472

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