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1 **Nalidixic Acid and Fe(II)/Cu(II) co-adsorption at goethite and**
2 **akaganéite surfaces**

3
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16 **ABSTRACT**

17 Interactions between aqueous Fe(II) and solid Fe(III) oxy(hydr)oxide surfaces play
18 determining roles on the fate of organic contaminants in nature. In this study, the adsorption of
19 nalidixic acid (NA), a representative redox-inactive quinolone antibiotic, on synthetic goethite
20 (α -FeOOH) and akaganéite (β -FeOOH) were examined under varying conditions of pH and
21 cation type and concentration, by means of adsorption experiments, attenuated total reflectance-
22 Fourier transform infrared spectroscopy, surface complexation modeling (SCM) and powder
23 X-ray diffraction. Batch adsorption experiments showed that Fe(II) had marginal effects on NA
24 adsorption onto akaganéite but enhanced NA adsorption on goethite. This enhancement is
25 attributed to the formation of goethite-Fe(II)-NA ternary complexes, without the need for
26 heterogeneous Fe(II)-Fe(III) electron transfer at low Fe(II) loadings (2 Fe/nm^2), as confirmed
27 by SCM. However, higher Fe(II) loadings required a goethite-magnetite composite in the SCM
28 to explain Fe(II)-driven recrystallization and its impact on NA binding. The use of a surface
29 ternary complex by SCM was supported further in experiments involving Cu(II), a prevalent
30 environmental metal incapable of transforming Fe(III) oxy(hydr)oxides, which was observed
31 to enhance NA loadings on goethite. However, Cu(II)-NA aqueous complexation and potential
32 Cu(OH)_2 precipitates counteracted the formation of ternary surface complexes, leading to
33 decreased NA loadings on akaganéite. These results have direct implications on the fate of
34 organic contaminants, especially those at oxic-anoxic boundaries.

35 **Keywords:** Fe(III) oxy(hydr)oxide; Fe(II); Cu(II); quinolones antibiotics; modeling.

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37

Synopsis

38 This work shows how the fate of antibiotics can be affected in Fe(II)- and Cu(II)- and

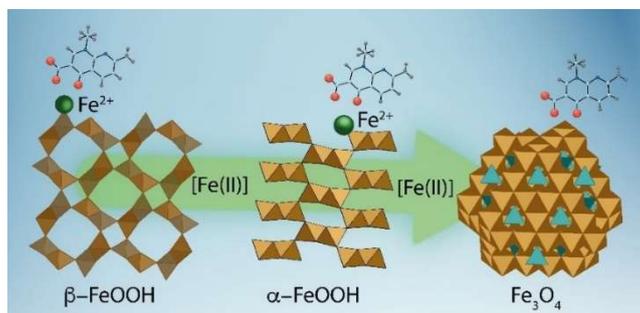
39 FeOOH-bearing environments, such as oxic-anoxic interfaces.

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41

Graphical Abstract

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44

45 1. INTRODUCTION

46 In natural waters and soils, iron can coexist as solid Fe(III) oxy(hydr)oxides minerals and
47 soluble Fe(II), especially at oxide-anoxic boundaries.^{1,2} Electron transfer between sorbed Fe(II)
48 species and solid Fe(III) oxy(hydr)oxide surfaces is an especially important mechanism³⁻⁵ in
49 these settings as it plays a significant role in triggering mineralogical transformations and
50 altering contaminant dynamics in the environment.⁶⁻⁹ Some Fe(III)-bearing phases can undergo
51 secondary mineralization reactions (ferrihydrite → goethite; lepidocrocite → magnetite)¹⁰⁻¹²
52 following Fe(II) adsorption, while other more stable (goethite,¹³ magnetite⁴ and hematite³)
53 phases can undergo intensive atom exchange without forming new product minerals.

54 Heterogeneous systems containing Fe(III) oxy(hydr)oxides and Fe(II) are very efficient in
55 environmental remediation due to their high reductive reactivity. Consequently, numerous
56 studies have focused on investigating their efficacy in remediation of both inorganic^{6, 14} and
57 organic contaminants.^{9, 15, 16} Redox reactions are driven by the high reactivity of adsorbed Fe(II),
58 as the complexation of Fe(II) with Fe(III) oxy(hydr)oxides can significantly lower the redox
59 potential of Fe(II), and thus enhance the reductive reactivity.^{9, 17, 18} However, the influence of
60 Fe(II) on the binding capacity of Fe(III) oxy(hydr)oxides has been less studied. The existing
61 research on this subject, limited to a few studies,^{7, 8, 19} has chiefly focused on inorganic
62 compounds. For instance, Fe(II) binding onto goethite and hematite was reported to increase
63 adsorption of sulfate and phosphate through ternary complexation and electrostatic
64 interactions.¹⁹ However, Fe(II) had only a minor effect on the fate of arsenate.⁷ In contrast,
65 Frierdich et al.⁸ found that Fe(II)-induced recrystallization of goethite and hematite

66 repartitioned Ni(II) at the mineral-water interface and substantially altered the fate of Ni(II).
67 Still, little is known about the impact of Fe(II) on the binding of organic, redox-inactive species
68 at Fe(III) oxy(hydr)oxide mineral surfaces. Previous work showed that Fe(II) bound to goethite
69 only slightly enhanced phthalic acid adsorption in the form of ternary outer-sphere species,⁹ yet
70 more information on how Fe(II)-organic binding alters Fe(III) oxy(hydr)oxide transformations
71 in these mixed redox systems is needed.

72 This knowledge is especially needed given the increasing scrutiny on the fate of antibiotics
73 (*e.g.* quinolone) in the environment, a consequence of their overuse and incomplete removal by
74 wastewater treatments.²⁰⁻²² Our recent studies have showed that Fe(III) oxy(hydr)oxides such
75 as goethite (α -FeOOH), akaganéite (β -FeOOH) and magnetite (Fe_3O_4) play key roles in the
76 mobility and fate of quinolone antibiotics.²³⁻³⁰ However, Fe(II) coexisting in soils and sediments
77 with Fe(III) oxy(hydr)oxides, resulting from microbial respiration and weathering of Fe-bearing
78 minerals, could also affect the fate of quinolone antibiotics. Two of these minerals were chosen
79 in this study include (i) goethite, which is the most thermodynamically stable iron oxyhydroxide
80 mineral at low-temperature and has significant implications for contaminant mobility in
81 terrestrial and aquatic environments,³¹ and (ii) akaganéite, a polymorph of goethite that forms
82 in environments rich in Fe(II) and Cl^- .³² In addition, OH populations, reactive hydroxyl groups
83 and intrinsic protonation and deprotonation constants were well documented for goethite^{23, 25,}
84 ^{33, 34} and akaganéite,³⁵⁻³⁷ which make them ideal model phases for fundamental interfacial
85 studies.

86 In this work, we investigated the impact of dissolved Fe(II) on the ability of goethite and

87 akaganéite in binding nalidixic acid (NA), a representative synthetic quinolone antibiotic that
88 is widely present in aquatic and terrestrial environments at concentrations ranging from ng/L to
89 $\mu\text{g/L}$.^{1,38-40} We resolved whether coexisting Fe(II) and NA (i) compete for sorption sites, (ii)
90 cooperatively bind via ternary complexation, and/or (iii) trigger mineralogical transformations.
91 To elucidate these mechanisms, we explored Fe(II) and NA loadings on goethite and akaganéite
92 by batch adsorption and surface complexation modeling, and tracked for phase changes by X-
93 ray diffraction and transmission electron microscopy. We also explored the role of Cu(II), a
94 common trace cation present in groundwater and surface waters alongside Fe(III)
95 oxy(hydr)oxides and antibiotics.^{27, 41-43} The inability of Cu(II) to induce transformation of Fe(III)
96 oxy(hydr)oxides provides an opportunity to explore the binding mechanisms in ternary systems
97 (cation/NA/goethite) using attenuated total reflectance-Fourier transform infrared (ATR-FTIR)
98 spectroscopy, without the complication rising from redox-induced mineral transformation
99 and/or possible Fe(II) oxidation. The zeta potential of minerals was also measured to account
100 for the electrostatic effects under various solution chemistry conditions. Our work provides
101 evidence for cation-NA-mineral ternary complexation, and a Fe(II)-concentration/surface
102 loading dependence on the recrystallization of Fe(III) oxy(hydr)oxides.

103

104 **2. MATERIALS AND METHODS**

105 **2.1 Chemicals**

106 Nalidixic acid (NA, $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_3$), iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ferric nitrate
107 nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), cupric chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), hydrochloric acid

108 (HCl), sodium hydroxide (NaOH), piperazine-1, 4-diethyl sulfonic acid (PIPES) and NaCl were
109 obtained from Sigma-Aldrich. All chemicals used in the study were of pro-analytical quality or
110 better and used as received. Ultrapure “Milli-Q” water (specific resistivity, $18.2 \text{ M}\Omega \text{ cm}^{-1}$) was
111 used for the preparation of all solutions. A stock solution of NA (purity >99%) was prepared by
112 dissolving 232 mg (1 mmole) of NA in 20 mL of 1 M NaOH, followed by dilution to a final
113 volume of 1 L with ultrapure water. All experiments were conducted in an anaerobic chamber
114 (N_2 -glovebox, MIKROUNA). All solutions were purged with N_2 for 4 h prior to their
115 introduction into the glovebox.

116

117 **2.2 Synthesis and characterization of goethite and akaganéite**

118 Goethite^{27, 33} and akaganéite³⁵⁻³⁷ were synthesized as described in previous studies, and the
119 detailed procedures are given in Text S1(Supporting Information). Phase identity and purity of
120 minerals were confirmed by powder X-ray diffraction (XRD), using a D8 ADVANCE X-ray
121 diffractometer (Bruker, Germany) equipped with a Co X-ray source ($\lambda=0.179 \text{ nm}$). The
122 diffractograms were recorded at 40 kV and 40 mA over 2θ range from 10° to 85° with a 0.02°
123 step size and a collection of 3 s per point. The phases were identified using a MDI Jade 6
124 software. The size and morphology of as-synthesized minerals were analyzed by transmission
125 electron microscopy (TEM, Tecnai G2 F30 S-TWIN, USA) operated at 300 kV and in bright-
126 field imaging mode. The TEM images indicated that goethite has a typical needle-like shape,
127 with length between 110-150 nm and width of 8-12 nm, while akaganéite presents acicular
128 particles of 4.5-5.7 nm in width and 25-31 nm in length (Figure S1). $\text{N}_2(\text{g})$

129 adsorption/desorption isotherms were recorded using a nitrogen adsorption apparatus (JWGB
130 SCI.& TECH, JW-BK132F, China) at 77 K before degassing overnight at 353 K, and the
131 calculated B.E.T. specific surface areas were 98 m²/g for goethite and 183 m²/g for akaganéite,
132 respectively. The zeta potential of minerals in the presence of different adsorbates was
133 determined using a zeta potential analyzer (NanoBrook 90Plus zeta, Brookhaven, USA). The
134 goethite or akageneite suspensions in the presence of NA and/or cations were adjusted to the
135 desired pH in 10 mM NaCl and equilibrated for 24 h under nitrogen. Aliquots were sampled for
136 ζ determinations and each sample was measured three times with 12 - 30 runs for every
137 measurement. The ζ potential values were averaged over 3 measurements.

138

139 **2.3 Batch experiments**

140 Adsorption batch experiments were carried out in a glovebox ($pO_2 < 1$ ppm) to eliminate any
141 O₂-driven redox reactions. Kinetic adsorption studies were conducted in 50 mL polypropylene
142 tubes containing suspensions of 50 m²/L goethite or akaganéite with 10 μ M NA or 300 μ M
143 Fe(II) in a background electrolyte of 10 mM NaCl. pH was maintained at 7.0 ± 0.1 using PIPES
144 solutions. Aliquots were sampled during the experiments and filtered (0.2 μ m, polyethersulfone
145 membrane filter) for analysis. Equilibrium adsorption experiments were conducted in 15 mL
146 polypropylene tubes. Briefly, solutions of 10 or 100 μ M NA were mixed with goethite or
147 akaganéite (50 m²/L) in 10 mM NaCl. FeCl₂ (50, 100, 200, 500 μ M) or CuCl₂ (10, 50, 100 and
148 200 μ M) were added to the solutions in order to study the effects of Fe(II) or Cu(II) on NA
149 adsorption. The pH was then adjusted to the desired value ($4 < \text{pH} < 10$) with 0.1 M HCl or

150 NaOH solutions. Preliminary experiments showed that adding NA or Fe(II) simultaneously or
151 sequentially after 24 hours of equilibration had negligible effects on adsorption results (Figure
152 S2). Desorption tests were conducted at pH 11 to check the mass balance, and an average
153 recovery of $99 \pm 1\%$ confirmed the mass balance. In another set of experiments, adsorption
154 isotherms were collected for varied Fe(II) concentrations (0-500 μM) with 10 μM NA, and the
155 pH was maintained using PIPES solutions at 7.1 ± 0.1 . All suspensions were equilibrated on a
156 platform shaker at room temperature for 24 h, and suspension pH values were measured again
157 before filtration (0.2 μm) with a benchtop pH/mV meter (ST3100, Ohaus) calibrated on a daily
158 basis. To investigate the mineral transformations under examination, mixtures of 50 m^2/L
159 goethite or akaganéite in 10 mM NaCl with 10 μM NA and varying concentrations of Fe(II)
160 were prepared at $\text{pH } 9.0 \pm 0.1$ for 24 h. The suspensions were then centrifuged and freeze-dried
161 before XRD and TEM characterization.

162 Aqueous NA concentrations were stored in a refrigerator and determined within 24 h using
163 an Ultimate 3000 high performance liquid chromatography (HPLC) system equipped with a
164 reversed-phase C18 column (250 \times 4.6 mm i.d., 5 μm) and a UV detector (258 nm). The mobile
165 phase was a mixture of acetonitrile/water (60:40 v/v) containing 0.1% of formic acid. The flow
166 rate of the mobile phase was set at 1 mL/min in the isocratic mode. Aqueous Fe(II) and Fe(III)
167 concentrations were determined immediately after filtration by the phenanthroline method.⁴⁴
168 Concentrations of Cu(II) were analyzed on an Atomic Absorption Spectrometer (Thermo, ICE-
169 3500). All experiments were performed at least twice, and the reproducibility of the
170 measurements was around 3% for NA and 5% for Fe(II) and Cu(II).

171 **2.4 ATR-FTIR Spectroscopy**

172 Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra of free NA
173 species and bound NA onto goethite with and without Cu(II) were recorded with a Bruker
174 Vertex 70/V FTIR spectrometer equipped with a DLaTGS detector. All spectra were collected
175 in the 600–4000 cm^{-1} range at a resolution of 4.0 cm^{-1} and at a forward/reverse scanning rate
176 of 10 Hz. Each spectrum was an average of 250 scans. The Blackman-Harris 3-term apodization
177 function was used to correct phase resolution. Sample preparation for the ATR-FTIR analysis
178 followed the same procedure as for batch sorption experiments. Two series of experiments were
179 conducted at pH 4–10 in 10 mM NaCl for 50 m^2/L goethite and (i) 100 μM NA or (ii) 100 μM
180 NA with 100 μM Cu(II). Spectra of goethite suspensions in 10 mM NaCl were also taken in the
181 absence of NA and Cu(II) and then subtracted from the spectra of sorbed NA and/or Cu(II) in
182 order to represent surface complexes only. Prior to ATR-FTIR analysis, tubes from batch
183 sorption experiments were centrifuged and then the centrifuged wet pastes were transferred
184 onto a diamond window of an Attenuated Total Reflectance (ATR) cell (Golden Gate, single-
185 bounce). A reference spectrum of aqueous NA was also acquired from a 10 mM NA solution in
186 1 M NaOH.

187 **2.5 Surface complexation modeling**

188 Surface complexation calculations were performed with PHREEQC (version 2),⁴⁵ and using
189 the “minteq.v4” database provided with this geochemical speciation code. The binding behavior
190 at goethite and akaganéite surfaces was described using the multisite complexation (MUSIC)
191 model approach.⁴⁶ Detailed information regarding the proportions of crystal planes and

192 corresponding reactive site densities are given in Text S2 in the SI. The electric double layer
193 and electrostatic interactions were described according to the three-plane model (TPM),⁴⁶
194 dividing the mineral–water interface into the 0-, 1-, and 2-planes. Charges of the adsorbates
195 were distributed among the 0 (H^+ , metal-bound complex), 1 (hydrogen-bound complex), and 2
196 (Na^+ , Cl^- , outer-sphere surface complexes) planes of the TPM and a charge distribution (CD)
197 term was employed for their description only if required. The values of surface site densities
198 and protonation constants, background electrolytes binding constants and capacitances for the
199 0-plane (C1) and 1-plane (C2) were taken from previous studies^{23, 24, 27} and are presented in
200 Table S1. The equilibrium constants for the formation of additional surface species are
201 documented in Table 1. The formation constants of NA–Fe(II) and NA–Cu(II) aqueous
202 complex were obtained from the literature.⁴⁷ Precipitation of $Fe(OH)_2(s)$ and $Cu(OH)_2(s)$ were
203 taken into account in the calculations (Table S1). Parameters of surface species in simple (binary)
204 systems were individually fitted using independent data sets, and then kept constant for
205 simulations in ternary systems. For example, NA–goethite surface complexation constants were
206 determined using NA adsorption data onto goethite, in close agreement with a previous study,²⁵
207 and then kept constant for the rest of simulations. The nature of Fe(II) surface complexes onto
208 goethite has been previously determined^{9, 19} and the corresponding surface complexation
209 constants were fitted using the Fe(II) adsorption data obtained in this study. Simulations were
210 then performed in the ternary goethite–Fe(II)–NA system without any parameter adjustment.
211 To mitigate the complexities arising from the precipitation of Cu(II) at high concentrations, we
212 exclusively used the data for Cu(II) at 200 μM for simulation purposes, without employing

213 them for the adjustment of constants. PhreePlot⁴⁸, which was used to estimate parameters,
214 employs a parameter optimization procedure that minimizes the weighted sum of squares of the
215 residuals to fit a model to experimental data. A modified Marquardt-Levenberg procedure⁴⁹
216 was applied. With this method, PhreePlot provides also a statistical uncertainty of the estimated
217 parameters (Table 1). For magnetite, we used the 2-pK_a-constant capacitance model approach
218 developed by Jolsterå et al.⁵⁰ The reactive site densities were determined as 1.50 sites nm⁻², and
219 the capacitance value was estimated as 2.1 F m⁻².

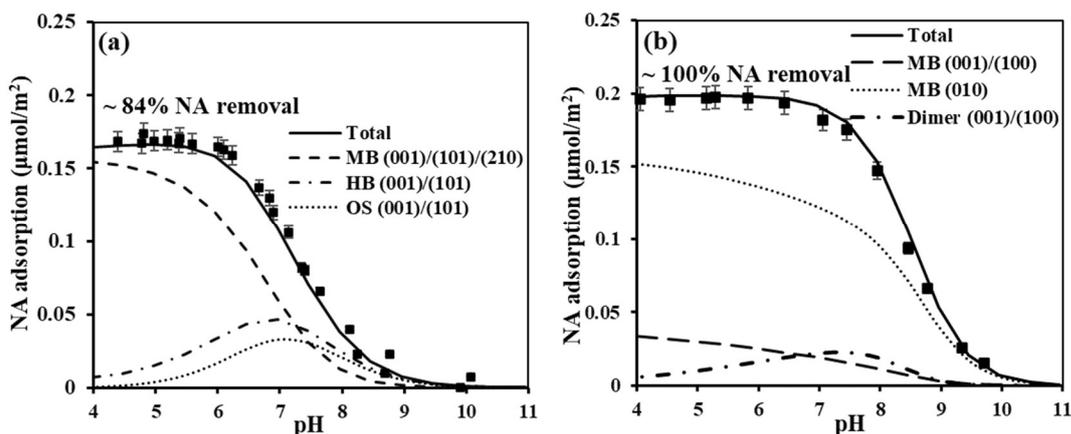
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221 3. RESULTS AND DISCUSSION

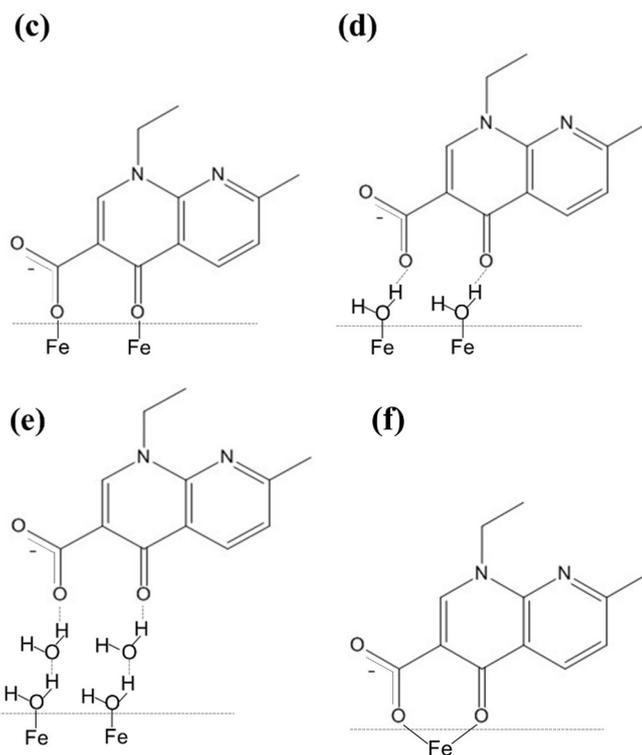
222 3.1. Nalidixic Acid adsorption onto goethite and akaganéite

223 Kinetics experiments showed that NA binding on goethite and akaganéite reached
224 equilibrium within 24 h (Figure S3), and mass balance confirmed that NA was removed only
225 by adsorption.

226



227



228

229 **Figure 1.** NA removal from solution for $[NA]_{tot} = 10 \mu\text{M}$ on $50 \text{ m}^2/\text{L}$ of (a) goethite and (b) akaganéite versus

230 pH in 10 mM NaCl at 25 °C. The corresponding percentage of NA removal at the plateau is also given. Lines

231 are model predictions for metal-bound (MB), hydrogen-bound (HB) and outer-sphere (OS) complexes. (c)

232 MB (d) HB (e) OS of NA at goethite (001)/(101)/(210) and akaganeité (001)/(100) surfaces, and (f) MB of

233 NA at akaganeité (010) surface.

234

235 NA adsorption follows the typically expected anion adsorption envelopes for quinolones.^{23,}

236 ²⁵ Here, surface loadings were highest in acidic to circumneutral pH, and substantially lower

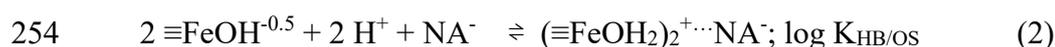
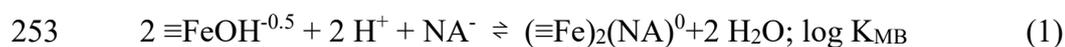
237 under alkaline conditions (Figure 1a). This can be explained by the increased electrostatic

238 repulsion between the deprotonated NA^- ($\text{pK}_a = 6.1$) species and negatively-charged mineral

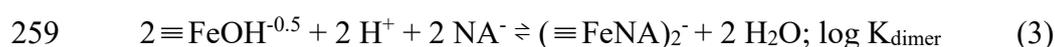
239 surface sites.

240 The ATR-FTIR spectra of NA bonded on goethite surfaces at different pH values showed

241 that the carbonyl group of bound NA was blue-shifted, and $\Delta\nu$ ($\Delta\nu = \nu_{\text{COO,as}} - \nu_{\text{COO,s}}$)^{51, 52}
 242 increased upon binding compared to the unbound NA (Text S4 and Figure S4a). Accordingly,
 243 the predominant NA binding mechanisms on goethite could involve the ketone group and one
 244 oxygen of the carboxylate group to (singly-coordinated) -OH groups of goethite.^{24, 25} This
 245 enables us to propose different surface complexes all involving carbonyl and carboxylic groups,
 246 in which -OH groups of goethite may or may not be of the same Fe(III) octahedron.⁵³ They
 247 include metal-bound (MB) complex with surface Fe sites, hydrogen-bound (HB) complex
 248 (surface hydration shared ion pair) with surface hydroxo groups and outer-sphere (OS) complex
 249 (solvent-surface hydration-separated ion pair) with protonated singly coordinated sites
 250 ($\equiv\text{FeOH}_2^{+0.5}$). The structures of the MB, HB, and OS surface complexes are shown in Figure
 251 1c-e, assuming the participation of two Fe(III) octahedra. These can be expressed through the
 252 following reactions (Table 1):



255 These reactions show similar stoichiometries but the charge distribution between 0-, 1-, and 2-
 256 planes differ depending on the position of NA at the mineral-water interface. In addition, at high
 257 NA loadings, a NA-NA dimer is formed through intermolecular interactions, in which the
 258 charge of one NA is located at the 0-plane, and the second one at the 1-plane:²⁵



260 NA adsorption on akaganéite was greater than that on goethite. At pH <7, ~100% of NA
 261 sorbed onto akaganéite, while the maximum NA uptake on goethite was only ~84% (Figure 1b).

262 We attribute this mineral-dependent adsorption to the larger (i) pH window for a positive surface
263 charge and (ii) reactive sites on akaganéite. The larger pH window for a positive charge stems
264 from the higher point-of-zero charge of akaganéite (9.6–10), compared to goethite (9.1–9.4).³³
265 ⁵⁴ The higher reactivity of akaganéite can be also explained by the occurrence of reactive
266 geminal $\equiv\text{Fe}(\text{OH}_2)_2^+$ groups at the (010) plane, which are known to have strong affinities for
267 anionic species.³⁵⁻³⁷

268 Based on previous crystallographic considerations and spectroscopic investigations,²³
269 surface complexes on the (001)/(100) planes of akaganéite are expected to be comparable to
270 those on the goethite (001)/(101) and (210) planes.²³ Therefore, the model for the (001)/(100)
271 planes of akaganéite includes the above surface reactions (eqs.1-3), i.e. bridging metal-bound,
272 hydrogen-bound complexes as well as a dimer. Additionally, to account for NA binding with
273 geminal $\equiv\text{Fe}(\text{OH}_2)_2^+$ groups at the (010) plane, a monocuclear six-membered chelate complex
274 was used, as follows (Figure 1f):



276 Surface complexation reactions and their corresponding constants for NA (Table 1) provide
277 insights into the pH-dependent behavior of NA loadings on goethite and akaganéite. NA surface
278 speciation on goethite suggests a predominance of MB complexes under acidic pH conditions
279 (Figure 1a) and a predominance of HB and OS complexes at high pH. In the case of akaganéite,
280 MB complexes are found to be the prominent species at all pH values for low NA loading (10
281 μM), primarily associated with the binding on the (010) plane (Figure 1). However, at high NA
282 loading (100 μM), the NA-NA dimer becomes the predominant species (Figure S5a). Moreover,

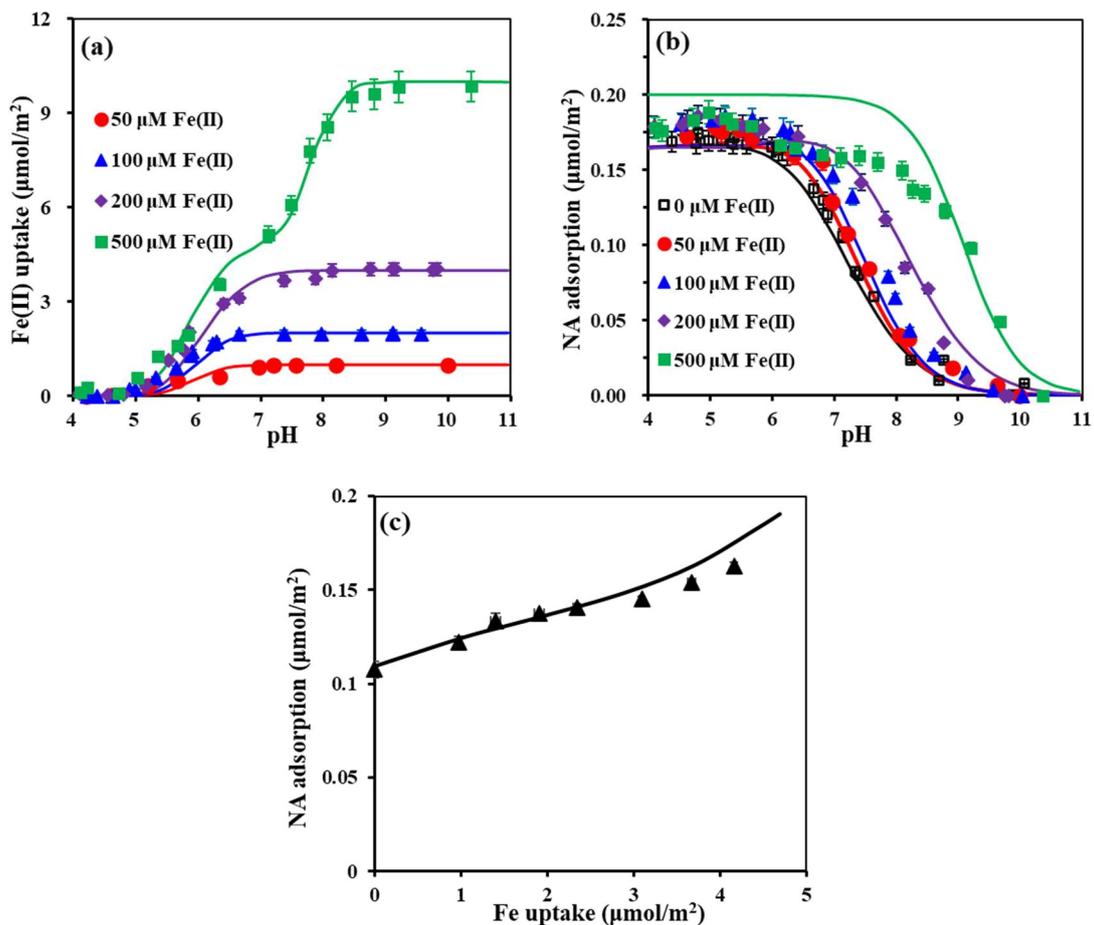
283 NaCl concentration variation (10-100 mM) exhibited negligible effect on NA adsorption,
284 aligning with the dominance of MB complexes on the akaganéite surface (Figure S5b).

285

286 3.2 Cation-NA co-binding on goethite and Fe(II)-driven catalytic recrystallization

287 As in the NA-minerals binary systems, kinetic experiments revealed that Fe(II) and NA
288 adsorption reactions reached equilibrium within 24 h (Figure S3). The presence of NA had no
289 effect on Fe(II) adsorption (Figure S6), and loadings were unaffected by the order of NA and
290 Fe(II) addition to the mineral suspensions (Figure S2).

291



292

293 **Figure 2.** (a) Fe(II) and (b) NA removal from solution for $[\text{NA}]_{\text{tot}} = 10 \mu\text{M}$ on $50 \text{ m}^2/\text{L}$ goethite in 10 mM

294 NaCl versus pH at different Fe(II) concentrations after 24 h reaction time. (c) NA adsorption versus Fe(II)

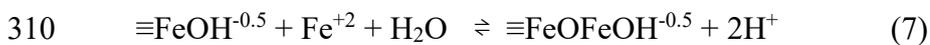
295 uptake. Experimental conditions: 10 μM NA and 0-500 μM Fe(II) adsorption onto 50 m^2/L goethite in 10
296 mM NaCl at $\text{pH} = 7.1 \pm 0.1$. Lines are modeling results for (a) Fe(II) and (c) NA adsorption onto goethite
297 without considering mineral transformations, (b) NA adsorption in the presence of 500 μM Fe(II) accounted
298 for the transformation of 25% of the initial goethite into magnetite.

299

300 Fe(II) enhanced NA adsorption onto goethite at $\text{pH} > 6$, with no significant influence at lower
301 pH values (Figure 2). While lower Fe(II) concentrations had only a minimal impact on NA
302 loadings, higher concentrations ($\geq 200 \mu\text{M}$) significantly increased NA loadings and even
303 changed the shape of the sorption edge. This observation suggests the existence of distinct
304 mechanisms governing the (co)binding of NA and Fe(II) species. Indeed, the presence of Fe(II)
305 could affect NA adsorption via several mechanisms. Firstly, Fe(II) can form aqueous complexes
306 with NA:⁴⁷

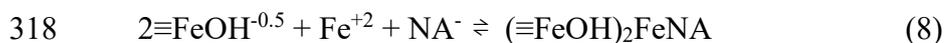


308 Secondly, Fe(II) can also adsorb onto goethite via the following reactions:^{9, 19, 55}



311 Here, the charge of the sorbed Fe(II) is located at the 0-plane. At the same time, alkaline
312 conditions favored Fe(II) precipitation as $\text{Fe}(\text{OH})_{2(\text{s})}$ (Figure S7). Eqs. 6-7, alongside
313 precipitation, fully accounted for the pH-dependent uptake of Fe(II) onto goethite (Figure 2a).
314 As a result, a change in the adsorption curve shape was observed at high amount of Fe(II) (500
315 μM) and at pH around pH 7, which can be attributed to the precipitation of $\text{Fe}(\text{OH})_{2(\text{s})}$.

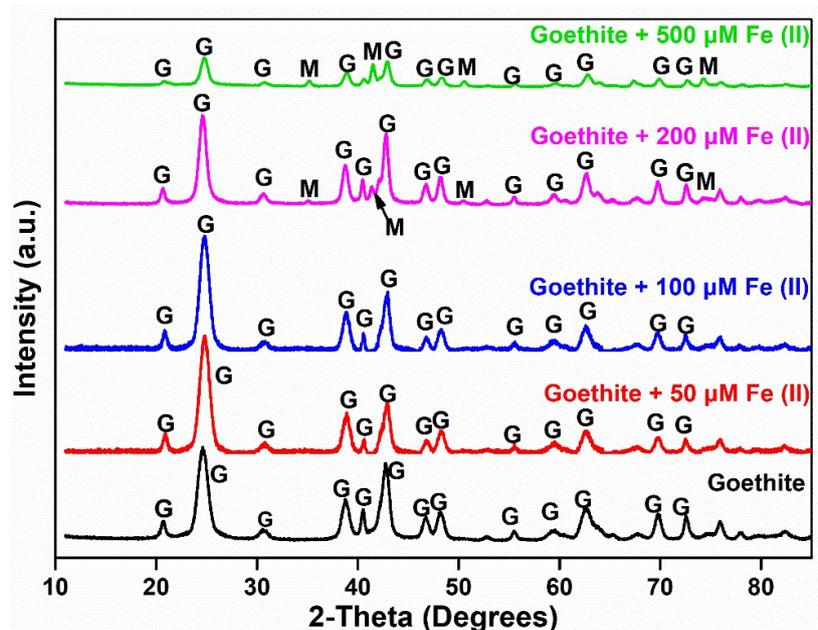
316 Finally, to account for the enhanced NA binding in the presence of Fe(II), a ternary
317 goethite–Fe(II)–NA complex was included in the model:



319 Our model successfully predicts NA binding to goethite at total loadings in the range of 50-200
320 μM Fe(II), by locating charges of Fe(II) and NA at the 0 plane. This is consistent with zeta
321 potential variation of goethite surface upon addition of Fe(II) or NA or both Fe(II) and NA
322 (Figure S8). For instance, addition of Fe(II) or Fe(II) and NA shifts the zeta potential towards
323 more positive values, creating a favorable condition for NA adsorption through ternary surface
324 complexation. Accounting for the electron transfer process between sorbed Fe(II) and Fe(III)
325 in goethite did not improve the modeling, as previously observed.¹⁹

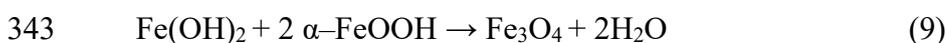
326 The effectiveness of the optimized model parameters for Fe(II) and NA adsorption was
327 validated by successfully predicting the co-adsorption of Fe(II) and NA at pH 7 (Figure 2c).
328 This model accurately predicted an increase in NA loadings associated with Fe(II) uptake, thus
329 providing further validation for including a ternary complex in the model. However, the model
330 tended to overestimate NA binding at a higher Fe(II) concentration (500 μM) (Figure S9a).
331 Based on XRD analysis (Figure 3), we observed that Fe(II) at concentrations of 200 and 500
332 μM catalytically recrystallized goethite to magnetite. This finding warranted the inclusion of
333 magnetite in the model to account for NA adsorption upon mineral transformations.

334



335
 336 **Figure 3.** Powder XRD patterns of the transformation products of 50 m² /L goethite with different
 337 concentrations of Fe(II) at pH 9. Peaks are identified as goethite (G) or magnetite (M). Magnetite (PDF#79-
 338 0419) was detected at 2θ at 35.1, 41.4, 50.4 and 74.1°.

339
 340 We propose that the formation of magnetite driven by Fe(II) can be attributed to a topotactic
 341 or reconstructive process resulting from the precipitation of white rust Fe(OH)_{2(s)} at high pH:⁵⁶⁻
 342 ⁵⁸

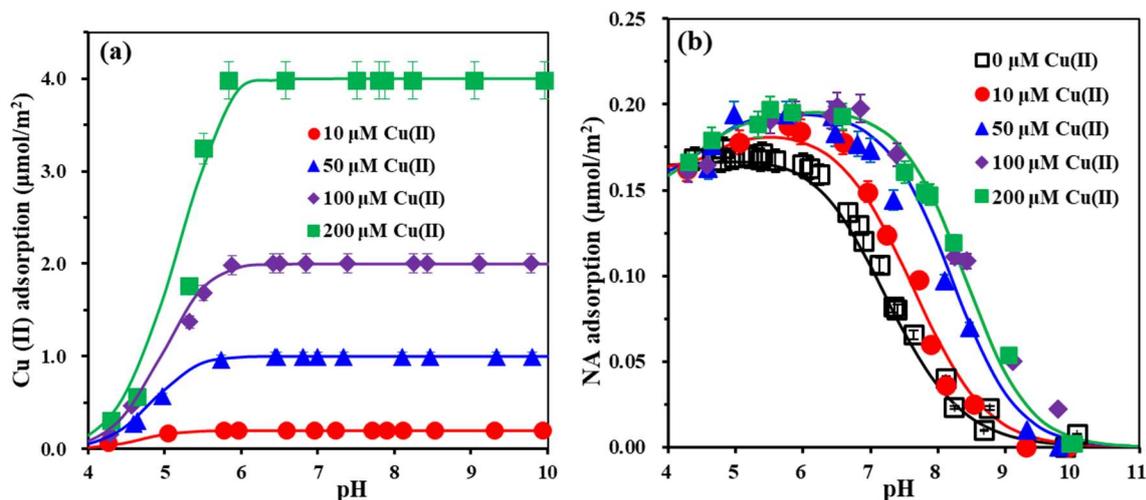


344 Using the XRD intensity (I) ratios of the most intense magnetite (2θ = 41.4°) and goethite (2θ
 345 = 24.7°), I_M/(I_M+I_G) peaks,⁵⁷ we find that 200 μM Fe(II) transformed only ~3% of goethite,
 346 whereas 500 μM Fe(II) transformed ~24% of the goethite into magnetite. Noting that after post-
 347 addition of 500 μM Fe(II), the goethite suspension contained a total of 6.2 mM Fe(III). As the
 348 maximum amount of iron in magnetite was 1.5 mM, we find that it represented 24 % of this
 349 total iron. This consequently supports the concept that all Fe(II) added to the suspension

350 converted to magnetite as resolved by XRD.

351 To describe NA binding onto goethite in the presence of 500 μM Fe(II), we imposed a 75%
352 goethite - 25% magnetite assemblage in the model, and simulated NA binding onto this
353 goethite-magnetite composite. We considered that NA bound to two surface hydroxy groups of
354 magnetite, similar to goethite (Eq.1).²⁶ All the modeling parameters are presented in Table S1.
355 Our best-fitting model predicted NA adsorption at high pH, where significant recrystallization
356 and transformation occurred (Figure 2b). The overestimation of NA adsorption at $\text{pH} < 8$ was
357 ascribed to the absence of goethite transformation to magnetite, which can be anticipated by the
358 lack of $\text{Fe}(\text{OH})_2$ precipitation (Figure S7). Therefore, at $\text{pH} < 8$, a model solely incorporating
359 goethite as the mineral phase predicted consistently higher NA loadings (see e.g. Figure S9b).

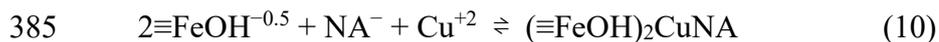
360 Because the reaction involving Fe(II) could have also modified the reactivity of goethite
361 surfaces towards NA binding, we investigated the effects of Cu(II) on NA adsorption onto
362 goethite. As typically encountered for cations, Cu(II) adsorption increased with pH and
363 concentration (Figure 4a). Since Cu(II)-goethite surface complexes have been well documented
364 and defined based on ab initio molecular geometries and EXAFS spectroscopy,⁵⁹ we describe
365 the pH-dependence of Cu(II) adsorption using the already reported equations of Cu(II) binding
366 onto goethite, as listed in Table 1.^{59, 60} The Cu(II) adsorption data can be accurately predicted
367 by keeping all parameters equal to literature values (Figure 4a).⁶⁰ In addition, the model also
368 predict the presence of Cu(II) precipitation as $\text{Cu}(\text{OH})_2(\text{s})$ for 200 μM Cu(II) (Figure S10).



369
 370 **Figure 4.** (a) Cu(II) and (b) NA removal from solution for $[NA]_{tot} = 10 \mu\text{M}$ on $50 \text{ m}^2 / \text{L}$ goethite in 10 mM
 371 NaCl versus pH at different Cu(II) concentrations after 24 h reaction time. Lines are modeling results.

372
 373 The FTIR spectra of bound NA species in the presence of Cu(II) exhibited major spectral
 374 variations for ketone and carboxyl groups compared to free NA species (Figure S4b), indicating
 375 the involvement of carboxylic and carbonyl groups of NA in the surface complexation. This is
 376 consistent with previous findings for metal complexation of quinolones,^{61, 62} which reported
 377 that the most common is the bidentate coordination mode involving the carbonyl and one of the
 378 carboxylate oxygen atoms (See Figure S11 for NA-Cu(II) complex).

379 Accordingly, the presence of Cu(II) significantly increased NA adsorption and shifted the
 380 sorption edge to higher pH (Figure 4b). NA sorption increased sharply at Cu(II) concentrations
 381 of less than 100 μM, while larger concentrations did not have any significantly higher impacts
 382 on loadings. As ternary surface-cation-ligand complexes generally enhance ligand binding by
 383 cations,^{27, 41, 60, 63} we modeled greater NA loadings using the following reaction, with locating
 384 charges of Cu(II) and NA at the 0 plane:



386 This ternary complexation is also consistent with the zeta potential variation of goethite
387 surface, where the excess positive charges induced by the adsorption of Cu(II) may favor the
388 adsorption of negative NA species, and thus the formation of goethite-Cu(II)-NA ternary
389 complexes (Figure S8). The difference in the influence of Cu(II) and Fe(II) on NA sorption can
390 be also related to the hard/soft acids/bases (HSABs) principle.⁶⁴ NA^{-} and OH^{-} are hard bases,
391 while Cu(II) and Fe(II) are hard acids, with Fe(II) being the harder one. As such, the interaction
392 is stronger in the bond of Cu(II)-OH/ Cu(II)-NA than that of Fe(II)-OH/ Fe(II)-NA,^{47, 64}
393 which explains the higher adsorption of NA in the presence of Cu(II) compared to Fe(II).

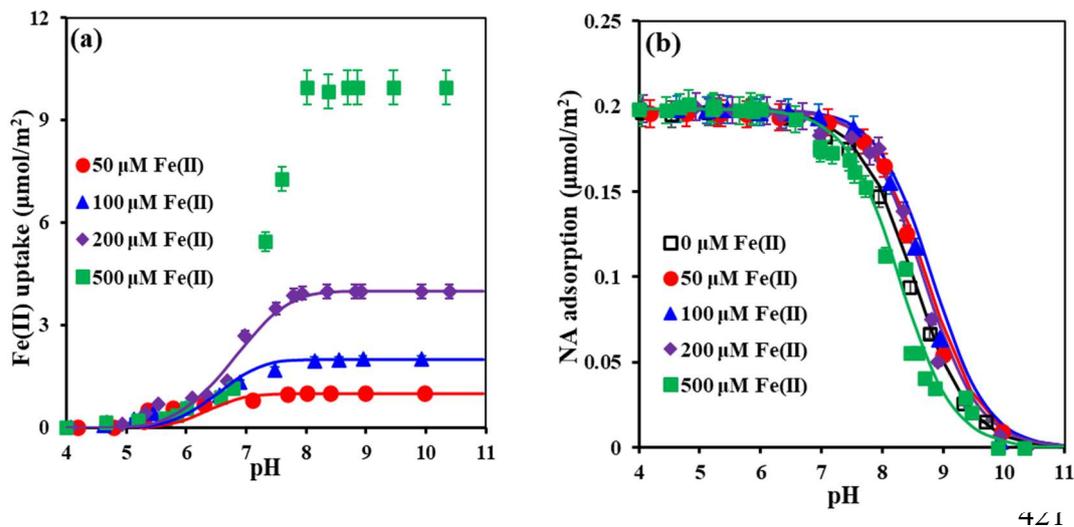
394 To further interpret the NA adsorption in the presence of 100 and 200 μM Cu(II), we
395 compared the surface species distribution of NA and Cu(II) (Figure S12). The increase in Cu(II)
396 concentration from 100 to 200 μM resulted in a significant increase in goethite-Cu(II) complex
397 and $\text{Cu}(\text{OH})_2$ precipitation. However, the amount of the goethite-Cu(II)-NA ternary complex
398 was very similar under these two Cu(II) concentrations. This falls in line with our experimental
399 findings where 100 μM Cu(II) and 200 μM Cu(II) induced the same NA sorbed amount,
400 corresponding to 100 % adsorption of initial added NA (10 μM). This model consequently
401 contributes to a mounting body of evidence for the importance of ternary surface complexation
402 in accounting for the binding of metal cations and quinolone antibiotics at goethite surfaces.^{27,}

403 ⁴¹

404 **3.3 Cation-NA co-binding on akaganéite and Fe(II)-driven catalytic recrystallization**

405 In contrast to the case of goethite, adsorption of Fe(II) from akaganéite suspensions

406 containing both Fe(II) and NA had marginal effects on NA loadings (Figures 5 and S13). As
 407 XRD (Figure 6) also revealed that no mineralogical transformations occurred at low Fe(II)
 408 concentrations, we modelled Fe(II) and NA binding using the same modeling strategy for
 409 predicting adsorption (Figure S14 and Text S3). Our model explains the insensitivity of NA
 410 loadings to 50-100 μM Fe(II), as the competition of Fe(II) for NA adsorption counteracts the
 411 enhancement in adsorption associated with ternary complexation. The model also predicts that
 412 the higher Fe(II) surface loadings were achieved in solutions of larger Fe(II) concentrations
 413 and/or higher pH.
 414

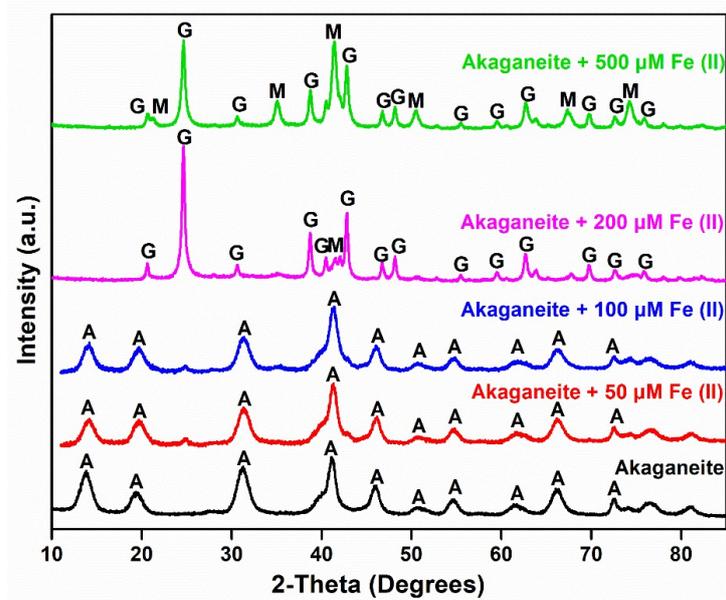


422 **Figure 5.** (a) Fe(II) and (b) NA removal from solution for $[\text{NA}]_{\text{tot}} = 10 \mu\text{M}$ on $50 \text{ m}^2/\text{L}$ akaganéite in 10 mM
 423 NaCl versus pH at different Fe(II) concentrations after 24 h reaction time. Lines are modeling results. The
 424 NA adsorption modeling result in the presence of 200 μM Fe(II) and 500 μM Fe(II) accounted for the
 425 transformation of the initial akaganéite into 100% goethite, and into 50% goethite and 50% magnetite,
 426 respectively. Because of greater akaganéite transformation at 500 μM Fe(II), the corresponding Fe(II) uptake
 427 was not modeled.

428 Based on XRD analysis (Figure 6), we also observed that akaganéite underwent
429 recrystallization into goethite when exposed to 200 μM Fe(II), while in the presence of 500 μM
430 Fe(II), it transformed into both goethite and magnetite. From the intensity ratios of the most
431 intense XRD peaks of the respective minerals, we find that $\sim 52\%$ goethite and $\sim 48\%$ magnetite
432 were formed after exposing akaganéite to 500 μM Fe(II). Interestingly, the proportion of
433 magnetite formed (48%) closely matched the Fe(II) reacted to the Fe(III) content of akaganéite
434 (42%). As goethite was found as the final product of akaganéite in the presence of 200 μM
435 Fe(II), we used our previously established NA-goethite surface complexation model to predict
436 NA adsorption. Our best fitting of the adsorption curve required an increasing of the NA-
437 goethite surface complex constant by only 1.2 log K units. This suggests that the newly formed
438 goethite exhibits a higher capacity for NA adsorption.

439 To account for the akaganéite transformation in the presence of 500 μM Fe(II), we adapted
440 our NA surface complexation model to include a 50% goethite - 50% magnetite composite
441 (Table S1). Notably, the updated model successfully predicted NA adsorption in the presence
442 of 500 μM Fe(II) across all pH values (Figure 5b and S15). It is worth noting that the resulting
443 magnetite exhibited distinct surface properties and reactivity towards NA adsorption as
444 compared to previous experiments, as it strongly depends on the type of ferric precursor
445 (goethite or akageneite).⁵⁸

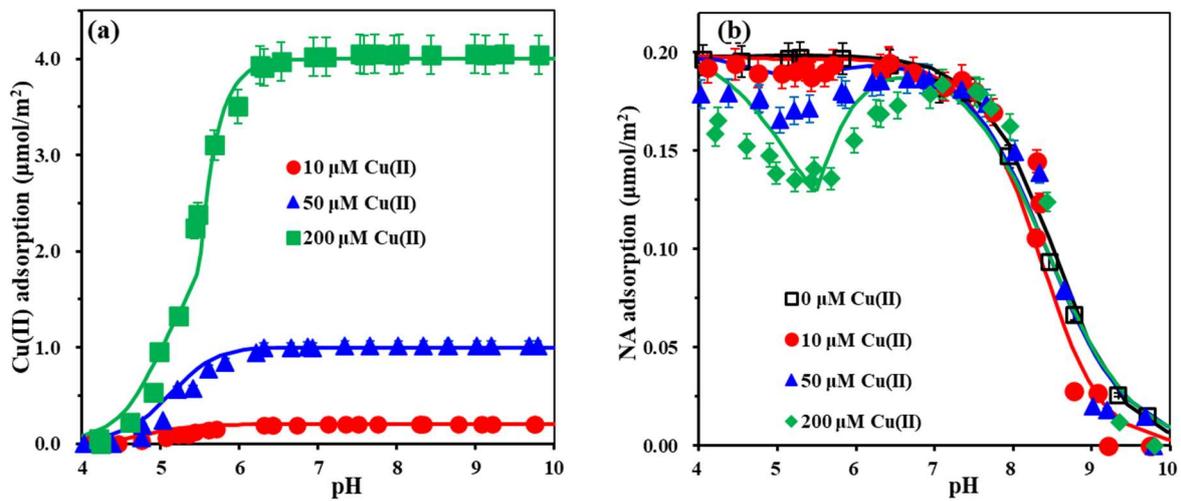
446



447
 448 **Figure 6.** Powder XRD patterns of the transformation products of 50 m² /L akaganéite with different
 449 concentrations of Fe(II) at pH 9. A, G and M refer to peaks of akaganéite, goethite and magnetite, respectively.

450

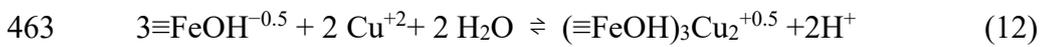
451



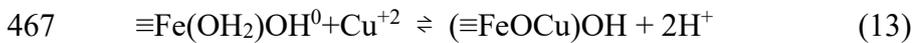
452
 453 **Figure 7.** (a) Cu(II) and (b) NA removal from solution for [NA]_{tot} = 10 µM on 50 m² /L akaganéite in 10 mM
 454 NaCl versus pH at different Cu(II) concentrations after 24 h reaction time. Lines are modeling results.

455

456 As in the case of goethite, we also investigated the role that Cu(II) species could play on NA
457 binding onto akaganéite. The results revealed that Cu(II) exerted a significant inhibitory effect
458 on NA adsorption under acidic pH conditions, with the extent of inhibition increasing with
459 higher Cu(II) concentrations (Figure 7b). Previous spectroscopic studies and theoretical
460 calculations indicated that Cu(II) forms bidentate and tridentate inner-sphere complexes with
461 the (100)/(001) planes of akaganéite.⁵⁹ These can be expressed as:

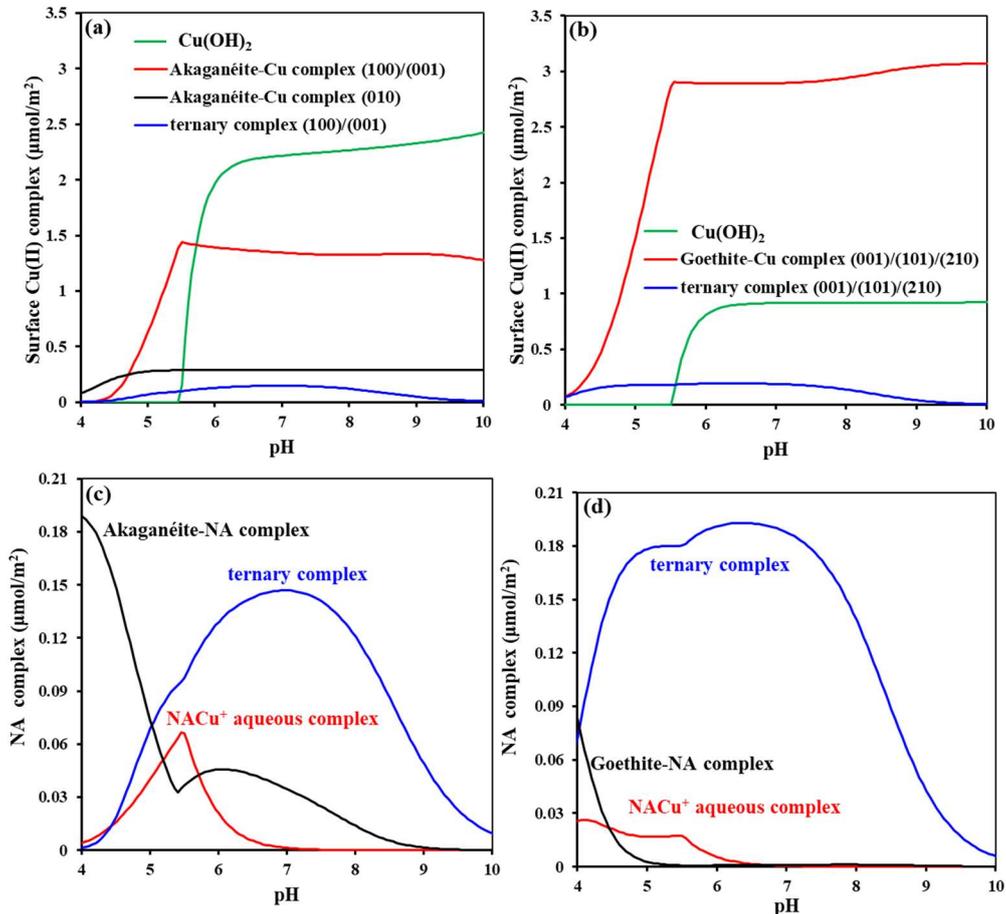


464 Although these added reactions (Table 1) effectively predicted Cu(II) loadings (Figure S16a),
465 the model overestimated NA loadings at low pH (Figure S16b). As an attempt to improve this
466 model, we introduced competitive Cu(II) binding reactions with the sites of the (010) plane:



468 While this reaction had limited NA-akaganéite loadings (Figure 1b), it still underestimated NA
469 adsorption in the presence of Cu(II) (Figure S16c). In contrast, incorporating an akaganéite-
470 Cu(II)-NA ternary complex into the model, as we did for goethite, and locating the charges of
471 Cu(II) and NA at the 0 plane and 1 plane, respectively (Table 1), made a considerable
472 improvement in the modeling predictions (Figure 7b). This improvement was observed even at
473 larger NA concentration (100 μM) in the presence of 100-200 μM Cu(II) (Figure S17).
474 Although there was no overall increase in total amount of sorbed NA observed in presence of
475 Cu(II) at high pH values, the modeling data suggests a significant role of ternary surface
476 complexation in NA binding onto akaganéite surfaces. Unlike goethite, where both NA and

477 Cu(II) bind to the same planes, our model suggests that NA preferentially targets the (010)
 478 planes while Cu(II) predominantly binds to the (100)/(001) planes, leading to the formation of
 479 ternary complex at the (100)/(001) planes (Figure 8a).



480
 481 **Figure 8.** Modeling results of different surface species. 10 μM NA and 200 μM Cu(II) adsorption onto 50
 482 m² /L (a, c) akaganéite and (b, d) goethite in 10 mM NaCl versus pH after 24 h reaction time. Surface Cu(II)
 483 complex on (a) akaganéite and (b) goethite. NA complex in the presence of (c) akaganéite and (d) goethite.

484
 485 To gain further insights into the mineral-dependent effect of Cu(II), we compared the surface
 486 distribution of Cu(II) complex between the two minerals in the presence of 200 μM Cu(II)
 487 (Figure 8). Despite similar Cu(II) uptake was observed on both minerals, there was clear
 488 difference in surface speciation. The akaganéite mineral demonstrated a significantly higher

489 amount of $\text{Cu}(\text{OH})_2$ precipitate compared to goethite, whereas the ternary complex on
490 akaganéite was much lower in comparison to goethite (Figure 8a,b). In addition, the NACu^+
491 aqueous complex was much larger in the presence of akaganéite (Figure 8c,d), which could
492 potentially explain the decreased NA binding onto akaganéite in the presence of $\text{Cu}(\text{II})$ at low
493 pH values.

494

495 **4. ENVIRONMENTAL IMPLICATIONS**

496 Through batch adsorption experiments, surface complexation modeling, ATR-FTIR and
497 XRD analysis, we have discovered that the co-binding of NA with cations ($\text{Fe}(\text{II})$ or $\text{Cu}(\text{II})$) is
498 strongly affected by pH, cation concentration and FeOOH phase. Furthermore, we also find that
499 the type of ternary complexation is strongly linked to the nature of the intervening cation and
500 mineral surface structure.

501 These findings have important implications for understanding the fate of quinolone
502 antibiotics in environments containing $\text{Fe}(\text{II})$ and $\text{Cu}(\text{II})$ and FeOOH , such as oxic-anoxic
503 boundaries in marine and freshwater basins, oxycline in sediments, and sediment–water
504 interfaces. For instance, $\text{Cu}(\text{II})$, commonly used as fungicide, could also have contrasting
505 effects by decreasing the affinity of quinolone antibiotics for akaganéite while increasing their
506 affinity for goethite. Additionally, $\text{Fe}(\text{II})$ produced through microbial respiration and weathering
507 of $\text{Fe}(\text{II})$ -bearing minerals, could have a considerable impact on quinolone antibiotics binding
508 on $\text{Fe}(\text{III})$ (oxyhydr)oxide minerals via ternary complexation and/or mineralogical
509 transformation. In addition to $\text{Cu}(\text{II})$ and $\text{Fe}(\text{II})$, other cations such as $\text{Ca}(\text{II})$,⁶⁵ $\text{Zn}(\text{II})$,⁶⁶ $\text{Pb}(\text{II})$,⁶⁷
510 $\text{Cd}(\text{II})$ ⁶⁸ and $\text{Ni}(\text{II})$ ⁶⁹ would also influence the adsorption of organic compounds through ternary

511 surface complexation. Given the prevalence of mineral-cation-ligand ternary complexes, we
512 propose that the intriguing phenomenon observed in this study extends beyond NA and can be
513 generalized to other organic pollutants containing carboxyl and carbonyl functional groups.

514 Considering that FeOOH-bound Fe(II) plays an important role in redox-driven
515 transformations occurring in natural environments, this study provides valuable insights that
516 can help guide future research on the fate of redox-active organic contaminants in
517 heterogeneous natural systems. Additionally, the transformation of Fe(III) oxy(hydr)oxides into
518 magnetite can occur upon exposure to Fe(II) at alkaline conditions, and the resulting magnetite
519 may exhibit varying reactivity depending on the ferric precursor. For example, magnetite
520 formed from akaganéite appears to possess higher reactivity compared to that derived from
521 goethite. These findings have thus important implications for better understanding the natural
522 attenuation of contaminants under reducing conditions, and/or the development of magnetite-
523 based remediation technologies. Future studies should explore Fe(II)-induced mineral
524 transformations as well as mineral-cation-ligand ternary interactions under real-world
525 conditions of water flow and natural chemical constituents.

526

527 **SUPPORTING INFORMATION**

528 Synthesis and characterization of goethite and akaganéite particles; ATR-FTIR investigations
529 and surface complexation modeling; Crystal planes and site densities of minerals and modeling
530 parameters; Zeta potentials of goethite and akaganéite; Kinetics data of Fe(II) and NA
531 adsorption onto minerals; Additional adsorption data of NA and/or Cu versus pH and NaCl

532 concentrations in single and binary systems; Additional experimental and modeling data on Cu
533 adsorption and precipitation, NA adsorbed species distribution under different Cu(II) or Fe(II)
534 concentrations, and NA adsorption on magnetite, akaganéite, goethite, and goethite/magnetite
535 composite.

536 **ACKNOWLEDGMENTS**

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538 Fundamental Research Funds for the Central Universities (CZQ21012), the Swedish Research
539 Council (2020-04853), and the CNRS (IRP CHEMICY, 2023-2027).

540

541 **Table 1.** Surface Complexation Model

Aqueous solutions		log K				ref
$\text{NAH}_{(s)} \rightleftharpoons \text{NAH}_{(aq)}$		-4.0				25
$\text{NA}^- + \text{H}^+ \rightleftharpoons \text{NAH}$		6.19				25
$\text{Fe}^{+2} + \text{NA}^- \rightleftharpoons \text{FeNA}^+$		3.99				47
$\text{NA} + \text{Cu}^{2+} \rightleftharpoons \text{NACu}^+$		6.155				47
Goethite ^a		log K	Δz_0	Δz_1	Δz_2	ref
$2 \equiv \text{FeOH}^{-0.5} + 2\text{H}^+ + \text{NA}^- \rightleftharpoons (\equiv \text{Fe})_2(\text{NA})^0 + 2\text{H}_2\text{O}$		20.2±0.1	+1	0	0	25
$2 \equiv \text{FeOH}^{-0.5} + 2\text{H}^+ + \text{NA}^- \rightleftharpoons (\equiv \text{FeOH}_2)_2^+ \cdots \text{NA}^-$		19.8±0.1	+2	-1	0	25
$2 \equiv \text{FeOH}^{-0.5} + 2\text{H}^+ + \text{NA}^- \rightleftharpoons (\equiv \text{FeOH}_2)_2^+ \cdots \text{NA}^-$		20.9±0.1	+2	0	-1	25
$2 \equiv \text{FeOH}^{-0.5} + 2\text{H}^+ + 2\text{NA}^- \rightleftharpoons (\equiv \text{Fe})_2(\text{NA})^0 \cdots \text{NA}^-$		22.2±0.1	+1	-1	0	25
$\equiv \text{FeOH}^{-0.5} + \text{Fe}^{+2} \rightleftharpoons \equiv \text{FeOFe}^{+0.5} + \text{H}^+$		1.3±0.1	+1	0	0	19
$\equiv \text{FeOH}^{-0.5} + \text{Fe}^{+2} + \text{H}_2\text{O} \rightleftharpoons \equiv \text{FeOFeOH}^{-0.5} + 2\text{H}^+$		-11.3±0.1	0	0	0	19
$2 \equiv \text{FeOH}^{-0.5} + \text{Fe}^{+2} + \text{NA}^- \rightleftharpoons (\equiv \text{FeOH})_2\text{FeNA}$		13±0.2	+10	0	0	This study
$2\equiv\text{FeOH}^{-0.5} + \text{Cu}^{+2} \rightleftharpoons (\equiv\text{FeOH})_2\text{Cu}^+$		9.18	0.84	1.16	0	60
$2\equiv\text{FeOH}^{-0.5} + \text{Cu}^{+2} + \text{H}_2\text{O} \rightleftharpoons (\equiv\text{FeOH})_2\text{CuOH} + \text{H}^+$		3.6	0.84	0.16	0	60
$2\equiv\text{FeOH}^{-0.5} + 2 \text{Cu}^{+2} + 2\text{H}_2\text{O} \rightleftharpoons (\equiv\text{FeOH})_2\text{Cu}_2(\text{OH})_2^+ + 2\text{H}^+$		3.65	0.84	1.16	0	60
$2\equiv\text{FeOH}^{-0.5} + 2 \text{Cu}^{+2} + 3\text{H}_2\text{O} \rightleftharpoons (\equiv\text{FeOH})_2\text{Cu}_2(\text{OH})_3 + 3\text{H}^+$		-3.1	0.84	0.16	0	60
$2\equiv\text{FeOH}^{-0.5} + \text{NA}^- + \text{Cu}^{+2} \rightleftharpoons (\equiv\text{FeOH})_2\text{CuNA}$		16.25±0.1	1	0	0	This study
Akaganéite ^b		log K	Δz_0	Δz_1	Δz_2	ref
$2 \equiv \text{FeOH}^{-0.5} + 2\text{H}^+ + \text{NA}^- \rightleftharpoons (\equiv \text{Fe})_2(\text{NA})^0 + 2\text{H}_2\text{O}$		20.6±0.2	+1	0	0	This study
$2 \equiv \text{FeOH}^{-0.5} + 2\text{H}^+ + \text{NA}^- \rightleftharpoons (\equiv \text{FeOH}_2)_2^+ \cdots \text{NA}^-$		20.6±0.1	+2	-1	0	This study
$\equiv \text{Fe}(\text{OH}_2)(\text{OH})^0 + \text{H}^+ + \text{NA}^- \rightleftharpoons \equiv \text{Fe}(\text{NA})^0 + 2\text{H}_2\text{O}$		13.4 ± 0.1	0	0	0	This study
$2\equiv\text{FeOH}^{-0.5} + 2 \text{H}^+ + 2 \text{NA}^- \rightleftharpoons (\equiv\text{FeNA})_2^- + 2 \text{H}_2\text{O}$		25.3 ± 0.1	1	-1	0	This study
$\equiv \text{FeOH}^{-0.5} + \text{Fe}^{+2} \rightleftharpoons \equiv \text{FeOHFe}^{+1.5}$		0.85±0.08	+2	0	0	This study
$\equiv \text{FeOH}^{-0.5} + \text{Fe}^{+2} + \text{H}_2\text{O} \rightleftharpoons \equiv \text{FeOFeOH}^{-0.5} + 2\text{H}^+$		-17.2±0.1	0	0	0	This study
$2 \equiv \text{FeOH}^{-0.5} + \text{Fe}^{+2} + \text{NA}^- \rightleftharpoons (\equiv \text{FeOH})_2\text{FeNA}$		13.7±0.2	1	0	0	This study
$2\equiv\text{FeOH}^{-0.5} + \text{Cu}^{+2} \rightleftharpoons (\equiv\text{FeOH})_2\text{Cu}^+$		insensitive	2	0	0	59
$3\equiv\text{FeOH}^{-0.5} + 2 \text{Cu}^{+2} + 2 \text{H}_2\text{O} \rightleftharpoons (\equiv\text{FeOH})_3\text{Cu}_2^{+0.5} + 2\text{H}^+$		6.56±0.1	2	0	0	59
$\equiv\text{Fe}(\text{OH}_2)\text{OH}^0 + \text{Cu}^{+2} \rightleftharpoons (\equiv\text{FeOCu})\text{OH} + 2\text{H}^+$		-4±0.1	0	0	0	This study
$2\equiv\text{FeOH}^{-0.5} + \text{NA}^- + \text{Cu}^{+2} \rightleftharpoons (\equiv\text{FeOH})_2\text{CuNA}$		16.2±0.1	2	-1	0	This study

542 ^aTPM with $C_1=2.3 \text{ F/m}^2$ and $C_2=1.07 \text{ F/m}^2$; Site densities: $[\equiv\text{FeOH}^{-0.5}] = 3.12 \text{ sites nm}^{-2}$ and $[\equiv\text{Fe}_3\text{O}^{-0.5}] = 3.12 \text{ sites nm}^{-2}$ on

543 (001)/(101) planes (90 % of the surface area), and $[\equiv\text{FeOH}^{-0.5}] = 7.4 \text{ sites nm}^{-2}$ on (210) plane (10 % of the surface area).

544 ^bTPM with $C_1=2.3 \text{ F/m}^2$ and $C_2=1.6 \text{ F/m}^2$. $[\equiv\text{FeOH}^{-0.5}] = 3.09 \text{ sites nm}^{-2}$, $[\equiv\text{Fe}_2\text{OH}] = 3.09 \text{ sites nm}^{-2}$, $[\equiv\text{Fe}_3\text{O}^{-0.5}] = 6.18 \text{ sites}$

545 nm^{-2} , $[\equiv\text{Fe}_3\text{O}^{-0.5}] = 3.09 \text{ sites nm}^{-2}$ on (001)/(100) planes (95% of the surface area), and $[\equiv\text{Fe}_2\text{OH}] = 7.06 \text{ sites nm}^{-2}$ and

546 $[\equiv\text{Fe}(\text{OH}_2)_2] = 3.53 \text{ sites nm}^{-2}$ on (010) plane (5% of the surface area)

547 REFERENCE

- 548 1. Xiu, W.; Yuan, W. J.; Polya, D. A.; Guo, H. M.; Lloyd, J. R., A critical review of abiotic and microbially-
549 mediated chemical reduction rates of Fe(III) (oxyhydr)oxides using a reactivity model. *Applied Geochemistry*
550 **2021**, *126*, 104895.
- 551 2. Huang, J. Z.; Jones, A.; Waite, T. D.; Chen, Y. L.; Huang, X. P.; Rosso, K. M.; Kappler, A.; Mansor, M.;
552 Tratnyek, P. G.; Zhang, H. C., Fe(II) Redox Chemistry in the Environment. *Chemical Reviews* **2021**, *121*, (13),
553 8161-8233.
- 554 3. Frierdich, A. J.; Helgeson, M.; Liu, C.; Wang, C.; Rosso, K. M.; Scherer, M. M., Iron Atom Exchange
555 between Hematite and Aqueous Fe(II). *Environ. Sci. Technol.* **2015**, *49*, (14), 8479-8486.
- 556 4. Gorski, C. A.; Handler, R. M.; Beard, B. L.; Pasakarnis, T.; Johnson, C. M.; Scherer, M. M., Fe Atom
557 Exchange between Aqueous Fe²⁺ and Magnetite. *Environ. Sci. Technol.* **2012**, *46*, (22), 12399-12407.
- 558 5. Handler, R. M.; Frierdich, A. J.; Johnson, C. M.; Rosso, K. M.; Beard, B. L.; Wang, C. M.; Latta, D. E.;
559 Neumann, A.; Pasakarnis, T.; Premaratne, W. A. P. J.; Scherer, M. M., Fe(II)-Catalyzed Recrystallization of
560 Goethite Revisited. *Environ. Sci. Technol.* **2014**, *48*, (19), 11302-11311.
- 561 6. Boland, D. D.; Collins, R. N.; Glover, C. J.; Payne, T. E.; Waite, T. D., Reduction of U(VI) by Fe(II) during
562 the Fe(II)-Accelerated Transformation of Ferrihydrite. *Environ. Sci. Technol.* **2014**, *48*, (16), 9086-9093.
- 563 7. Catalano, J. G.; Luo, Y.; Otemuyiwa, B., Effect of Aqueous Fe(II) on Arsenate Sorption on Goethite and
564 Hematite. *Environ. Sci. Technol.* **2011**, *45*, (20), 8826-8833.
- 565 8. Frierdich, A. J.; Luo, Y.; Catalano, J. G., Trace element cycling through iron oxide minerals during redox-
566 driven dynamic recrystallization. *Geology* **2011**, *39*, (11), 1083-1086.
- 567 9. Huang, J. Z.; Wang, Q. H.; Wang, Z. M.; Zhang, H. C., Interactions and Reductive Reactivity in Ternary
568 Mixtures of Fe(II), Goethite, and Phthalic Acid Based on a Combined Experimental and Modeling Approach.
569 *Langmuir* **2019**, *35*, (25), 8220-8227.
- 570 10. Hansel, C. M.; Benner, S. G.; Fendorf, S., Competing Fe(II)-Induced Mineralization Pathways of
571 Ferrihydrite. *Environ. Sci. Technol.* **2005**, *39*, (18), 7147-7153.
- 572 11. Pedersen, H. D.; Postma, D.; Jakobsen, R.; Larsen, O., Fast transformation of iron oxyhydroxides by the
573 catalytic action of aqueous Fe(II). *Geochimica et Cosmochimica Acta* **2005**, *69*, (16), 3967-3977.
- 574 12. Yang, L.; Steefel, C. I.; Marcus, M. A.; Bargar, J. R., Kinetics of Fe(II)-Catalyzed Transformation of 6-line
575 Ferrihydrite under Anaerobic Flow Conditions. *Environ. Sci. Technol.* **2010**, *44*, (14), 5469-5475.
- 576 13. Handler, R. M. B., B. L.; Johnson, C. M.; Scherer, M. M., Atom Exchange between Aqueous Fe(II) and
577 Goethite: An Fe Isotope Tracer Study. *Environ. Sci. Technol.* **2009**, *43*, 1102-1107.
- 578 14. Hu, Y.; Xue, Q.; Tang, J.; Fan, X.; Chen, H. H., New insights on Cr(VI) retention by ferrihydrite in the
579 presence of Fe(II). *Chemosphere* **2019**, *222*, 511-516.
- 580 15. Hao, T. W.; Huang, Y.; Li, F. B.; Wu, Y. D.; Fang, L. P., Facet-dependent Fe(II) redox chemistry on iron
581 oxide for organic pollutant transformation and mechanisms. *Water Research* **2022**, *219*, 118587.
- 582 16. Cárdenas-Hernández, P. A.; Anderson, K. A.; Murillo-Gelvez, J.; Di Toro, D. M.; Allen, H. E.; Carbonaro,
583 R. F.; Chiu, P. C., Reduction of 3-Nitro-1,2,4-Triazol-5-One (NTO) by the Hematite-Aqueous Fe(II) Redox
584 Couple. *Environ. Sci. Technol.* **2020**, *54*, (19), 12191-12201.
- 585 17. Orsetti, S.; Laskov, C.; Haderlein, S. B., Electron Transfer between Iron Minerals and Quinones:
586 Estimating the Reduction Potential of the Fe(II)-Goethite Surface from AQDS Speciation. *Environ. Sci.*
587 *Technol.* **2013**, *47*, (24), 14161-14168.
- 588 18. Silvester, E.; Charlet, L.; Tournassat, C.; G é hin, A.; Gren è che, J.-M.; Liger, E., Redox potential
589 measurements and Mössbauer spectrometry of FeII adsorbed onto FeIII (oxyhydr)oxides. *Geochimica et*
590 *Cosmochimica Acta* **2005**, *69*, (20), 4801-4815.
- 591 19. Hinkle, M. A. G.; Wang, Z. M.; Giammar, D. E.; Catalano, J. G., Interaction of Fe(II) with phosphate and
592 sulfate on iron oxide surfaces. *Geochimica Et Cosmochimica Acta* **2015**, *158*, 130-146.
- 593 20. Ardo, S. G.; Nelieu, S.; Ona-Nguema, G.; Delarue, G.; Brest, J.; Pironin, E.; Morin, G., Oxidative
594 degradation of nalidixic acid by nano-magnetite via Fe²⁺/O₂-mediated reactions. *Environ Sci Technol*
595 **2015**, *49*, (7), 4506-4514.
- 596 21. Lorphensri, O.; Intravijit, J.; Sabatini, D. A.; Kibbey, T. C.; Osathaphan, K.; Saiwan, C., Sorption of
597 acetaminophen, 17 α -ethynyl estradiol, nalidixic acid, and norfloxacin to silica, alumina. and a
598 hydrophobic medium. *Water Res* **2006**, *40*, (7), 1481-1491.
- 599 22. Kovalakova, P.; Cizmas, L.; McDonald, T. J.; Marsalek, B.; Feng, M. B.; Sharma, V. K., Occurrence and
600 toxicity of antibiotics in the aquatic environment: A review. *Chemosphere* **2020**, *251*, 126351.
- 601 23. Marsac, R.; Martin, S.; Boily, J. F.; Hanna, K., Oxolinic Acid Binding at Goethite and Akaganeite Surfaces:
602 Experimental Study and Modeling. *Environ. Sci. Technol.* **2016**, *50*, (2), 660-668.

- 603 24. Xu, J.; Marsac, R.; Costa, D.; Cheng, W.; Wu, F.; Boily, J. F.; Hanna, K., Co-Binding of Pharmaceutical
604 Compounds at Mineral Surfaces: Molecular Investigations of Dimer Formation at Goethite/Water Interfaces.
605 *Environ. Sci. Technol.* **2017**, *51*, (15), 8343-8349.
- 606 25. Xu, J.; Marsac, R.; Wei, C.; Wu, F.; Boily, J. F.; Hanna, K., Cobinding of Pharmaceutical Compounds at
607 Mineral Surfaces: Mechanistic Modeling of Binding and Cobinding of Nalidixic Acid and Niflumic Acid at
608 Goethite Surfaces. *Environ. Sci. Technol.* **2017**, *51*, (20), 11617-11624.
- 609 26. Cheng, W.; Marsac, R.; Hanna, K., Influence of Magnetite Stoichiometry on the Binding of Emerging
610 Organic Contaminants. *Environ. Sci. Technol.* **2018**, *52*, (2), 467-473.
- 611 27. Cheng, W.; Kalahroodi, E. L.; Marsac, R.; Hanna, K., Adsorption of Quinolone Antibiotics to Goethite
612 under Seawater Conditions: Application of a Surface Complexation Model. *Environ. Sci. Technol.* **2019**,
613 *53*, (3), 1130-1138.
- 614 28. Cheng, W.; Zhou, L.; Marsac, R.; Boily, J. F.; Hanna, K., Effects of organic matter-goethite interactions
615 on reactive transport of nalidixic acid: Column study and modeling. *Environ Res* **2020**, *191*, 110187.
- 616 29. Luo, T.; Xu, J.; Cheng, W.; Zhou, L.; Marsac, R.; Wu, F.; Boily, J. F.; Hanna, K., Interactions of Anti-
617 Inflammatory and Antibiotic Drugs at Mineral Surfaces Can Control Environmental Fate and Transport.
618 *Environ. Sci. Technol.* **2022**, *56*, (4), 2378-2385.
- 619 30. Zhou, L.; Cheng, W.; Marsac, R.; Boily, J. F.; Hanna, K., Silicate surface coverage controls quinolone
620 transport in saturated porous media. *J Colloid Interf Sci* **2022**, *607*, 347-356.
- 621 31. Liu, H. B.; Chen, T. H.; Frost, R. L., An overview of the role of goethite surfaces in the environment.
622 *Chemosphere* **2014**, *103*, 1-11.
- 623 32. Rémazeilles, C.; Refait, P., On the formation of β -FeOOH (akaganéite) in chloride-containing
624 environments. *Corrosion Science* **2007**, *49*, (2), 844-857.
- 625 33. Gaboriaud, F.; Ehrhardt, J.-J., Effects of different crystal faces on the surface charge of colloidal goethite
626 (α -FeOOH) particles: an experimental and modeling study. *Geochimica et Cosmochimica Acta* **2003**, *67*,
627 (5), 967-983.
- 628 34. Hanna, K.; Martin, S.; Quilès, F.; Boily, J.-F., Sorption of phthalic acid at goethite surfaces under flow-
629 through conditions. *Langmuir : the ACS journal of surfaces and colloids* **2014**, *30* 23, 6800-6807.
- 630 35. Kozin, P. A.; Boily, J.-F., Proton Binding and Ion Exchange at the Akaganéite/Water Interface. *The*
631 *Journal of Physical Chemistry C* **2013**, *117*, (12), 6409-6419.
- 632 36. Song, X.; Boily, J.-F., Competitive ligand exchange on akaganéite surfaces enriches bulk chloride
633 loadings. *J Colloid Interf Sci* **2012**, *376*, (1), 331-333.
- 634 37. Song, X.; Boily, J.-F., Surface Hydroxyl Identity and Reactivity in Akaganéite. *The Journal of Physical*
635 *Chemistry C* **2011**, *115*, (34), 17036-17045.
- 636 38. Grover, G.; Kini, S. G., Synthesis and evaluation of new quinazolone derivatives of nalidixic acid as
637 potential antibacterial and antifungal agents. *Eur J Med Chem* **2006**, *41*, (2), 256-262.
- 638 39. Fatta-Kassinos, D.; Meriç, S.; Nikolaou, A. D., Pharmaceutical residues in environmental waters and
639 wastewater: current state of knowledge and future research. *Analytical and Bioanalytical Chemistry* **2011**,
640 *399*, 251-275.
- 641 40. Gothwal, R.; Shashidhar, T., Antibiotic Pollution in the Environment: A Review. *Clean - Soil, Air, Water*
642 **2015**, *43*, (4), 479-489.
- 643 41. Gu, X. Y.; Tan, Y. Y.; Tong, F.; Gu, C., Surface complexation modeling of coadsorption of antibiotic
644 ciprofloxacin and Cu(II) and onto goethite surfaces. *Chem Eng J* **2015**, *269*, 113-120.
- 645 42. Kong, X.; Feng, S.; Zhang, X.; Li, Y., Effects of bile salts and divalent cations on the adsorption of
646 norfloxacin by agricultural soils. *J Environ Sci* **2014**, *26*, (4), 846-854.
- 647 43. Li, X.; Bi, E., The impacts of Cu(II) complexation on gatifloxacin adsorption onto goethite and hematite.
648 *Journal of Environmental Quality* **2020**, *49*, (1), 50-60.
- 649 44. Vogel, A. I., Vogel's textbook of quantitative chemical analysis. In 6th ed. / ed.; Mendham, J.; Denney,
650 R. C.; Barnes, J. D.; Thomas, M., Eds. Prentice Hall: Harlow, England, 2000.
- 651 45. Parkhurst, D. L.; Appelo, C. A. J. *User's guide to PHREEQC (Version 2): A computer program for*
652 *speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*, 99-4259;
653 1999.
- 654 46. Hiemstra, T.; Van Riemsdijk, W. H., A Surface Structural Approach to Ion Adsorption: The Charge
655 Distribution (CD) Model. *J Colloid Interf Sci* **1996**, *179*, (2), 488-508.
- 656 47. Timmers, K.; Sternglanz, R., Ionization and divalent cation dissociation constants of nalidixic and
657 oxolinic acids. *Bioinorganic Chemistry* **1978**, *9*, (2), 145-155.
- 658 48. Kinniburgh, D. G.; Cooper, D. In *PhreePlot: Creating graphical output with PHREEQC*, 2011; 2011.
- 659 49. Powell, M. J. D., A Method for Minimizing a Sum of Squares of Non-Linear Functions Without
660 Calculating Derivatives. *The Computer Journal* **1965**, *7*, (4), 303-307.

- 661 50. Jolsterå, R.; Gunneriusson, L.; Holmgren, A., Surface complexation modeling of Fe₃O₄-H⁺ and Mg(II)
662 sorption onto maghemite and magnetite. *J Colloid Interf Sci* **2012**, *386*, (1), 260-267.
- 663 51. Nakamoto, K., Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part B:
664 Applications in Coordination, Organometallic, and Biorganic Chemistry,. *Wiley-Interscience::New York* **2009**,
665 424 p.
- 666 52. Tackett, J. E., FT-IR characterization of metal acetates in aqueous solution. *Appl. Spectrosc* **1989**, *43*
667 (3), 483.
- 668 53. Boily, J.-F.; Persson, P.; Sjöberg, S., Benzenecarboxylate surface complexation at the goethite (α -
669 FeOOH)/water interface: II. Linking IR spectroscopic observations to mechanistic surface complexation
670 models for phthalate, trimellitate, and pyromellitate. *Geochimica et Cosmochimica Acta* **2000**, *64*, (20),
671 3453-3470.
- 672 54. Lutzenkirchen, J.-F. o. B. J., Modeling proton binding at the goethite (α -FeOOH)-water. *Colloids and*
673 *Surfaces A: Physicochemical and Engineering Aspects* **2001**, *179* (1), 11-27.
- 674 55. Hiemstra, T.; van Riemsdijk, W. H., Adsorption and surface oxidation of Fe(II) on metal (hydr)oxides.
675 *Geochimica et Cosmochimica Acta* **2007**, *71*, (24), 5913-5933.
- 676 56. Ahn, T.; Kim, J. H.; Yang, H.-M.; Lee, J. W.; Kim, J.-D., Formation Pathways of Magnetite Nanoparticles
677 by Coprecipitation Method. *The Journal of Physical Chemistry C* **2012**, *116*, (10), 6069-6076.
- 678 57. Usman, M.; Abdelmoula, M.; Faure, P.; Ruby, C.; Hanna, K., Transformation of various kinds of goethite
679 into magnetite: Effect of chemical and surface properties. *Geoderma* **2013**, *197-198*, 9-16.
- 680 58. Usman, M.; Abdelmoula, M.; Hanna, K.; Grégoire, B.; Faure, P.; Ruby, C., FeII induced mineralogical
681 transformations of ferric oxyhydroxides into magnetite of variable stoichiometry and morphology. *Journal*
682 *of Solid State Chemistry* **2012**, *194*, 328-335.
- 683 59. Peacock, C. L.; Sherman, D. M., Copper(II) sorption onto goethite, hematite and lepidocrocite: a surface
684 complexation model based on ab initio molecular geometries and EXAFS spectroscopy1 Associate editor:
685 D. L. Sparks. *Geochimica et Cosmochimica Acta* **2004**, *68*, (12), 2623-2637.
- 686 60. Weng, L. P.; Van Riemsdijk, W. H.; Hiemstra, T., Cu²⁺ and Ca²⁺ adsorption to goethite in the presence
687 of fulvic acids. *Geochimica Et Cosmochimica Acta* **2008**, *72*, (24), 5857-5870.
- 688 61. Turel, I., The interactions of metal ions with quinolone antibacterial agents. *Coordination Chemistry*
689 *Reviews* **2002**, *232*, (1), 27-47.
- 690 62. Chen, Z.; Xiong, R. G.; Zuo, J.; Guo, Z.; You, X.-z.; Fun, H.-K., X-Ray crystal structures of Mg²⁺ and
691 Ca²⁺ dimers of the antibacterial drug norfloxacin. *Journal of The Chemical Society-dalton Transactions*
692 **2000**, 4013-4014.
- 693 63. Yan, Y. P.; Wan, B.; Mansor, M.; Wang, X. M.; Zhang, Q.; Kappler, A.; Feng, X. H., Co-sorption of metal
694 ions and inorganic anions/organic ligands on environmental minerals: A review. *Sci Total Environ* **2022**,
695 149918.
- 696 64. Xu, H.; Xu, D. C.; Wang, Y., Natural Indices for the Chemical Hardness/Softness of Metal Cations and
697 Ligands. *Acs Omega* **2017**, *2*, (10), 7185-7193.
- 698 65. Audette, Y.; Smith, D. S.; Parsons, C. T.; Chen, W.; Rezanezhad, F.; Van Cappellen, P., Phosphorus
699 binding to soil organic matter via ternary complexes with calcium. *Chemosphere* **2020**, *260*, 127624.
- 700 66. Yan, Y.; Wan, B.; Zhang, Y.; Zhang, L.; Liu, F.; Feng, X., In situ ATR-FTIR spectroscopic study of the co-
701 adsorption of *myo*-inositol hexakisphosphate and Zn(II) on goethite. *Soil Research* **2018**, *56*, (5),
702 526-534.
- 703 67. Lenhart, J. J.; Bargar, J. R.; Davis, J. A., Spectroscopic Evidence for Ternary Surface Complexes in the
704 Lead(II)-Malonic Acid-Hematite System. *J Colloid Interf Sci* **2001**, *234*, (2), 448-452.
- 705 68. Wan, B.; Yan, Y. P.; Zhu, M. Q.; Wang, X. M.; Liu, F.; Tan, W. F.; Feng, X. H., Quantitative and
706 spectroscopic investigations of the co-sorption of *myo*-inositol hexakisphosphate and cadmium(II) on to
707 haematite. *European Journal of Soil Science* **2017**, *68*, (3), 374-383.
- 708 69. Flynn, E. D.; Catalano, J. G., Competitive and Cooperative Effects during Nickel Adsorption to Iron
709 Oxides in the Presence of Oxalate. *Environ. Sci. Technol.* **2017**, *51*, (17), 9792-9799.