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1 **Fate and Transport of Pharmaceuticals in Iron and Manganese Binary Oxide**
2 **Coated Sand Columns**

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4 Tao Luo^{a,c,†}, Rasesh Pokharel^{b,†}, Tao Chen^a, Jean-François Boily^c, Khalil Hanna^{a,d,*}

5
6 ^a Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR-UMR 6226, F-
7 35000, Rennes, France.

8 ^b Department of Earth Sciences, Utrecht University, 3584 CB Utrecht, Netherlands

9 ^c Department of Chemistry, Umeå University, Umeå, SE-901 87, Sweden

10 ^d Institut Universitaire de France (IUF), MESRI, 1 rue Descartes, 75231 Paris, France.

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13 *Corresponding author: Tel.: +33 2 23 23 80 27, khalil.hanna@ensc-rennes.fr

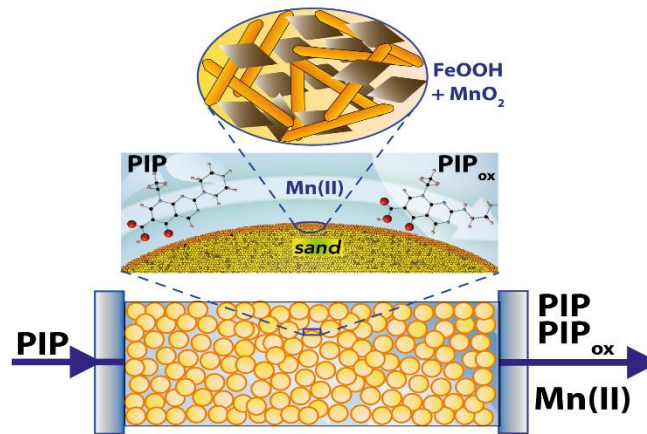
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Graphical Abstract

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28



29 **Abstract**

30 Predicting the fate and transport of pharmaceuticals in terrestrial environments requires knowledge
31 of their interactions with complex mineral assemblages. To advance knowledge along this front,
32 we examined the reactivity of pipemidic acid (PIP), a typical quinolone antibiotic, with quartz
33 particles coated with a mixture of manganese oxide (MnO_2) and goethite ($\alpha\text{-FeOOH}$) under static
34 and dynamic flow conditions. Batch and dynamic column experiments showed that PIP binding to
35 MnO_2 proceeded through a heterogeneous redox reaction while binding to goethite was not redox-
36 reactive. Mixed columns of aggregated goethite-manganese particles however enhanced redox
37 reactivity because (i) goethite facilitated the transport of dissolved Mn(II) ion and increased the
38 retention of PIP oxidation products, and (ii) MnO_2 was protected from passivation. This mobility
39 behavior was predicted using transport models accounting for adsorption and transformation
40 kinetics of PIP on both goethite and MnO_2 . This work sheds new light on reactivity changes of
41 mixtures of Fe and Mn oxides under flow-through conditions, and will have important implications
42 in predicting the fate and transport of redox-active organic compounds as well as development of
43 new geomedia filters for environmental remediation.

44

45 **Keywords:** pharmaceuticals; goethite; manganese oxide; redox; geomedia filter; transport;
46 modeling.

47

48

Synopsis

49

50 This work shows how goethite may overcome the drawbacks of Mn-oxides to be used as a
51 geomeia-filter for environmental remediation

52

53

54 **Introduction**

55 Iron (Fe) and manganese (Mn) are the two most common redox-active elements in the
56 Earth's crust. They are present in wide range of environments with different composition,
57 mineralogy, and morphology^{1,2}. For example, Fe and Mn-oxides may co-exist with each other as
58 discrete particles, mixture of component phases or particulate coatings in soils and sediments³. In
59 deep sea waters, Mn and Fe are oxidized to form ferromanganese crusts and nodules on the oceans
60 floor, a mineral of immense economic interest. Because of their specific nanoscale properties, high
61 surface area, low cost, strong oxidation and sorption abilities, iron and manganese oxides are
62 widely used in various environmental applications⁴⁻⁸. They play a key role in controlling the fate
63 and mobility of elements and toxic compounds in nature, and can also be used as an
64 environmentally friendly geomedia filter in water treatment technologies and/or aquifer recharge
65 management⁹⁻¹¹.

66 Goethite (α -FeOOH) is one of the most thermodynamically stable iron oxyhydroxide under
67 ambient conditions, and the most abundant one in natural settings^{2,12}. For this reason, numerous
68 theoretical and experimental studies explored organic or inorganic compounds binding
69 mechanisms to goethite surfaces and their impact on migration in nature^{13,14}. Birnessite-type
70 layered manganese oxides are, at the same time, of great interest given their strong redox- and
71 cation exchange reactivity^{8,15,16}. Their interest is also motivated by their structural similarity to the
72 biogenically precipitated natural manganese oxides, which are the most commonly occurring forms
73 of MnO₂ in surficial environments¹.

74 Although the reactivity of each individual or single phase has been widely investigated^{7,17-}
75 ²¹, knowledge is limited on how binary mixture of these two phases, goethite and MnO₂, alter the
76 overall reactivity of environmental compounds. Previous studies²²⁻²⁴ have reported that binary

77 mixture of $\text{Fe}(\text{OH})_3$ with $\text{Al}(\text{OH})_3$ or $\text{SiO}_{2(\text{am})}$ have exhibited different adsorption properties from
78 their component parts due to changes in surface site availability and surface charge. This has been
79 ascribed to the dissolution of $\text{Al}(\text{OH})_3$ or $\text{SiO}_{2(\text{am})}$ and sorption/precipitation of the dissolved ions
80 at Fe-oxides surfaces. Other studies²⁵ have reported that mixtures of MnO_2 with other oxides like
81 Al_2O_3 or $\text{SiO}_{2(\text{am})}$ or TiO_2 inhibited MnO_2 reactivity mainly through heteroaggregation between
82 particles and/or adsorption of metal ions released from the second oxides on the MnO_2 surface.
83 Two recent studies^{26,27} even showed that Fe oxides inhibited MnO_2 reactivity through
84 heteroaggregation of positively charged Fe oxides particles with negatively charged MnO_2
85 particles, thereby reducing the number of surface sites of MnO_2 . However, little is known on how
86 this reactivity is affected under dynamic, flow-through, conditions that are far more prevalent in
87 environmental and/or engineered systems than the static (batch) modes more commonly employed
88 in laboratory studies. This is particularly relevant because dissolved ions and/or redox by-
89 products (*e.g.* dissolved Mn(II)) concurrently affect surface reactivity of manganese and iron
90 oxides minerals and the mobility of target compounds. As such, experimental work under
91 continuous flow conditions can better emulate natural environments (*e.g.* geochemical systems
92 containing Fe- and Mn- oxides) or engineered infiltration systems (*e.g.* managed aquifer recharge
93 (MAR) and water treatment systems), where the target pollutants and the generated reaction
94 products travel through and are then flushed out of the column system. In addition, most traditional
95 environmental models are based on a single phase or simple system, and little is known on the
96 redox reactivity within complex mineral assemblages. Knowledge of the adsorption and redox
97 reactions that take place in the mixed mineral phases or complex environmental systems and under
98 flow-through conditions is consequently needed to explore contaminant transport.

99 This study aims to assess the roles that co-existing iron and manganese oxides play on the
100 fate and transport of contaminants under conditions of water flow. This was achieved by working

101 with columns packed with sand microparticles (CS) coated by MnO₂ (MCS), goethite (GCS), or
102 mixed goethite-MnO₂ (MGCS). Pipemidic acid (PIP) was, in turn, chosen as a representative
103 redox-active quinolone antibiotic widely used in human and veterinary medicine²⁸, and commonly
104 found in ng/L to µg/L levels ^{29–31} in aquatic environments and agricultural settings^{32–34}.
105 Investigation of redox transformation of compounds contacted to reactive minerals is also required
106 for an accurate assessment of ecological impacts of quinolone antibiotics. As the redox reaction is
107 strongly depended on pH value and MnO₂/compound ratio, dynamic flow experiments of PIP were
108 performed with two different MnO₂ amounts in the MGCS system and at pH 5.2 and 7.0, which
109 are within the typical pH range for shallow groundwater and soil pore waters³⁵. A transport model
110 that accounts for adsorption and oxidation kinetics was used to predict changes in PIP transport in
111 coated sands under flow. This work additionally explains how goethite-MnO₂ interactions affect
112 PIP reactivity, and potentially how these mechanisms affect similar other environmental emerging
113 contaminants.

114 **2. Materials and Methods**

115 **2.1 Synthesis of minerals and coated phases**

116 Pure Fontainebleau quartz sand (200-300 µm; ≤ 0.06 m²/g) was chosen as an inert support,
117 due to its very low reactivity and aqueous solubility under our experimental conditions³⁶. The
118 quartz sand was cleaned with HCl, H₂O₂ and ultrapure water to remove any colloidal or amorphous
119 silica particles and organic/inorganic contaminants (see SI for detailed cleaning procedure). Acid
120 birnessite (MnO₂) prepared according to McKenzie³⁷ was coated on quartz sand (MCS) as in our
121 previous study¹⁷, and summarized in the SI. Likewise, goethite (α-FeOOH) goethite-coated quartz
122 sand (GCS) were synthesized as described in previous studies^{18,38–40}, and summarized in the SI.
123 The B.E.T. specific surface area of uncoated goethite and birnessite phases was 81 ± 4 and 65 ± 1
124 m² g⁻¹ respectively, and the point of zero charge (PZC) determined at 298 K in 0.01, 0.1 and 1 M

125 NaCl solutions by the potentiometric titration method, was pH 9.1 for goethite and 2.4 for
126 birnessite. Coating coverage was thereafter evaluated by total Mn and Fe concentrations of acid
127 digested MCS and GCS. Concentrations, measured by Inductively Coupled Plasma-atomic
128 Emission Spectrometry (ICP-AES), revealed 0.60 ± 0.02 (SD) mg Mn per 1 g of MCS and 6.2 mg
129 ± 0.20 (SD) Fe per 1 g of GCS. These coating amounts are within the previously reported range
130 for natural coated subsurface materials^{35,41}, and they allow stable coated minerals to be achieved.

131 The possible dissolution of the used quartz sand was, additionally checked in 1 and 10 g/L
132 sand suspensions that were continuously stirred over a range of pH values (4-10) in pure water or
133 0.01 M NaCl for up to one month. In all cases, the dissolved silicate concentrations were below the
134 detection limit of the molybdenum blue spectrophotometric method ($<1 \mu\text{M}$) and ICP-AES (<0.2
135 μM).

136 Binary mixtures of iron and manganese oxides (MGCS) were prepared by adding different
137 amounts of MnO_2 suspension to GCS. Small aliquots of MnO_2 suspension were pipetted
138 homogeneously over the GCS surface, then mixed with a polypropylene spatula, and dried overnight
139 at room temperature. The resulting solid was thereafter washed four times with 10 mM NaCl to
140 remove any uncoated MnO_2 , then dried again at room temperature. Two different MGCS were
141 prepared: 1) 0.05 MGCS and 2) 0.1 MGCS, where 0.05 and 0.1 indicate the percentage of MnO_2
142 in the MGCS system.

143 The Mn content in the MGCS was determined by dissolving in 30 mM ascorbic acid
144 following the protocol of Charbonnet et al.⁴² and analyzed by ICP/AES. The measured amount was
145 0.29 ± 0.02 (SD) mg of Mn in 1 g of 0.05 MGCS and 0.60 ± 0.02 (SD) mg of Mn in 1 g of 0.1
146 MGCS. Scanning electron microscopy (SEM) was applied to study the surface morphology of the
147 MGCS matrix. Samples were examined with a JSM JEOL 7100 F microscope with a field emission
148 gun and an OXFORD Genesis energy-dispersive Xray spectrometer at 20 kV at a working distance

149 of 5–10 mm and magnifications from 15000× to 30000×. SEM images of MGCS showed a mixture
150 of goethite and MnO₂ particles deposited on the sand (Fig.S1). Due to the extremely low Mn
151 amount in the MGCS, X-ray diffraction could not be used for MGCS characterization.

152 **2.2 Batch and column experiments**

153 Three different sets of batch experiments were conducted to determine the 1) pH dependent
154 adsorption of PIP on GCS with or without Mn(II), 2) pH dependent Mn(II) adsorption on GCS
155 with or without PIP, 3) kinetics of PIP removal on 0.05 MGCS at pH 5.2, and 4) kinetic Mn(II)
156 sorption on MCS and MGCS at pH 5.2 under static conditions. Details on the experimental setup
157 are provided in the SI.

158 Dynamic breakthrough experiments were conducted at room temperature and under water-
159 saturated conditions. Briefly, 15 g of GCS, MCS or MGCS were packed in glass columns with an
160 internal diameter of 1.6 cm and bed length of 4.7 cm. The column was wrapped with aluminum
161 foils to avoid any photo-induced degradation. The bulk density of the packed MGCS was $1.52 \pm$
162 0.05 g/cm^3 , and the column pore volume (PV or V_p) was $4 \pm 0.1 \text{ mL}$. The column was first saturated
163 with a background solution of 10 mM NaCl (previously purged with N₂) at pH 5.2 or 7.0
164 (depending on the experimental pH) with a constant flow rate of 0.5 mL/min (residence time of 8
165 min). A bromide tracer experiment was performed using an input solution containing 10 mM NaBr
166 in 10 mM NaCl at pH 5.2 or 7.0. Br⁻ breakthrough curves for different columns (GCS, MCS, 0.05
167 MGCS, 0.1 MGCS) were obtained by analysis of the effluent solution using ion chromatography
168 (Fig. S2).

169 Different column experiments were performed by injecting input solutions consisting of a
170 constant amount of 10 mM NaCl and 10 μM PIP but at two different pH values, 5.2 (± 0.1) or 7.0
171 (± 0.1). The investigated inflow concentration of PIP may appear higher than the level amounts of
172 pharmaceuticals commonly detected in environmental systems²⁹⁻³¹, but close to total dose of

173 organic compounds found in industrial effluents or urban stormwater and municipal wastewater
174 used in aquifer recharge⁴². Furthermore, since the Mn-based redox reaction is strongly dependent
175 on red/ox ratio, different MnO₂ amounts and thus different PIP/MnO₂ ratio were investigated. The
176 experimental flow-rate was constant throughout the course of the experiment at 0.5 ml/min. The
177 input solution was purged with N₂ to avoid CO₂ contamination and to maintain the experimental
178 pH throughout the course of the experiment. Flow interruption method was applied in selected
179 experiments to check the occurrence of kinetic limitations. All effluent solutions were collected
180 using a fractional collector. The pH of the effluent solution was determined through the experiment
181 by using an online pH meter. The effluent solution was also analysed for PIP and by-products with
182 high-performance liquid chromatography (HPLC) and an ultrahigh-performance liquid
183 chromatography–tandem mass spectrometry (UPLC-MS/MS) system, and for dissolved metal ions
184 using ICP-AES. More details about experimental conditions and measurements are reported in the
185 SI (Table S1).

186

187 **2.4 Transport modeling**

188 First, the hydrodynamic parameters were obtained by fitting the bromide breakthrough data
189 using classical Advection Dispersion Equation (ADE):

$$190 \quad \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \quad (1)$$

191 Breakthrough curves (BTC) for Br⁻ suggest the absence of great dispersion/diffusion or physical
192 nonequilibrium effect (Fig. S2 in the SI). Macroscopic dispersivity (~ 1.89 mm) was obtained by
193 the ratio of the dispersion coefficient (*D*) and of pore velocity (*v*). Molecular diffusion was
194 considered negligible with respect to the dynamic dispersion. The Péclet number (*Pe* = *vL*/*D*) was
195 ~25 in the column, suggesting the predominance of a convective regime, and the flow can be
196 assumed to be homogeneous. During water saturation and tracer experiments, total dissolved Mn,

197 Fe and Si in the outflow was below the ICP-AES detection limit (0.1 μM for Mn, 0.2 μM for Fe
 198 and 0.2 μM of Si), and therefore the possibility of mobilization and/or dissolution of minerals can
 199 be excluded. Blank tests conducted also confirmed no adsorption of Mn(II) ions to the quartz sand
 200 ($\leq 0.06 \text{ m}^2/\text{g}$).

201 The reactive transport model is based on a two-site, advective-dispersive transport model with
 202 degradation and Freundlich-Langmuir kinetic sorption. The liquid and sorbed concentrations are
 203 ruled by the following differential equation that governs the chemical non-equilibrium transport
 204 for a homogeneous system under steady-state water flow^{43,44}:

$$205 \quad \frac{\partial C}{\partial t} + \frac{\rho \partial(S)}{\theta \partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \mu_1 C - \frac{\rho}{\theta} \mu_s S \quad (2)$$

206 where θ is the volumetric water content (L^3/L^3), C is the volume-averaged solution concentration
 207 (M/L^3), t is time (T), ρ is solid bulk density, S is the sorbed concentration (M/M), D is the dispersion
 208 coefficient in the liquid phase (L^2/T), v is the water velocity (L/T), μ_1 and μ_s are first-order
 209 degradation rate constants (T^{-1}) for the liquid and sorbed phases.

210 Because quinolones binding to oxide surfaces may proceed through a non-specific and fast surface
 211 complexation reaction, such as outer-sphere or hydrogen-bound, and a specific surface
 212 complexation reaction, generally slower, such as metal-bound complexes, we assume that
 213 adsorption sites can be divided into two fractions, instantaneous (Type-1) and kinetic (Type-2)
 214 sites⁴⁴.

$$215 \quad S = S_1 + S_2 \quad (3)$$

216 Where S_1 and S_2 are solid phase concentrations associated with Type-1 and Type-2 sites
 217 respectively. Considering Type-1 adsorption sites are always at equilibrium, S_1 can be expressed
 218 as:

$$219 \quad S_1 = fK \frac{C^\beta}{1 + \eta C^\beta} \quad (4)$$

220 The Type-2 adsorption sites are assumed to be a first-order kinetic rate process:

$$221 \quad \frac{\partial S_2}{\partial t} = \alpha \left[(1 - f)K \frac{C^\beta}{1 + \eta C^\beta} - S_2 \right] - \mu_s S_2 \quad (5)$$

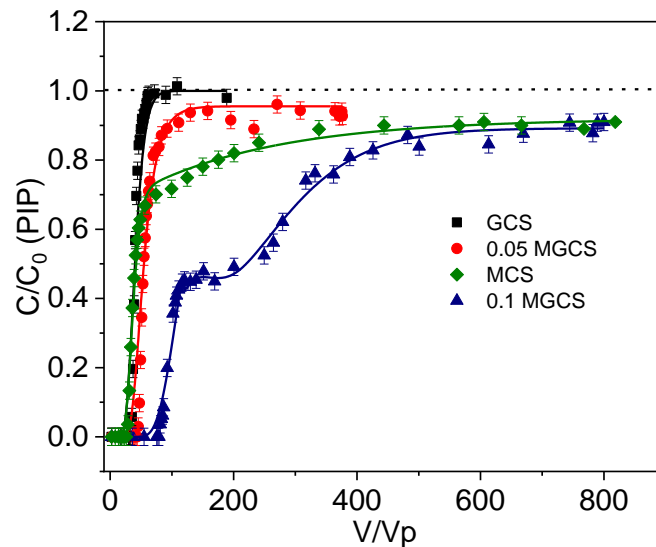
222 where α is a first-order kinetic rate coefficient (T^{-1}), f is the fraction of instantaneous adsorption
223 sites (Type-1), and K , β and η are empirical coefficients.

224 Transport modeling was performed with HYDRUS 1D⁴³. This code allows for the numerical
225 resolution of equations 2-5 for several boundary and initial conditions: concentration flux at the
226 inlet, zero concentration gradient at the outlet, and no solute at time zero. By using a least-squares
227 optimization routine, HYDRUS 1D also allows inverse modeling to fit the model solution to the
228 data to estimate fate and transport parameters⁴³. Because of PIP transformation reactions only
229 occurred at MnO_2 surfaces and not in solution, μ_1 was set to 0. This also allows reducing the number
230 of estimated parameters, and thus avoiding non-uniqueness issues (a sensitivity analysis has been
231 done in previous work⁷). Values for the sorption parameter K , fraction of equilibrium sites f ,
232 kinetics adsorption α and the first-order degradation rate μ_s were determined through fitting the
233 breakthrough curves of PIP, and are reported in Table S2.

234

235 3. Results and Discussion

236 3.1. Influence of goethite and/or birnessite coating on the PIP breakthrough

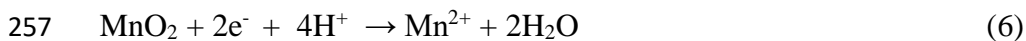


237
238 **Figure 1.** PIP Breakthrough curves MnO₂-bearing columns (0.60 mg Mn/g MCS; 0.29 mg Mn/g
239 0.05 MGCS; 0.60 mg Mn/g 0.1 MGCS). The dashed line indicates the theoretical complete
240 breakthrough of PIP ($C/C_0 = 1$), and solid lines are model predictions. Inflow conditions: 10 μ M
241 PIP; pH 5.2 ± 0.1 ; 10 mM NaCl; PV 4 mL; flow rate 0.5 mL/min. V/V_p is the ratio of injected
242 volume and pore volume).

243
244 MnO₂ in MGCS columns strongly slows down PIP mobility with respect to the (MnO₂-free)
245 GCS column (Figure 1). This can be appreciated by extensive tailing of the breakthrough curve
246 (BTC) and incomplete breakthrough of PIP in the MCS column (0.60 mg Mn/g 0.1 MCS),
247 compared to the GCS column with a sigmoidal-shaped low-tailing BTC with total breakthrough
248 ($C/C_0 = 1$) by 60 PV. In strong contrast, the 0.1 MGCS with the same Mn loading as MCS (0.60
249 mg Mn/g 0.1 MGCS) exhibited breakthrough at 81 PV, achieved a brief steady-state just below
250 ~ 200 PV at $C/C_0 \sim 0.45$ and a final steady-state at $C/C_0 \sim 0.91$, just as in MCS, after 744 PV.
251 However, halving Mn loadings to 0.29 mg Mn/g in 0.05 MGCS produced BTC attributes

252 intermediate to those of GCS and MCS, with the breakthrough point of PIP at 45 PV and a steady
253 breakthrough at $C/C_0 \sim 0.94$ at 308 PV.

254 The pH of the output solution from the GCS column initially slightly decreased by ~ 0.4
255 unit but finally returned to 5.5 when steady-state breakthrough was reached (Fig. S3). However,
256 the transformation of PIP on MnO_2 or the reductive conversion of MnO_2 released Mn(II) through:



258 As this is a proton-promoted process, pH initially increased to 5.9 and then decreased to initial pH
259 value on MCS column (Fig. S3). In the MGCS column, no pH changes in 0.05 MGCS, while pH
260 followed the same behavior as for the MCS column in 0.1 MGCS (Fig. S3). As PIP was mostly
261 present in the zwitterionic form ($pK_{a1} = 5.20$, $pK_{a2} = 6.38$) (Fig. S4), adsorption to goethite
262 occurred via surface complexation reactions involving carboxylic and keto groups, with a
263 possibility of oxidation reaction involving the piperazine ring.⁴⁵ However, the BTC shape and the
264 lack of by-products in the effluent did not provide evidence for PIP oxidation by goethite. The
265 modeling results also support the absence of PIP oxidation since no heterogeneous degradation rate
266 (μ_s) was required to fit the BTC of PIP (Fig. 1, Table S2). Conversely, modeling of the partial PIP
267 breakthrough in the Mn-bearing MCS and MGCS columns did require μ_s (Fig. 1, Table S2).

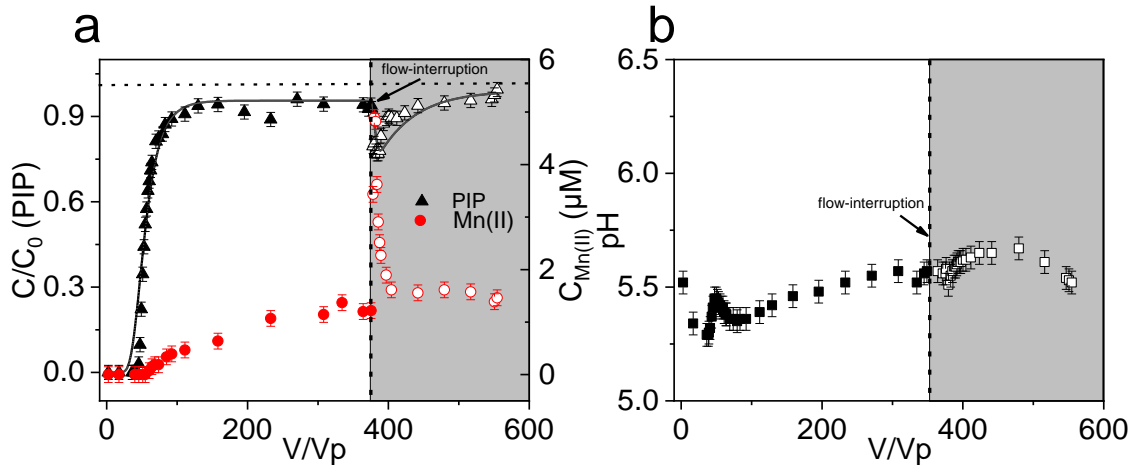
268 The total amount of PIP removal (by adsorption and/or oxidation) was calculated by
269 integrating of the area above the BTC of PIP. In the MCS column, the total PIP removal was ~ 5
270 μmol at ~ 800 PV, while the same Mn loadings in the 0.1 MGCS column removed ~ 11 μmol PIP
271 at the same breakthrough time. This consequently implies that the 0.1 MGCS column removed
272 almost twice the amount of PIP than in the MCS column despite having the same Mn loading. As
273 the 0.1 MGCS and GCS columns contained the same goethite loadings, the contribution of goethite
274 in PIP removal can be estimated at ~ 1.5 μmol .

275 Enhanced MnO₂ content not only improved PIP removal in the MGCS column (3.2 μmol
276 PIP removal in 0.05 MGCS column vs 11 μmol in 0.1 MGCS column), but also modified the
277 breakthrough behavior. Indeed, a two-step behavior, two fronts and two plateaus, was observed
278 corresponding to the pH variation during the transport experiment (Fig.S3). This breakthrough
279 behavior can be described by considering three stages, and different parameters are necessary to
280 describe each stage of the full BTC of PIP (Table S2). If the same adsorption and oxidation
281 parameters (i.e. α , K , f , μ_s) were used for full BTC description, the calculated curve failed to
282 describe the transport process of PIP, especially for the transitional plateau (Fig. S5). This mobility
283 behavior could be explained by the pH impact on heterogeneous redox reaction and/or
284 (re)adsorption of redox products. It has been reported that fluoroquinolone binding to negatively
285 charged Mn-oxide surfaces proceeds through a heterogeneous redox reaction, whereby two one-
286 electron-transfer or a single two-electron transfer oxidize PIP and reduce surface-bound metal sites
287 ^{17,19,46}. This will be investigated in the next section.

288

289 **3.2. Impact of manganese oxide content on PIP oxidation in column**

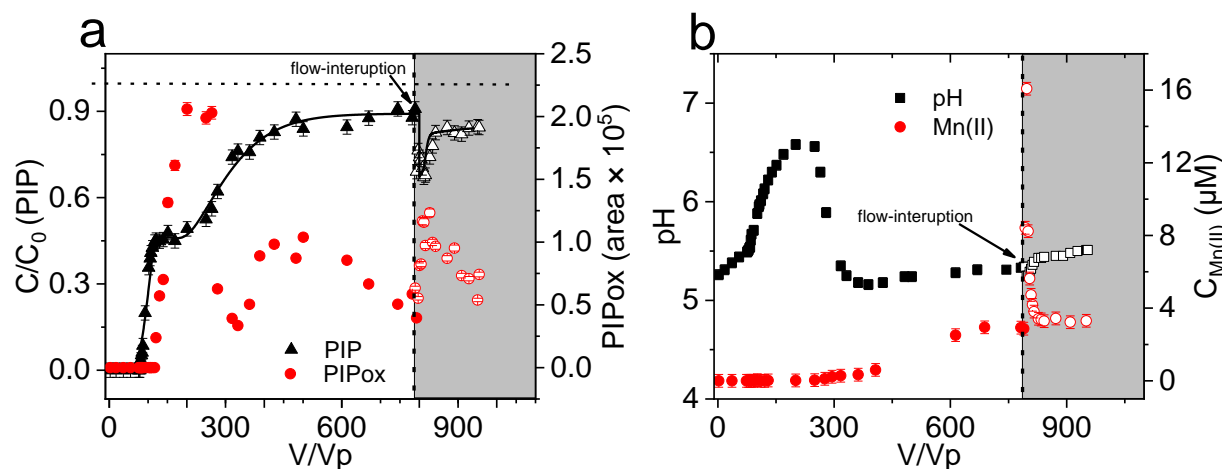
290 To further investigate PIP transport in MGCS columns, redox by-products (dissolved Mn(II) and
291 oxidized by-product of PIP) were monitored in the outflow solution throughout the breakthrough
292 experiment and upon flow interruption. Our flow/no flow/flow sequence protocol allowed us to
293 check kinetic limitations through determination of BTC of species before interruption and after
294 resumption of flow.



295
 296 **Figure 2.** Breakthrough curves of a) PIP, Mn(II), and b) pH in the 0.05 MGCS column. The
 297 horizontal dashed line indicates the theoretical complete breakthrough of PIP ($C/C_0 = 1$) and solid
 298 lines are model predictions. The vertical dashed lines indicate the moment of flow interruption
 299 (duration 24 h). The empty symbols in the shadow area indicate the second-stage after flow
 300 resumption. Inflow conditions: 10 μM PIP; pH 5.2 ± 0.1 ; 10 mM NaCl; PV 4 mL; flow rate 0.5
 301 mL/min. V/V_p is the ratio value of injected volume and pore volume.

302
 303 In the 0.05 MGCS column, Mn(II) was detected in the effluent solution at the same time as
 304 PIP, then reached a steady-state concentration of 1.2 μM . Increasing the residence time of PIP in
 305 the 0.05 MGCS column by interrupting the flow for 24 h (376 PV) did not influence the incomplete
 306 breakthrough as the same partial breakthrough ($C/C_0 = 0.94$) was still observed upon flow
 307 resumption (Fig. 2a). This flow interruption period allowed species to react over a longer period
 308 during flow-through conditions. Here, relative concentrations of PIP dropped from 0.94 to 0.76
 309 while those of Mn(II) increased sharply from 1.2 to 5 μM , yet solution pH values were stable
 310 throughout the course of the experiment (Fig. 2b). This behavior pointed to rate-limited
 311 sorption/redox processes from co-occurring adsorption reactions and heterogeneous redox
 312 reactions. Note that BTC curves in separate bromide tracer experiments did not change following

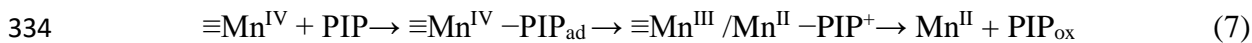
313 a flow/no-flow/flow sequence, thereby excluding the possibility of physical non-equilibrium or
 314 diffusive mass transfer that might cause changes in PIP and Mn(II) concentrations. Upon flow
 315 resumption, both PIP and Mn(II) concentrations reached the steady-state concentrations prior to
 316 the stop-flow. Although Mn(II) was detected by ICP-AES as the reduced by-product, no oxidized
 317 by-product of PIP (hereafter referred as PIP_{ox}) was detected in the effluent throughout the course
 318 of the experiment (Fig. 2a). This could be explained by the very low concentrations of generated
 319 redox products and/or strong binding to minerals at the working pH value (5.2).



320
 321 **Figure 3.** Breakthrough curves of (a) PIP and PIP_{ox} (peak area of PIP by-product; M-26) and (b)
 322 Mn(II), pH in 0.1 MGCS column. The horizontal dashed line indicates the theoretical complete
 323 breakthrough of PIP ($C/C_0 = 1$) and solid lines are model predictions. The vertical dashed lines
 324 indicate the moment of flow interruption (duration 24 h). The empty symbols in the shadow area
 325 indicate the second-stage after flow resumption. Inflow conditions: 10 μM PIP; pH 5.2 ± 0.1 ; 10
 326 mM NaCl; PV 4 mL; flow rate 0.5 mL/min. V/V_p is the ratio of injected volume and pore volume.

327
 328 In the 0.1 MGCS column, redox products (Mn(II) and PIP_{ox}) were detected throughout the
 329 course of the experiment (Fig. 3a). LC/MS analysis confirmed the PIP_{ox} had a m/z value of 227
 330 (M-26), formed through N-dealkylation of the piperazine ring of PIP (Fig. S6). As previously

331 observed for quinolone compounds^{17,19}, one electron is transferred from sorbed compound to the
332 surface-bound Mn^{IV}, yielding radical intermediates, and Mn^{III} that can be further reduced to give
333 Mn^{II} as follows:



335 As seen in Figure 3a, PIP_{ox} concentration in the effluent solution reached its maximum, and then
336 decreased after ~175 PV. Prior to flow-interruption, the BTC of PIP_{ox} followed the outflow pH
337 values, as PIP_{ox} binding to minerals is pH-dependent. However, the peak area of LC/MS data
338 corresponding to PIP_{ox} was not constant (no-steady-state values) during the course of the
339 experiment. Increasing the residence in the column with flow-interruption, decreased PIP
340 concentration but increased that of PIP_{ox}. When the flow was resumed, PIP concentration reached
341 again a plateau, with a steady-state value lower than that before flow interruption (0.9 to 0.8). High
342 MnO₂ content exhibited greater removal ability of PIP and more Mn(II) generation. For example,
343 a higher *k* value, first-order degradation rate coefficient (including sorption and oxidation), was
344 obtained in the 0.1 MGCS (*k* = 2.1 × 10⁻⁴ min⁻¹) compared to 0.05 MGCS (*k* = 1.4 × 10⁻⁴ min⁻¹), by:

$$345 \quad k = - \frac{\ln\left(\frac{C_a}{C_b}\right)}{t} \quad (8)$$

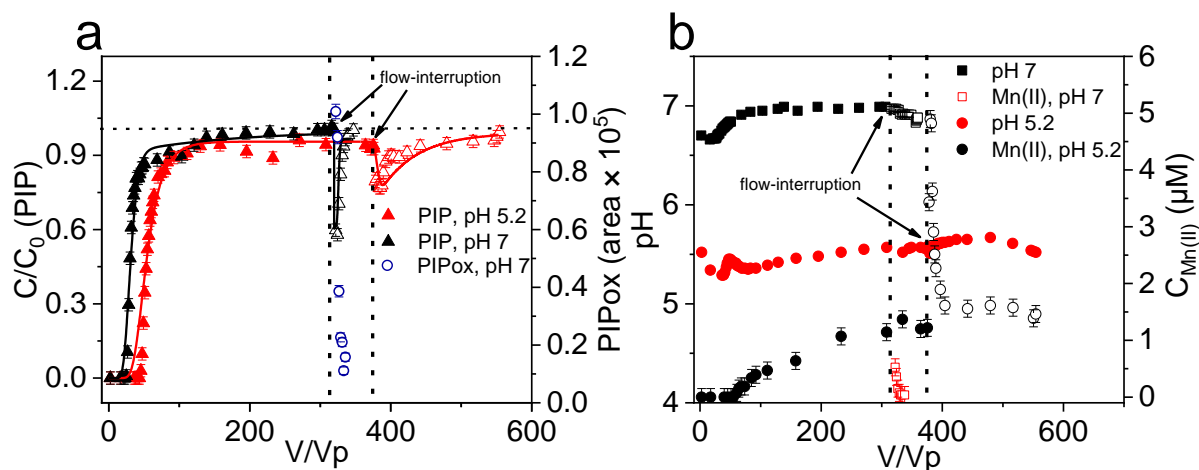
346 Here, C is the PIP effluent concentration before (C_b) and after (C_a) flow-interruption, and *t* is the
347 duration of interruption (24 h).

348 The shape of the breakthrough curve of Mn(II) in the 0.1 MGCS column was similar to that
349 of 0.05 MGCS column. However, Mn(II) did not exhibit breakthrough with PIP (as the 0.05 MGCS
350 column) and was only detected after injection of ~300 PV. This delayed Mn(II) breakthrough
351 corresponds to an increase in the outflow pH value (see Fig. 3b), and thus can be explained by
352 increasing in Mn(II) binding onto goethite with increasing pH (See batch data in Fig. S7). The
353 effluent concentration of Mn(II) thereafter reached a plateau-like, steady-state, value when the pH

354 decreased down to the inflow pH (~5.2). In MCS no Mn(II) desorbed into the effluent solution (Fig.
355 S8). The presence of dissolved Mn(II) in outflow solutions of MGCS columns (0 μ M in MCS
356 column vs. 2.5 μ M in 0.1 MGCS column at pH 5.2) suggests that the presence of goethite altered
357 Mn(II) uptake by MnO₂ at this pH value, and thus increased its mobility through the column system.
358 This was confirmed further by Mn(II) batch adsorption data on MCS and MGCS (Fig. S9), where
359 70% of dissolved Mn(II) were removed by MCS while only 40% was removed with MGCS under
360 the same experimental conditions (See Fig. S9). Additional batch experiments showed that PIP was
361 continuously removed (sorption + oxidation) by MGCS, yet only Mn(II) (no PIP_{ox}) was detected
362 in solution (Fig. S10). As observed in the column system, the presence of goethite likely ensured
363 preferential adsorption of PIP or PIP_{ox} over Mn(II) onto MGCS at pH 5.2. This aligns with our
364 batch adsorption tests (Fig. S7) revealing strong PIP and weak Mn(II) loadings at this pH value.
365 PIP binding was also lower and Mn(II) binding greater at larger pH, and even because competitive
366 sorption at pH > 6. Taken together, these findings confirmed that interactions between positively
367 charged goethite (PZC 9.1) and negatively charge MnO₂ (PZC 2.4) particles decreased overall
368 cation adsorption in the MGCS system. As a result, dissolved Mn(II) ion was flushed out of the
369 column, thus preventing further interactions with MnO₂ and mitigating surface passivation, which
370 is generally observed in MnO₂-based redox reactions (*e.g.* as in MCS column)^{4,17,42}. Indeed, it has
371 been reported that Mn(II) binding at the MnO₂ surface may decrease the oxidation rate of organic
372 compounds because (i) Mn(II) may block redox reactive sites on the oxide surface, preventing
373 adsorption of the organic compound or competitively reacting with MnO₂ and (ii) surface bound
374 Mn(II) may decrease the average oxidation state of MnO₂, and therefore slow the rate of electron
375 transfer^{4,17,42,46}. This may explain the higher reactivity of the MGCS system in total PIP removal
376 with respect to MCS.

377

378 **3.3. PIP transport at two pH values**



379
 380 **Figure 4.** Breakthrough curves of (a) PIP and PIP_{ox} (peak area of PIP by-product; M-26) and (b)
 381 Mn(II), pH on different pHs in 0.05 MGCS column. The horizontal dashed line indicates the
 382 theoretical complete breakthrough of PIP ($C/C_0 = 1$) and solid lines are model predictions. The
 383 vertical dashed lines indicate the PIP moment of flow interruption (duration 24 h). The empty symbols
 384 indicate the second-stage after flow resumption. Inflow conditions: $10 \mu\text{M}$ PIP, $\text{pH} 5.2 \pm 0.1$ and
 385 7.0 ± 0.1 , 10 mM NaCl , PV 4 mL , flow rate 0.5 mL/min . V/V_p is the ratio of injected volume and
 386 pore volume.

387
 388 An additional PIP breakthrough experiment in 0.05 MGCS column was repeated but at pH
 389 7.0. In contrast to experiments at pH 5.2 (Fig. 4), no variations in pH occurred. Only $1.8 \mu\text{mol}$ of
 390 PIP was removed at neutral pH, compared to that at pH 5.2 ($3.2 \mu\text{mol}$), because acidic conditions
 391 favored PIP oxidation and adsorption onto MnO_2 and/or goethite. Steeper BTC and earlier
 392 breakthrough point, with complete breakthrough were achieved, whereas no PIP_{ox} or Mn(II) was
 393 detected in the column effluent, indicating extreme low or no PIP transformation occurred at pH 7.
 394 This observation is consistent with our modeling result since setting $\mu_s = 0$ can well fit the BTC of
 395 PIP at pH 7 (Table S2).

396 No oxidation occurred during the first stage, but when the residence time is increased, Mn(II)
397 and PIP_{ox} were detected upon flow resumption. The PIP relative concentration drops to 0.6 at pH
398 7 but only to 0.8 at pH 5.2 when the flow was resumed (Fig. 4a). According to Eq. 8, more PIP was
399 removed and a higher k value was obtained during flow interruption period at pH 7 ($1.4 \times 10^{-4} \text{ min}^{-1}$
400 1 at pH 5.2, $3.5 \times 10^{-4} \text{ min}^{-1}$ at pH 7, Table S3). As only sorption happened in the first step, we
401 suppose that the pristine MnO₂ surfaces may enable more PIP oxidation during flow interruption
402 period. Furthermore, less MnO₂ passivation can be expected, as more Mn(II) can be adsorbed by
403 goethite at pH 7 (see batch data in Fig. S7).

404 In summary, both experimental and modeling results show that binary mixtures of
405 manganese oxides and goethite are capable of oxidizing and removing PIP more efficiently than in
406 the single phase. MGCS may overcome the major drawbacks of MCS to be used as a potential
407 geomeedia for antibiotic removal. Indeed, preferential adsorption of Mn(II) on negatively charged
408 MnO₂, and the progressive build-up of Mn(II) in the column decreased the reactivity of the MCS
409 column over breakthrough time. However, MGCS preferential adsorbed PIP or PIP_{ox} over Mn(II)
410 and thereby reduced the passivation effect by dissolved Mn(II).

411

412 **4. Environmental significance**

413 This study contributed to mounting evidences that the environmental fate of pollutants can
414 not be predicted based on the sorption/oxidation data of single minerals. A thorough examination
415 of the redox reactivity within complex mineral assemblages under both batch and continuous flow
416 conditions is necessary for an accurate assessment of contaminant transport in natural environments
417 (e.g. soils and sediments) or engineered infiltration systems (e.g. MAR). Here, we showed that
418 coexisting minerals, in our case goethite, can alter the overall reactivity of the redox-active MnO₂.
419 In particular, interactions between the positively charged goethite and the negatively charged MnO₂

420 particles decreased Mn(II) surface loadings, thus facilitating its mobility through the column. In
421 addition to advancing ideas on environmental processes, knowledge that goethite-MnO₂
422 interactions decrease MnO₂ passivation could be used to design novel geomedia filters. Fe and Mn
423 binary oxide may overcome the major drawbacks of Mn-oxides to be used as a potential geomedia
424 for antibiotic removal. As manganese oxides have the potential to be applied as filter to prevent
425 organic contaminants from percolating into the groundwater sources in both natural soils and
426 artificial infiltration systems, this work could help in designing efficient geomedia in treatment
427 technologies (industrial and/or municipal wastewater, agricultural runoff, stormwater, etc.). Those
428 contaminated systems contain diverse organic groups such as pharmaceuticals and personal care
429 products, pesticides and detergents, with varying concentrations. Therefore, the amount MnO₂
430 and/or goethite coated on sand should be optimized to further enhance the reactivity and longevity
431 of geomedia, and prior to the application of GMCS in infiltration systems. Finally, as Fe and Mn-
432 oxides may co-exist with each other as particulate coatings, the transport model developed here
433 will help in understanding fate and transformation of emerging compounds in natural environments
434 such as soils and sediments.

435

436 **Supporting Information**

437 Synthesis of minerals and coatings materials; pH dependent PIP and Mn(II) adsorption onto GCS;
438 Kinetics of PIP removal with 0.05 GMCS; Kinetic sorption of Mn(II) on MCS and 0.05 GMCS;
439 PIP and PIP_{ox} detection methods; SEM images of GCS, 0.05 MGCS, 0.1 MGCS; Breakthrough
440 curves of pH in the different MnO₂ content packed columns.

441 **Author Contributions**

442 † T.L. and R.P. contributed equally to this work.

443 **Notes**

444 The authors declare no competing financial interest.

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451

452 **References**

- 453 (1) Post, J. E. Manganese Oxide Minerals: Crystal Structures and Economic and Environmental
454 Significance. *Proc. Natl. Acad. Sci. U. S. A.* **1999**, *96* (7), 3447–3454.
- 455 (2) Cornell, R. M.; Schwertmann, U. *The Iron Oxides: Structure, Properties, Reactions, Occurrences and*
456 *Uses*; Weinheim: Wiley-vch, 2003.
- 457 (3) Lion, L. W.; Altmann, R. S.; Leckie, J. O. Trace-Metal Adsorption Characteristics of Estuarine
458 Particulate Matter: Evaluation of Contributions of Fe/Mn Oxide and Organic Surface Coatings. *Environ.*
459 *Sci. Technol.* **1982**, *16* (10), 660–666.
- 460 (4) Remucal, C. K.; Ginder-Vogel, M. A Critical Review of the Reactivity of Manganese Oxides with
461 Organic Contaminants. *Environ. Sci. Process. Impacts* **2014**, *16* (6), 1247–1266.
- 462 (5) Li, J.; Zhao, L.; Zhang, R.; Teng, H. H.; Padhye, L. P.; Sun, P. Transformation of Tetracycline
463 Antibiotics with Goethite: Mechanism, Kinetic Modeling and Toxicity Evaluation. *Water Res.* **2021**, *199*,
464 117196.
- 465 (6) Huang, X.; Chen, Y.; Walter, E.; Zong, M.; Wang, Y.; Zhang, X.; Qafoku, O.; Wang, Z.; Rosso, K. M.
466 Facet-Specific Photocatalytic Degradation of Organics by Heterogeneous Fenton Chemistry on Hematite
467 Nanoparticles. *Environ. Sci. Technol.* **2019**, *53* (17), 10197–10207.
- 468 (7) Zhou, L.; Martin, S.; Cheng, W.; Lassabatere, L.; Boily, J. F.; Hanna, K. Water Flow Variability Affects
469 Adsorption and Oxidation of Ciprofloxacin onto Hematite. *Environ. Sci. Technol.* **2019**, *53* (17), 10102–
470 10109.
- 471 (8) Chen, Y.; Lu, X.; Liu, L.; Wan, D.; Chen, H.; Zhou, D.; Sharma, V. K. Oxidation of B-Blockers by
472 Birnessite: Kinetics, Mechanism and Effect of Metal Ions. *Chemosphere* **2018**, *194*, 588–594.
- 473 (9) Liang, M.; Xu, S.; Zhu, Y.; Chen, X.; Deng, Z.; Yan, L.; He, H. Preparation and Characterization of Fe-
474 Mn Binary Oxide/Mulberry Stem Biochar Composite Adsorbent and Adsorption of Cr(VI) from Aqueous
475 Solution. *Int. J. Environ. Res. Public Health* **2020**, *17*, 676.

- 476 (10) Ricko, A. N.; Psoras, A. W.; Sivey, J. D. Reductive Transformations of Dichloroacetamide Safeners:
477 Effects of Agrochemical Co-Formulants and Iron Oxide + Manganese Oxide Binary-Mineral Systems.
478 *Environ. Sci. Process. Impacts* **2020**, 22 (10), 2104–2116.
- 479 (11) Zhang, G.; Liu, F.; Liu, H.; Qu, J.; Liu, R. Respective Role of Fe and Mn Oxide Contents for Arsenic
480 Sorption in Iron and Manganese Binary Oxide: An X-Ray Absorption Spectroscopy Investigation. *Environ.*
481 *Sci. Technol.* **2014**, 48 (17), 10316–10322.
- 482 (12) Liu, H.; Chen, T.; Frost, R. L. An Overview of the Role of Goethite Surfaces in the Environment.
483 *Chemosphere* **2014**, 103, 1–11.
- 484 (13) Evanko, C. R.; Dzombak, D. A. Surface Complexation Modeling of Organic Acid Sorption to Goethite.
485 *J. Colloid Interface Sci.* **1999**, 206, 189–206.
- 486 (14) Cheng, W.; Zhou, L.; Marsac, R.; Boily, J. F.; Hanna, K. Effects of Organic Matter–Goethite
487 Interactions on Reactive Transport of Nalidixic Acid: Column Study and Modeling. *Environ. Res.* **2020**,
488 *191*, 110187.
- 489 (15) Wang, L.; Cheng, H. Birnessite (γ -MnO₂) Mediated Degradation of Organoarsenic Feed Additive p -
490 Arsanilic Acid. *Environ. Sci. Technol.* **2015**, 49 (6), 3473–3481.
- 491 (16) Zhao, W.; Tan, W.; Wang, M.; Xiong, J.; Liu, F.; Weng, L.; Koopal, L. K. CD-MUSIC-EDL Modeling
492 of Pb²⁺ Adsorption on Birnessites: Role of Vacant and Edge Sites. *Environ. Sci. Technol.* **2018**, 52 (18),
493 10522–10531.
- 494 (17) Pokharel, R.; Li, Q.; Zhou, L.; Hanna, K. Water Flow and Dissolved Mn(II) Alter Transformation of
495 Pipemidic Acid by Manganese Oxide. *Environ. Sci. Technol.* **2020**, 54 (13), 8051–8060.
- 496 (18) Hanna, K.; Boily, J. F. Sorption of Two Naphthoic Acids to Goethite Surface under Flow through
497 Conditions. *Environ. Sci. Technol.* **2010**, 44 (23), 8863–8869.
- 498 (19) Zhang, H.; Huang, C. H. Oxidative Transformation of Fluoroquinolone Antibacterial Agents and
499 Structurally Related Amines by Manganese Oxide. *Environ. Sci. Technol.* **2005**, 39 (12), 4474–4483.

500 (20) Wang, A.; Wang, H.; Deng, H.; Wang, S.; Shi, W.; Yi, Z.; Qiu, R.; Yan, K. Controllable Synthesis of
501 Mesoporous Manganese Oxide Microsphere Efficient for Photo-Fenton-like Removal of Fluoroquinolone
502 Antibiotics. *Appl. Catal. B Environ.* **2019**, *248* (July 2018), 298–308.

503 (21) Cheng, W.; Elaheh, Lot, K.; Remi, M.; Hanna, K. Adsorption of Quinolone Antibiotics to Goethite
504 under Seawater Conditions: Application of a Surface Complexation Model. *Environ. Sci. Technol.* **2019**,
505 *53*, 1130–1138.

506 (22) Anderson, P. R.; Benjamin, M. M. Surface and Bulk Characteristics of Binary Oxide Suspensions.
507 *Environ. Sci. Technol.* **1990**, *24* (5), 692–698.

508 (23) Anderson, P. R.; Benjamin, M. M. Modeling Adsorption in Aluminum-Iron Binary Oxide Suspensions.
509 *Environ. Sci. Technol.* **1990**, *24* (10), 1586–1592.

510 (24) Meng, X.; Letterman, R. D. Effect of Component Oxide Interaction on the Adsorption Properties of
511 Mixed Oxides. *Environ. Sci. Technol.* **1993**, *27* (5), 970–975.

512 (25) Taujale, S.; Zhang, H. Impact of Interactions between Metal Oxides to Oxidative Reactivity of
513 Manganese Dioxide. *Environ. Sci. Technol.* **2012**, *46*, 2764–2771.

514 (26) Zhang, H.; Taujale, S.; Huang, J.; Lee, G. Effects of NOM on Oxidative Reactivity of Manganese
515 Dioxide in Binary Oxide Mixtures with Goethite or Hematite. *Langmuir* **2015**, *31*, 2790–2799.

516 (27) Huang, J.; Zhang, H. Redox Reactions of Iron and Manganese Oxides in Complex Systems. *Front.*
517 *Environ. Sci. Eng.* **2020**, *14* (5), 76.

518 (28) Shimizu, M.; Nakamura, S.; Kurobe, N.; Takase, Y. Absorption, Distribution and Excretion of
519 Pipemidic Acid. *Chemotherapy* **1975**, *23* (9), 2724–2729.

520 (29) Golet, E. M.; Alder, A. C.; Giger, W. Environmental Exposure and Risk Assessment of
521 Fluoroquinolone Antibacterial Agents in Wastewater and River Water of the Glatt Valley Watershed,
522 Switzerland. *Environ. Sci. Technol.* **2002**, *36* (17), 3645–3651.

523 (30) Kolpin, D. W.; Furlong, E. T.; Meyer, M. T.; Thurman, E. M.; Zaugg, S. D.; Barber, L. B.; Buxton, H.
524 T. Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999-2000:
525 A National Reconnaissance. *Environ. Sci. Technol.* **2002**, *36* (18), 1202–1211.

526 (31) Hartmann, A.; Golet, E. M.; Gartiser, S.; Alder, A. C.; Koller, T.; Widmer, R. M. Primary DNA
527 Damage but Not Mutagenicity Correlates with Ciprofloxacin Concentrations in German Hospital
528 Wastewaters. *Arch. Environ. Contam. Toxicol.* **1999**, *36* (2), 115–119.

529 (32) Weist, K.; Högberg, L. D. ECDC Publishes 2015 Surveillance Data on Antimicrobial Resistance and
530 Antimicrobial Consumption in Europe. *Eurosurveillance* **2016**, *21*, 30401.

531 (33) Ma, Y.; Li, M.; Wu, M.; Li, Z.; Liu, X. Occurrences and Regional Distributions of 20 Antibiotics in
532 Water Bodies during Groundwater Recharge. *Sci. Total Environ.* **2015**, *518–519*, 498–506.

533 (34) Manyi-Loh, C.; Mamphweli, S.; Meyer, E.; Okoh, A. Antibiotic Use in Agriculture and Its
534 Consequential Resistance in Environmental Sources: Potential Public Health Implications. *Molecules* **2018**,
535 *23*, 795.

536 (35) Sposito, G. *The Surface Chemistry of Soils*; Oxford university press. 1984.

537 (36) Zhou, L.; Cheng, W.; Marsac, R.; Boily, J. F.; Hanna, K. Silicate Surface Coverage Controls Quinolone
538 Transport in Saturated Porous Media. *J. Colloid Interface Sci.* **2022**, *607*, 347–356.

539 (37) McKenzie, R. M. The Synthesis of Birnessite, Cryptomelane, and Some Other Oxides and Hydroxides
540 of Manganese. *Miner. Mag.* **1971**, *38*, 493–502.

541 (38) Gaboriaud, F.; Ehrhardt, J. J. Effects of Different Crystal Faces on the Surface Charge of Colloidal
542 Goethite (α -FeOOH) Particles: An Experimental and Modeling Study. *Geochim. Cosmochim. Acta* **2003**,
543 *67* (5), 967–983.

544 (39) Hanna, K.; Martin, S.; Quilès, F.; Boily, J.-F. Sorption of Phthalic Acid at Goethite Surfaces under
545 Flow-Through Conditions. *Langmuir* **2014**, *30* (23), 6800–6807.

546 (40) Rusch, B.; Hanna, K.; Humbert, B. Coating of Quartz Silica with Iron Oxides: Characterization and
547 Surface Reactivity of Iron Coating Phases. *Colloids Surfaces A Physicochem. Eng. Asp.* **2010**, *353* (2–3),
548 172–180.

549 (41) Stumm, W. *Chemistry of the Solid–Water Interface: Processes at the Mineral–Water and Particle–*
550 *Water Interface in Natural Systems*; John Wiley & Son Inc., 1992.

- 551 (42) Charbonnet, J. A.; Duan, Y.; Van Genuchten, C. M.; Sedlak, D. L. Chemical Regeneration of
552 Manganese Oxide-Coated Sand for Oxidation of Organic Stormwater Contaminants. *Environ. Sci. Technol.*
553 **2018**, 52 (18), 10728–10736.
- 554 (43) Šimůnek, J.; van Genuchten, M. T. Modeling Nonequilibrium Flow and Transport Processes Using
555 HYDRUS. *Vadose Zo. J.* **2008**, 7 (2), 782–797.
- 556 (44) Van Genuchten, M. T.; Wagenet, R. J. Two-Site/Two-Region Models for Pesticide Transport and
557 Degradation: Theoretical Development and Analytical Solutions. *Soil Sci. Soc. Am. J.* **1989**, 53 (5), 1303–
558 1310.
- 559 (45) Zhang, H.; Huang, C. H. Adsorption and Oxidation of Fluoroquinolone Antibacterial Agents and
560 Structurally Related Amines with Goethite. *Chemosphere* **2007**, 66 (8), 1502–1512.
- 561 (46) Li, Q.; Pokharel, R.; Zhou, L.; Pasturel, M.; Hanna, K. Coupled Effects of Mn(II), pH and Anionic
562 Ligands on the Reactivity of Nanostructured Birnessite. *Environ. Sci. Nano* **2020**, 7 (12), 4022–4031.
- 563