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1 **Mineralization enhancement of pharmaceutical contaminants by radical-**
2 **based oxidation promoted by oxide-bound metal ions**

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26

27 **Abstract**

28 While the use of transition metal oxides in catalyzing advanced oxidation reactions has
29 been widely investigated, very few reports have focused on how the preliminary contact of
30 oxides with target compounds may affect the succession of reaction. In this study, we
31 examined the adsorption and electron transfer reactions of two fluoroquinolones, flumequine
32 (FLU) and norfloxacin (NOR), with goethite (α -FeOOH) or manganese (Mn) oxide, and their
33 impact on the subsequent mineralization of target compounds using H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ under
34 UVA irradiation. Intriguingly, higher total organic carbon (TOC) removal was achieved when
35 antibiotics and metal-oxides were allowed for pre-equilibration before starting the oxidation
36 reaction. The rate and extent of TOC removal is strongly dependent on the molecule structure
37 and the redox-active mineral used, and much less on the pre-equilibration time. This high
38 efficiency can be ascribed to the presence of reduced metal ions, chemically or
39 photochemically generated during the first stage, onto oxide minerals. Oxide-bound Mn^{II}
40 plays a crucial role in catalyzing oxidant decomposition and then producing greater amounts
41 of radical species through a photo-assisted redox cycle, regardless of the underlying surface,
42 $\text{Mn}^{\text{IV}}\text{O}_2$ or $\text{Mn}^{\text{III}}\text{OOH}$. This finding will be of fundamental and practical significance to Mn-
43 based oxidation reactions and wastewater treatment processes.

44

45 **1. Introduction**

46 Fe- and Mn- oxyhydroxides, commonly found in the Earth's near-surface environment,
47 are generally the dominant sorbents and redox-active compounds in the environment ¹⁻².
48 Interactions of these oxides with organic compounds may involve the adsorption associated or
49 not with a heterogeneous redox reaction. The latter, which is typically attributed to sequential
50 one electron-transfer reactions, results in reductive dissolution of the oxide into reduced ions
51 (e.g. Fe^{II} or Mn^{II}) and oxidative transformation of the molecule into oxidized products ³⁻⁵.
52 These interactions are mainly affected by solution pH, oxide surface properties, and structural
53 characteristics of target compound ⁶⁻¹³.

54 The heterogeneous electron transfer reactions are generally studied in the context of
55 characterization of affected environments, as the fate of organic contaminants is often tied to
56 their affinities to surfaces of soil and sediment mineral particles. Some reports contend that
57 these reactions can also be applied in water and wastewater treatment technologies¹¹⁻¹³, even
58 though there is no total effective destruction of target contaminants. Indeed, one electron-
59 transfer reactions with Mn- or Fe-oxides produce a suite of products, including ring-cleavage
60 products or dehalogenated products⁵⁻¹⁰. Although they could modify the contaminant
61 structure, they are not able to achieve total mineralization, *i.e.*, their complete conversion to
62 CO₂ and/or inorganic ions. The latter may be achieved by advanced oxidation processes
63 which are a set of techniques based on the catalytic decomposition of oxidants, hydrogen
64 peroxide (H₂O₂) or persulfate (S₂O₈²⁻)¹⁴⁻¹⁶, and then the formation of strongly reactive
65 transient species such as the hydroxyl radical, •OH (2.8 V), or the sulfate radical, SO₄•⁻ (2.5-
66 3.1 V) ¹⁷⁻¹⁸.

67 In this work, we examined, for the first time, how the electron transfer reactions between
68 organic contaminants and redox-active minerals can determine the subsequent total removal
69 or mineralization of target compounds. For this purpose, we first studied the reaction (*i.e.*,

70 adsorption and/or heterogeneous redox reactions) of two kinds of fluoroquinolone antibiotics
71 with goethite (α -FeOOH) and manganese oxide (MnO_2), which are the most common redox-
72 active minerals in terrestrial and marine environments. The formation of byproducts and
73 reduced metal ions during the first stage of reaction was also monitored. Flumequine (FLU)
74 and norfloxacin (NOR) were selected because of their growing use in human and veterinary
75 medicine and continuous release into the environment, resulting in their large presence in
76 surface waters, groundwaters and sediments at concentrations levels ranging from ng to μg
77 per L ¹⁹⁻²⁰. Fluoroquinolones such as NOR are electron donor–acceptor compounds with the
78 piperazinyll group serving as the electron donor and 4-oxoquinoline-3-carboxylic acid as the
79 electron acceptor in the neutral and zwitterion forms.

80 The catalytic decomposition of H_2O_2 or $\text{Na}_2\text{S}_2\text{O}_8$ and degradation/mineralization of target
81 compounds were then investigated in presence of MnO_2 or α -FeOOH, under dark and UVA
82 irradiation. We also evaluated the impact of pre-equilibration time (*i.e.*, first contact between
83 molecules and oxides) on the mineralization of compounds through hydroxyl/sulfate radical -
84 based oxidation processes. Radical scavengers and Laser Flash Photolysis (LFP) experiments
85 were performed to assess the involved radical species and their reactivity with generated
86 byproducts. To assess the contribution of Mn^{IV} and Mn^{III} in the overall reaction, Mn-oxides
87 with lower valence states as in manganite (γ - $\text{Mn}^{\text{III}}\text{OOH}$) were investigated, and the role
88 played by mineral-bound Mn^{II} on the heterogeneous oxidation process was discussed.

89

90 **2. Materials and methods**

91 **2.1. Chemicals**

92 All chemicals were of pro-analytical quality or better and purchased from Sigma-
93 Aldrich, France. FLU (purity > 99%) and NOR (purity > 98%) stock solutions were prepared
94 separately by dissolving 20 mg of both chemicals in 0.5 mL of 1 M NaOH, then diluted to 1 L
95 with ultrapure water. Hydrogen peroxide (H₂O₂, 35% w/w) and sodium persulfate (PS)
96 (Na₂S₂O₈ > 99.5% purity) were also provided by Sigma-Aldrich. Sulfuric acid, Sodium
97 hydroxide, Manganese (II) nitrate tetrahydrate (Mn(NO₃)₂·4H₂O), 2-propanol (2-Pr, C₃H₈O),
98 *t*-butanol (*t*-but, C₄H₁₀O) were obtained from Sigma–Aldrich. Solutions were prepared with
99 high-purity water obtained from a Millipore Milli-Q system.

100 Goethite (α -FeOOH), manganite (γ -MnOOH) and manganese oxide (MnO₂) particles
101 were synthesized as described in previous studies ²¹⁻²³. The nature of goethite and manganite
102 was confirmed by X-ray diffraction (XRD) (Fig. S1). The diffractogram of manganese oxide
103 corresponds to that of pyrolusite (Fig S1). The B.E.T. specific surface area of α -FeOOH, γ -
104 MnOOH and MnO₂ were 85 ± 1, 64 ± 1 and 371 ± 5 m² g⁻¹, respectively. The point of zero
105 charge (PZC) determined from potentiometric titration of MnO₂ and MnOOH were 2.4 and
106 6.3, respectively, whereas that of goethite was 9.1. Mn average oxidation state (AOS) of
107 pyrolusite was measured by a back-titration method using a KMnO₄ standard solution. ²⁴ AOS
108 of the MnO₂ used in this study was determined as 3.95.

109 **2.2. Adsorption, redox and Laser Flash Photolysis experiments**

110 Solubility experiments were conducted by suspending separately FLU and NOR
111 powders (~4-6 mg) in 10 mL water solution containing NaCl (10 mM) as a function of pH.
112 The suspensions were equilibrated for 24 h, thereafter the supernatants were filtered (0.2 μ m).
113 Then, FLU and NOR concentrations were measured by high-performance liquid

114 chromatography (HPLC, Waters 600 controller with a C18 column (250 mm×4.6 mm i.d., 5
115 μm). Solubility is relatively low at acidic pH for FLU ($\sim 80 \mu\text{M}$) and between pH 7 and 8 for
116 NOR ($\sim 1200 \mu\text{M}$) (Fig. S2).

117 Adsorption and redox kinetics were then evaluated at $\text{pH} = 6.5 \pm 0.1$, NaCl
118 concentration = 10 mM, NOR initial concentration = 24 μM , FLU initial concentration = 24
119 μM with $\alpha\text{-FeOOH}$ and MnO_2 concentration = 10 $\text{m}^2 \text{L}^{-1}$. All batch experiments were
120 performed under an atmosphere of $\text{N}_2(\text{g})$ to purge dissolved CO_2 from the aqueous solutions.
121 Because the adsorption of target compounds is negligible at pH higher than 10 (according to
122 preliminary adsorption tests), desorption tests were conducted at $\text{pH} = 11$ as a means to check
123 the mass balance. Amount of Mn^{II} released in the reaction solution was monitored by Atomic
124 Absorption Spectrometer (Varian AA 140). Possible generation of dissolved ferrous ion was
125 assessed by UV-visible spectrophotometry (Cary 50 probe, Varian) using the 1-10
126 phenanthroline method.

127 Aqueous concentrations of NOR and FLU were determined using a Waters 600
128 controller high performance liquid chromatography (HPLC) system equipped with an
129 autosampler (Waters 717 plus), a C18 column (250 mm×4.6 mm i.d., 5 μm) and a UV
130 detector (246 nm for FLU or 277 nm for NOR, Waters 2489). The mobile phase was a
131 mixture of water/acetonitrile (60:40 v/v) containing 0.1 % of formic acid. The flow rate of the
132 mobile phase was set at 1 mL min^{-1} in an isocratic mode. Under these conditions, the retention
133 times of FLU and NOR were 6.5 and 7.5 min, respectively.

134 Oxidation by-products were analyzed with a water ultrapure HPLC-MS/MS (Acquity
135 UPLC) system, equipped with a BEH C18 column (100 mm x 2.1mm, 1.7 μm). The mobile
136 phase consisted of acetonitrile containing 0.1 % of formic acid (eluant A) and mixture
137 acetonitrile/water (*i.e.*, 10 % / 90 %) containing 0.1 % of formic acid (eluant B) with gradient
138 0 min / 0 % A – 1 min/0 % A – 9 min/100 % A – 12 min / 0 % A and a flow rate equal to 400

139 $\mu\text{L min}^{-1}$. An electrospray ionization (ESI) was used for the MS measurements in positive
140 ionization mode and full scan acquisition.

141 The reactivity of NOR or FLU and their byproducts with radical species was monitored
142 using a Laser Flash Photolysis apparatus (LFP), following previously reported procedure.²⁵
143 Briefly, a laser flash photolysis system using 266 nm excitation wavelength (pulse energy of
144 45 mJ) is used to generate hydroxyl and sulfate radical from H_2O_2 and PS solutions in the
145 presence of different concentrations of fluoroquinolone. Aliquots of chemical solutions (FLU,
146 NOR, $\text{S}_2\text{O}_8^{2-}$, H_2O_2 , etc.) were mixed just before each LFP experiment to obtain the desired
147 concentrations. Reactivity of FLU with hydroxyl radical was determined by using chemical
148 competition kinetics with thiocyanate anion (SCN^-) and consequent formation of di-
149 thiocyanate radical anion ($\text{SCN}_2^{\bullet-}$) detected at 470 nm. Absorption of $\text{SCN}_2^{\bullet-}$ transient was
150 correlated to the competitive reactivity between $\bullet\text{OH}$ and fluoroquinolones in solution to
151 obtain the second order rate constant.²⁵ The second-order rate constant for the reactivity
152 between $\text{SO}_4^{\bullet-}$ and NOR or FLU, was determined from the slope of the linear correlation
153 between the first-order decay constant of the radical, determined from the regression lines of
154 the logarithmic decays of $\text{SO}_4^{\bullet-}$ signal monitored at 450 nm, and the initial concentration of
155 fluoroquinolone. Each error was obtained from the scattering of the experimental data from
156 the fitting line. The constant was reported as $\text{L mgC}^{-1} \text{ s}^{-1}$ after determination of carbon
157 concentration (mgC L^{-1}) using TOC analyser of each sample. Experiments were performed at
158 pH 3 and 9 for FLU (pKa 6.3) and at pH 3.5, 7.5 and 11 for NOR (pKa 6.2 and 8.5) in order
159 to determine the reactivity of neutral and deprotonated forms, which coexist at pH 6.5.

160 **2.3. UVA irradiation experiments**

161 A photoreactor (made of borosilicate glass) of 500 mL capacity was used to perform all
162 experiments at $\text{pH } 6.5 \pm 0.1$. The tubular reactor, 34 cm high and 3.8 cm in diameter, was
163 designed. This setup has an enclosed chamber comprising this reactor; an UVA lamp 24 W

164 (Philips PL-L) placed in the center of the glass cell emitting in a wavelength region 320-400
165 nm with the emission peak centered at $\lambda_{\text{max}} = 360$ nm, yielding a irradiation intensity of 16
166 mW cm^{-2} quantified with an UVA Radiometer (VLX- 3W equipped with a sensor CX 365,
167 ALYS Technologies, Switzerland). The solution with catalysts was continuously stirred with
168 a magnetic bar at 180 rpm. The pH of the sample solution was measured with a VWR
169 instruments 6000 pH-meter. Monitoring of suspension temperature indicated no significant
170 fluctuation (20 ± 2 °C) along the experiment.

171 Two different experiments were conducted at room temperature. In the first series of
172 experiments, FLU or NOR, oxidants (H_2O_2 or $\text{S}_2\text{O}_8^{2-}$) and oxides ($\alpha\text{-FeOOH}$ or MnO_2) were
173 mixed simultaneously few minutes before UVA irradiation. In the second experimental series,
174 suspensions containing antibiotics and goethite or manganese oxide were stirred in the dark
175 for a certain time (1, 24, or 48 h) before adding oxidant and/or starting UVA irradiation.

176 In both experiments, 0.059 g of goethite or 0.0135 g of MnO_2 were added to 500 mL of
177 contaminant solution and the pH was kept constant (6.5 ± 0.1) using NaOH or H_2SO_4 . At each
178 time interval, an aliquot of solution was collected to determine the aqueous concentration of
179 FLU or NOR by HPLC/UV. Total Organic Carbon (TOC) was determined using a TOC-
180 meter (Shimadzu TOC-VCSH). All experiments were conducted in triplicates and showed a
181 good reproducibility within 5 % of relative standard deviation.

182

183 **Results and discussion**

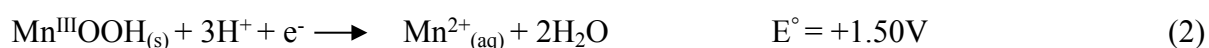
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185 **3.1. Assessment of adsorption and electron transfer reactions on mineral surfaces**

186 Sorption kinetics of FLU onto $10 \text{ m}^2 \text{ L}^{-1}$ of oxide ($\alpha\text{-FeOOH}$ or MnO_2) with 10 mM
187 NaCl at $\text{pH} = 6.5 \pm 0.1$ conducted over a 6-day period showed that a steady-state was
188 achieved within approximately 20 h of reaction time (Fig. S3). Mass balance showed that
189 FLU was removed only by adsorption (*i.e.*, ~ 40 % of FLU was sorbed onto $10 \text{ m}^2 \text{ L}^{-1}$ of $\alpha\text{-$

190 FeOOH or MnO₂, respectively), and that transformation by oxidation did not occur under the
 191 experimental conditions of this study. As widely reported for organic ligands, adsorption
 192 kinetics onto mineral surfaces could be described according to the pseudo-first-order
 193 equation. The pseudo-first-order apparent rate constant k_{app} (min⁻¹) obtained by linear
 194 regression of $-\ln([FLU]_{aq}/[FLU]_0)$ versus time were found close for α -FeOOH (0.15 min⁻¹)
 195 and MnO₂ (0.17 min⁻¹).

196 Both adsorption and oxidation appear to be involved in the removal of NOR in presence
 197 of α -FeOOH or MnO₂ (See [NOR]_{tot} and [NOR]_{aq} in Fig. S3), which is in agreement with
 198 previous works ^{6,26}. This oxidation reaction was more pronounced for MnO₂ likely due to its
 199 higher redox potential, *i.e.*, Mn^{III}/Mn^{II} being more electron acceptor than Fe^{III}/Fe^{II} ³⁻⁵:

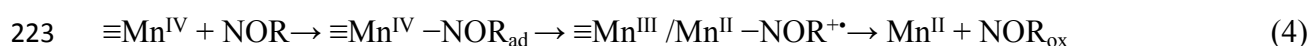


200
 201 The disappearance kinetics of compounds undergoing adsorption/transformation process on
 202 metal oxides cannot be described by simple equations that include classical exponential
 203 functions (*e.g.*, pseudo-first order model). Instead, we calculated an initial rate constant (k_{in} in
 204 min⁻¹) over the first stage of reaction (*i.e.*, 60 min) by plotting a linear regression of -
 205 $\ln([NOR]_{aq}/[NOR]_0)$ versus time, and we found 0.19 min⁻¹ for α -FeOOH and 0.32 min⁻¹ for
 206 MnO₂. This behavior has been attributed to the complexity of involved reactions including
 207 formation of precursor complex, dissolution of reduced metal, accumulation of reaction
 208 products and/or a gradual change of the reactivity of surface sites.

209 In MnO₂/NOR system, an increase in dissolved Mn^{II} concentration was observed over
 210 time, confirming that NOR has been oxidized by MnO₂ under dark conditions (Fig. 1).
 211 However, the measured amount does not correspond to the stoichiometric amount with

212 respect to the NOR degradation, most likely due to strong adsorption of Mn^{II} ions to MnO_2
213 surfaces at pH 6.5 (see below for more details). In case of goethite, dissolved Fe^{II} ion was
214 below detection limit (i.e. $0.2 \mu\text{M}$), probably because of the low amount of generated Fe^{II} (low
215 oxidation extent, Fig. S3), and strong binding of Fe^{II} to FeOOH surfaces at pH 6.5 and
216 subsequent oxidation of adsorbed Fe^{II} ¹⁰.

217 Unlike FLU, NOR binding is followed by an electron transfer process resulting in the
218 concomitant oxidation of NOR and reduction of surface-bound metal. In case of MnO_2 , one
219 electron is transferred from ligand to the surface-bound Mn^{IV} to yield radical intermediate and
220 Mn^{III} that can be further reduced to give Mn^{II} . Subsequently, the formed radical intermediate
221 (NOR°) may undergo several different reaction pathways to yield a range of byproducts as
222 follows:



224
225 Although both FLU and NOR may form similar surface complexes with metal surfaces (i.e.
226 metal-bonded complexes with surface sites and/or directly hydrogen-bonded complexes with
227 surface hydroxo groups) ^{10,21,27}, oxidative transformation was only observed for NOR. Since
228 FLU does not contain a piperazine ring, we may suppose that the piperazine moiety, the
229 electron donor group, should play a critical role in the molecular transformation with FeOOH
230 or MnO_2 . This phenomenon has been proposed in previous work⁶ to explain why four
231 fluoroquinolones all containing a piperazine moiety exhibited a very similar oxidation rate.
232 The nature of primary oxidation byproducts identified in the present work as a result of
233 dealkylation and hydroxylation at the piperazine moiety⁶, further supports this hypothesis.
234 Indeed, two main byproducts were detected by LC/MS/MS analysis conducted on NOR
235 solution reacted with MnO_2 for 22h (Fig. S4). The first ($m/z = 251$, $M - 69$) is supposed to
236 form through N-dealkylation of the piperazine ring with a final aniline functional group, while

237 the second ($m/z = 350$, $M+30$) could correspond to C-hydroxylation of the piperazine moiety,
238 with two additional $>C=O$ groups in the $M + 30$ product (Fig. S4).

239
240 **3.2. Assessment of radical-based oxidation in presence of H_2O_2 or PS under UVA**

241 **irradiation**

242
243 The addition of oxidant to the initial suspension allowed much better removal extent in
244 MnO_2 than in goethite after 300 min of reaction time (Figs. S5 & S6). In all experiments, the
245 direct photolysis of two pollutants is less than 10 % and the degradation resulting from
246 photochemical activation of oxidants less than 20 % (Figs. S5 & S6). The removal resulting
247 upon irradiation of solids (*i.e.* oxide/UV systems) is depended on the oxide surface and
248 molecule. For NOR, 90 % with MnO_2 and 20% with goethite were observed (Figs. S6), which
249 are similar to those observed under dark conditions (*i.e.* through sorption and heterogeneous
250 redox reactions, Fig. S3), ruling out additional contribution of light. For FLU, almost 30 % of
251 FLU removal was observed for both solids under UVA irradiation (Fig. S5), which
252 corresponds to the sorption reaction (Fig. S3), confirming that contribution of ligand to metal
253 charge transfer is small to negligible under our experimental conditions.

254 MnO_2 exhibited more efficiency for thermal activation of oxidants (H_2O_2 or PS) than
255 goethite, while the combination with UVA showed the best performance (*i.e.* > 95 % of FLU
256 or NOR were removed). To account for the adsorption on solids (goethite or MnO_2),
257 desorption tests (adding NaOH to reach pH 11) were carried out and total amounts of FLU or
258 NOR were plotted against time (Figs. S5 & S6). We also monitored the time-trend of TOC in
259 oxidation systems. About 30 % of mineralization of NOR was obtained for H_2O_2/MnO_2 and
260 PS/ MnO_2 systems, while 16 % and 20 % were achieved for $H_2O_2/goethite$ and PS/goethite,
261 respectively (Fig. 2). UVA irradiation allowed more TOC removal, but did not achieve
262 complete mineralization (Fig. 2 for NOR and Fig.S7 for FLU).

263 Previous works reported that superoxide radical ($O_2^{\bullet-}$) is the dominant reactive species
264 generated in the thermal catalyzed decomposition of H_2O_2 by MnO_2 at neutral pH, and at high
265 concentration of H_2O_2 (i.e. > 7.5 mM)^{14, 28}. In the case of MnO_2 -catalyzed activation of PS,
266 several works showed that the Mn(IV)-oxides catalytically decompose PS into sulfate radicals
267 ($SO_4^{\bullet-}$) and hydroxyl radicals ($\bullet OH$)^{9, 29-30}. However, a recent work has identified singlet
268 oxygen (1O_2) as the primary species during PS activation by pyrolusite (β - MnO_2), which can
269 be generated by direct oxidation or recombination of superoxide ions and radicals from a
270 metastable manganese intermediate at neutral pH³¹. In the present work and under UVA
271 irradiation, insights into degradation pathways with minerals + oxidants + UVA could be
272 obtained by studying the effects of 2-propanol (2-Pr) and tert-butyl alcohol (*t*-but), because of
273 their different selectivity (i.e., second-order rate constants) with hydroxyl and sulfate radicals.
274 2-Pr reacts with both $\bullet OH$ and $SO_4^{\bullet-}$, with the second-order reaction constant $k_{HO\bullet,2-Pr} =$
275 1.9×10^9 $M^{-1} s^{-1}$ and $k_{SO_4^{\bullet-},2-Pr} = 4-7.42 \times 10^7$ $M^{-1} s^{-1}$ ³²⁻³³, while *t*-but can be considered to be
276 more selective toward $\bullet OH$ ($k_{HO\bullet,t-but} = 6.0 \times 10^8$ $M^{-1} s^{-1}$) than $SO_4^{\bullet-}$ ($k_{SO_4^{\bullet-},t-but} = 4-8.4 \times 10^5$
277 $M^{-1} s^{-1}$)³²⁻³⁴. For an accurate assessment of reactivity with radical species, we have also
278 determined the bimolecular reaction rate constants with $\bullet OH$ and $SO_4^{\bullet-}$ at different pH values
279 (Table 1 and Fig. S8). At the working pH (6.5), both protonated and ionized forms of FLU
280 may co-exist (See Fig. S2 for distribution of species vs pH). Radical scavenging experiments
281 were only performed with FLU, because of the fast heterogeneous oxidation reaction of NOR
282 with metal oxides.

283 According to scavenging experiments, 2-propanol has strongly inhibited the FLU degradation
284 at 0.5 mM of H_2O_2 (Fig. S9), suggesting that the $\bullet OH$ was by far the dominant reactive species
285 accounting for almost 95 % of degradation. When PS was used instead of H_2O_2 , inhibition
286 observed with *t*-but used as selective scavenger of $\bullet OH$ compared to 2-Pr suggested that the
287 degradation would prevalently take place upon reaction with $SO_4^{\bullet-}$ (Fig. S9, Table S1). From

288 the data, $\text{SO}_4^{\cdot-}$ contribution up to 90% of total FLU degradation can be estimated (Table S1).

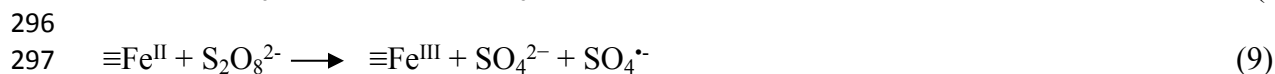
289 At pH 6.5, reaction of $\text{SO}_4^{\cdot-}$ with HO^{\cdot} in order to generate $\cdot\text{OH}$ must be of less extent,

290 because of the low concentration of HO^{\cdot} in solution at this pH value and the low reaction rate,

291 $k_{\text{HO}^{\cdot} \text{SO}_4^{\cdot-}} = 7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ^{29, 35}.

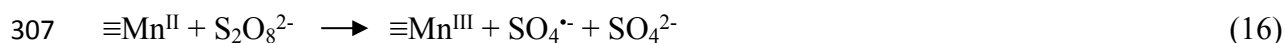
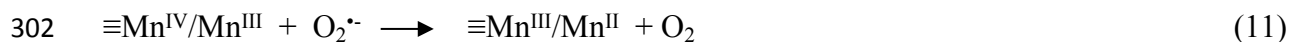
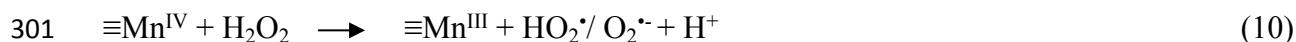
292 Therefore, decomposition of H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ by FeOOH could proceed through a

293 reaction chain, which lead to the production of radical species ^{14, 15, 36}:



299 Likewise, Mn could also initiate H_2O_2 or PS decomposition to generate radical species

300 following equations ^{29, 37, 38, 39}:



308

309 Because the conduction bands of Mn^{IV} (hydr)oxides are at much lower energies than

310 those of the Fe^{III} (hydr)oxides (band gaps in Pyrolusite is 1.0 eV vs 2.5 eV for goethite)⁴⁰, the

311 photoreductive dissolution of Mn^{IV} -oxides is more energetically feasible. However, two one-

312 electron transfer steps or a single two-electron step may be operative during photo-assisted

313 reduction of MnO_2 , *i.e.*, Mn^{IV} can be photochemically reduced to Mn^{III} with or without further
314 reduction into Mn^{II} ⁴³⁻⁴⁵. Waite et al., ⁴³ have reported that the 365-nm light irradiation MnO_2
315 can produce Mn^{II} , while other authors reported that photo-generation of Mn^{III} occurs under
316 400-nm light irradiation of MnO_2 , with no further reduction into Mn^{II} ⁴⁴. Furthermore,
317 creation of photoexcited precursor species, which exhibits more facile electron transfer than
318 occurs thermally, may take place under irradiation⁴⁰⁻⁴⁵.

319 In the present work, Mn^{II} aqueous concentration did not exceed 2 μM even after 10h
320 of irradiation of MnO_2 suspension in N_2 purging solution at pH 6.5, most likely due to strong
321 binding of Mn^{2+} to MnO_2 surfaces at pH 6.5. Consistently, environmental concentrations of
322 Mn^{2+} under oxic conditions are found generally very low, particularly in absence of dissolved
323 organic matter⁴¹⁻⁴³.

324 Taken together, these results shows that the greater efficiency achieved under
325 irradiation could be explained by the higher production of active species, *i.e.*, hydroxyl or
326 sulfate radicals and/or reduced metal ions ($\text{Fe}(\text{II})$ or $\text{Mn}(\text{II})$) ³⁵⁻³⁷. The UVA irradiation may
327 promote the photo-assisted reduction of Fe^{III} to Fe^{II} or Mn^{IV} to Mn^{III} and/or Mn^{II} , which
328 subsequently reacts with H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ generating $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$.

329

330

331 **3.3. Impact of pre-equilibration time on the mineralization extent**

332 As total mineralization is not achieved by UVA and oxidants (H_2O_2 or PS), we examine
333 here the implications of the one-electron transfer reaction in enhancing the elimination of
334 target compounds by hydroxyl/sulfate radical-based technology. For this purpose, we
335 investigated the impact of pre-equilibration time between antibiotics and metal-oxides on the
336 mineralization extent.

337 When oxidants and solids were simultaneously added to FLU solution under UVA
338 irradiation (*i.e.*, without pre-equilibration), the mineralization extent increased progressively
339 and achieved a steady-state after 32 h of reaction time (Fig. S7). An equilibration of solid with
340 FLU for 24 h before oxidant addition and UVA irradiation did not affect the mineralization
341 extent (Fig. S10). Note that only adsorption occurs during the pre-equilibration period (solid +
342 FLU) according to the mass balance. In both cases, the highest mineralization extent was
343 found for the UVA/MnO₂ system whatever the used oxidant.

344 When NOR and solids are allowed for equilibration in aqueous solution over 24 h
345 before adding the oxidant, the mineralization extent increased from 0 to 23, 32, 44 and 52 %
346 for H₂O₂/Goethite, PS/Goethite, H₂O₂/MnO₂ and PS/MnO₂ systems, respectively (Fig.3).
347 UVA irradiation after the pre-equilibration time allowed higher mineralization extent, but the
348 complete mineralization was only achieved in the PS/UVA/MnO₂ system (Fig. 3).

349 As the electron transfer reaction between NOR and MnO₂ was relatively fast, we have
350 repeated the previous experiments but by lowering the pre-equilibration time to 1h (Fig. 4).
351 Similar mineralization extents were obtained in the PS/MnO₂ and PS/UVA/MnO₂ systems, but
352 within a shorter total time (*i.e.*, 40 h instead of 54 h of total reaction time). On the other hand,
353 longer pre-equilibration time (*i.e.*, 48 h) was tested for goethite since its reaction kinetic with
354 NOR was relatively slow (See Fig. S11). Only a slight improvement in TOC removal (*i.e.*,
355 less than 8%) was observed, suggesting that larger pre-equilibration time does not
356 significantly affect the mineralization extent in the case of goethite.

357

358 **3.4. Role of oxide-bound Mn^{II} in mineralization enhancement**

359 The mineralization improvement takes place only when NOR and the metal oxide are
360 allowed for equilibration before adding the oxidant. The enhancement factor is more
361 important in presence of MnO₂ (more redox active), and more particularly when PS was used

362 as an oxidant in the second stage. These results can be explained if the reaction products, *i.e.*
363 NOR byproducts and Mn species generating during the first stage, are more reactive than the
364 starting compounds. To assess the reactivity of NOR byproducts with sulfate radicals, Laser
365 Flash Photolysis (LFP) experiments were performed for the mother NOR solution ($t=0$, called
366 NOR) and those reacted with MnO_2 after 1h and 24 h of reaction (called here NOR_{ox}). The
367 results showed very similar reactivity constants with sulfate radicals, *i.e.* $k_{(\text{NOR}, \text{SO}_4^{\cdot-})} =$
368 $1.7 \cdot 10^7 \text{ L mgC}^{-1} \text{ s}^{-1}$ close to the values determined after oxidation by MnO_2 (*i.e.*, $k_{(\text{NOR}_{\text{ox}}, \text{SO}_4^{\cdot-})}$
369 $)_{1\text{h}} = k_{(\text{NOR}_{\text{ox}}, \text{SO}_4^{\cdot-})_{24\text{h}}} = 1.6 \cdot 10^7 \text{ L mgC}^{-1} \text{ s}^{-1}$) (See Table S2). This result may rule out the
370 hypothesis that the higher mineralization rate results from the greater reactivity of NOR
371 byproducts with radical species.

372 Reductive dissolution of MnO_2 by NOR may lead to generate reduced Mn ions and thus
373 Mn^{II} or Mn^{III} -rich MnO_2 system. Because of the great tendency for manganese ions to be
374 adsorbed at the oxide surface at the working pH, the exact concentration of Mn^{2+} generated
375 from the redox reaction MnO_2/NOR cannot be determined. However, adsorption isotherm
376 determined at pH 6.5 indicated a great affinity of Mn^{2+} to MnO_2 with an adsorption capacity
377 lying at $\sim 0.1 \mu\text{mol m}^{-2}$ (Fig. S12). In addition, AOS of Mn in the reacted solid decreased to
378 3.76, thereby underscoring a partial reduction of MnO_2 though no structural modification was
379 observed by XRD (Fig. S13). Only UVA irradiation seems to induce oxygen depletion in the
380 pyrolusite structure, yet no visible structural change can be determined (Table S3, Fig. S13).
381 This is in agreement with previous works which showed a great stability (low solubility) of
382 pyrolusite under well-oxidized conditions.⁴⁶⁻⁴⁷

383

384 To assess the contribution of Mn^{II} in the advanced oxidation reaction (*i.e.* the second
385 stage), we added Mn^{2+} (24 μM to be equivalent to the stoichiometric amount of NOR) in
386 MnO_2 suspension before adding NOR and starting the oxidation reaction (Fig. S14). The

387 results showed a complete mineralization of NOR after 60 h of reaction, while increasing of
388 Mn^{II} concentration to 48 μM led to a complete mineralization within a shorter time (*i.e.*, 44 h
389 instead of 60 h) (Fig. S14). Therefore, complete NOR mineralization could be achieved either
390 by performing a pre-equilibration stage between NOR and MnO_2 or by adding Mn^{II} to the
391 MnO_2 suspension. It is worth noting that Mn^{II} ions in homogeneous solution are not active for
392 PS activation and NOR degradation (Fig. S15), and the mineralization is only achieved when
393 Mn^{II} was added to MnO_2 suspension. As it is generally reported for Fe^{II} ⁴⁸, this higher
394 reactivity of surface-bound Mn^{II} compared to aqueous Mn^{II} may be ascribed to its bandgap
395 decrease, which warrants future research.

396 The contribution of the solid was further confirmed by repeating the oxidation
397 experiment but by removing the solid from solution (*e.g.*, through filtration) after the pre-
398 equilibration period (Fig. S16). Indeed, the mineralization extent of NOR dropped to less than
399 $21 \pm 2\%$. When the same experiment was performed with goethite a slight decrease of
400 mineralization was observed, $53 \pm 2\%$ when goethite was removed from the solution after 24
401 h of pre-equilibration time against $69 \pm 2\%$ in presence of goethite (Fig. S16).

402 As a further attempt to gain insights into the enhanced reactivity of reacted MnO_2
403 system, Mn oxides with lower valence states (Mn^{III}) as in manganite ($\gamma\text{-Mn}^{\text{III}}\text{OOH}$) were
404 investigated. 37 % and complete mineralization were obtained with PS/ MnOOH and
405 PS/ MnOOH /UVA processes, respectively (Fig. 5), compared to 30 and 65 % with PS/ MnO_2
406 and PS/ MnO_2 /UVA processes, respectively (Fig. 2). When NOR and manganite were allowed
407 for 1h pre-equilibration before starting the oxidation reaction, complete mineralization was
408 also observed in the PS/ MnOOH /UVA system, but only after 35 h of reaction time (Fig. 5).
409 This implies that the photo-generation of Mn^{II} enhances the oxidation performance, regardless
410 of the starting solid, *e.g.* $\text{Mn}^{\text{IV}}\text{O}_2$ or $\text{Mn}^{\text{III}}\text{OOH}$.

411 Taken together, these results suggest that oxide-bound Mn^{II} is key in catalyzing the
412 oxidation reaction and enhancing the mineralization rate under UVA irradiation through a
413 redox cycle. Mn^{II} species or photogenerated Mn^{II} species react first with oxidants to produce
414 radicals through eqs. 13 and 16. Then, Mn^{II} species could be re-generated via photo-reduction
415 of active sites on MnO_x or MnOOH surfaces, which in turn react with PS or H_2O_2 to generate
416 $\text{SO}_4^{\cdot-}$ or $\cdot\text{OH}$. The higher fluoroquinolone degradation in the presence of PS compared to
417 H_2O_2 can be probably ascribed to the *i*) higher ability of Mn^{II} in PS activation compared to
418 H_2O_2 and *ii*) higher selectivity of generated sulfate radical (e.g. less subjected for scavenging
419 effects compared to $\cdot\text{OH}$) toward fluoroquinolones. It is worth noting that photo-assisted
420 generation and/or regeneration of Mn^{II} may require a certain time, as TOC removal kinetics
421 exhibited a *two-step* behavior, *i.e.* sharp decay after a first slow phase, particularly in the
422 PS/UVA system, and regardless of the underlying surface, $\text{Mn}^{\text{IV}}\text{O}_2$ (Fig. 4) or $\text{Mn}^{\text{III}}\text{OOH}$ (Fig.
423 5).

424 3. Environmental implications

425 We have notably demonstrated that a short pre-equilibration time between redox-active
426 minerals and antibiotics is crucial to achieve total elimination or mineralization of
427 compounds. Reduced metal ions generated during the pre-equilibration stage and
428 contacted/adsorbed to oxide minerals are highly active in triggering oxidation reactions and
429 achieving complete mineralization. This key promoter of oxidation reaction is generated *in*
430 *situ* with no other reactant added. MnO_x system exhibits more reactivity than FeOOH because
431 (i) of its higher reduction potential ($\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$ being more electron acceptor than $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$),
432 (ii) two one-electron transfer steps or a single two-electron step may be operative during
433 $\text{Mn}^{\text{IV}}\text{O}_2$ reduction, and/or (iii) photoreductive dissolution of $\text{Mn}^{\text{IV}}\text{O}_x$ is more
434 thermodynamically favorable, irrespective of the presence or absence of complexing ligands.

435 In the first stage, the oxidative transformation is attributed to sequential one electron-
436 transfer reactions, i.e., electron transfer within the precursor complex formed between the
437 molecule and the surface-bound metal, that result in reductive dissolution of the oxide and
438 oxidation of the molecule. In the second stage, the byproducts are attacked by radical species,
439 generated upon addition of H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ under UVA irradiation, which achieved
440 mineralization via probably ring-opening reactions. If the compound (e.g. FLU) solely
441 adsorbs to oxide surfaces with no redox reaction during the first stage of reaction, a pre-
442 equilibration period does not impact the mineralization extent regardless of the duration of the
443 first stage.

444 Oxide-bound Mn^{II} is essential in catalyzing oxidation reaction and then producing greater
445 amounts of radical species through a photo-assisted redox cycle. Light enhanced the rate of
446 Mn^{2+} generation, which in turn reacts with H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ to produce more radical species and
447 then oxidize/mineralize target compounds. This shows the greater ability of MnO_2 as
448 compared to iron oxides, in inducing electron transfer reactions with antibiotics, and then
449 triggering their subsequent radical-based degradation. These results provide a novel strategy
450 towards the application of redox active minerals in a dynamic two-step treatment process,
451 where the redox byproducts generated *in-situ* during the first stage strongly contribute in
452 achieving total removal of TOC. Because of the great affinity of manganese ions for Mn-
453 oxide surfaces at neutral pH, the Mn^{2+} leaching from the oxide surface is very limited, and
454 much below the wastewater discharge limits. Therefore, the developed system will be of
455 scientific significance in both Mn-based oxidation reactions and practical wastewater
456 treatment processes.

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460

461 **Supporting Information Available.** Solubility tests and speciation vs pH, additional kinetics
462 data in sorption/desorption and formation of byproducts; adsorption of Mn^{2+} to MnO_2 ;
463 oxidation/mineralization kinetics for FLU and NOR under different experimental conditions,
464 LFP experimental datasets. This information is available free of charge via the Internet at
465 <http://pubs.acs.org/>.

466

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Tables

Table 1. Second-order rate constants between flumequine (FLU) and norfloxacin (NOR) determined by laser flash photolysis with hydroxyl and sulfate radicals at different pH values.

Molecule	pH	$k_{HO\cdot}(M^{-1} s^{-1})$	$k_{SO_4^{\cdot-}}(M^{-1} s^{-1})$
FLU	3	$1.80 \pm 0.17 \times 10^{10}$	$1.86 \pm 0.30 \times 10^9$
	9	$6.34 \pm 0.13 \times 10^9$	$1.81 \pm 0.12 \times 10^9$
NOR	3.5		$2.09 \pm 0.17 \times 10^9$
	7.5	$6.18 \pm 0.18 \times 10^9$ (ref.49)	$1.36 \pm 0.14 \times 10^9$
	11		$1.31 \pm 0.30 \times 10^9$

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Figure captions

Figure 1: Kinetics of NOR removal and Mn^{2+} release under dark conditions at $\text{pH } 6.5 \pm 0.1$:

$[\text{NOR}] = 24 \mu\text{M}$; $[\text{MnO}_2] = 0.027 \text{g L}^{-1}$ ($10 \text{ m}^2 \text{ L}^{-1}$).

Figure 2: Removal kinetics of NOR_{tot} (empty symbols) and TOC_{tot} (full symbols) with simultaneous addition of solids and oxidants under dark and irradiation conditions at $\text{pH } 6.5 \pm$

0.1 . $[\text{NOR}]_0 = 24 \mu\text{M}$; $[\text{H}_2\text{O}_2]_0 = [\text{S}_2\text{O}_8^{2-}]_0 = 0.5 \text{ mM}$; $[\text{goethite}]_0 = 0.118 \text{g L}^{-1}$ ($10 \text{ m}^2 \text{ L}^{-1}$);

$[\text{MnO}_2]_0 = 0.027 \text{g L}^{-1}$ ($10 \text{ m}^2 \text{ L}^{-1}$).

Figure 3: Removal kinetics of NOR_{tot} (empty symbols) and TOC_{tot} (full symbols) after 24 h of pre-equilibration time under dark and irradiation conditions at $\text{pH } 6.5 \pm 0.1$: $[\text{NOR}]_0 = 24$

μM ; $[\text{H}_2\text{O}_2]_0 = [\text{S}_2\text{O}_8^{2-}]_0 = 0.5 \text{ mM}$; $[\text{goethite}]_0 = 0.118 \text{g L}^{-1}$ ($10 \text{ m}^2 \text{ L}^{-1}$); $[\text{MnO}_2]_0 = 0.027 \text{g L}^{-1}$

($10 \text{ m}^2 \text{ L}^{-1}$). The arrow indicates the moment where oxidant addition and/or UVA irradiation take place.

Figure 4: Removal kinetics of NOR_{tot} (empty symbols) and TOC_{tot} (full symbols) with MnO_2

and $\text{S}_2\text{O}_8^{2-}$ (PS) under dark and irradiation conditions at $\text{pH } 6.5 \pm 0.1$: $[\text{NOR}]_0 = 24 \mu\text{M}$;

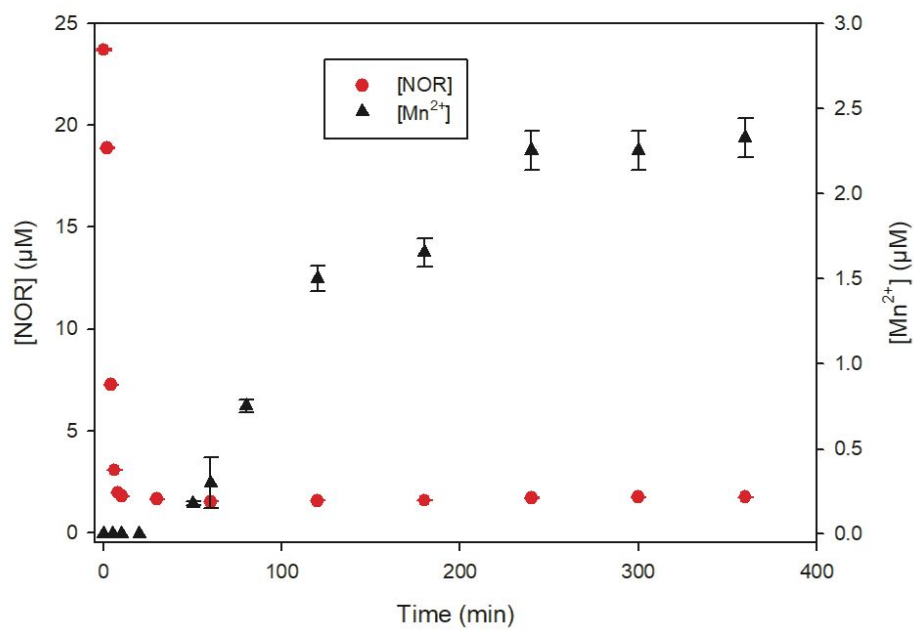
$[\text{S}_2\text{O}_8^{2-}]_0 = 0.5 \text{ mM}$; $[\text{MnO}_2]_0 = 0.027 \text{g L}^{-1}$ ($10 \text{ m}^2 \text{ L}^{-1}$); Pre-equilibration time = 1h.

Figure 5: Removals kinetic of NOR_{tot} (empty symbols) and TOC_{tot} (full symbols) using

MnOOH without or with pre-equilibration time under dark and irradiation conditions and at

$\text{pH } 6.5 \pm 0.1$: $[\text{NOR}]_0 = 24 \mu\text{M}$; $[\text{S}_2\text{O}_8^{2-}]_0 = 0.5 \text{ mM}$; $[\text{MnOOH}]_0 = 0.154 \text{g L}^{-1}$ ($10 \text{ m}^2 \text{ L}^{-1}$). The

vertical dashed line indicates the moment (1h) where oxidant addition and/or UVA irradiation take place.



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Figure 1

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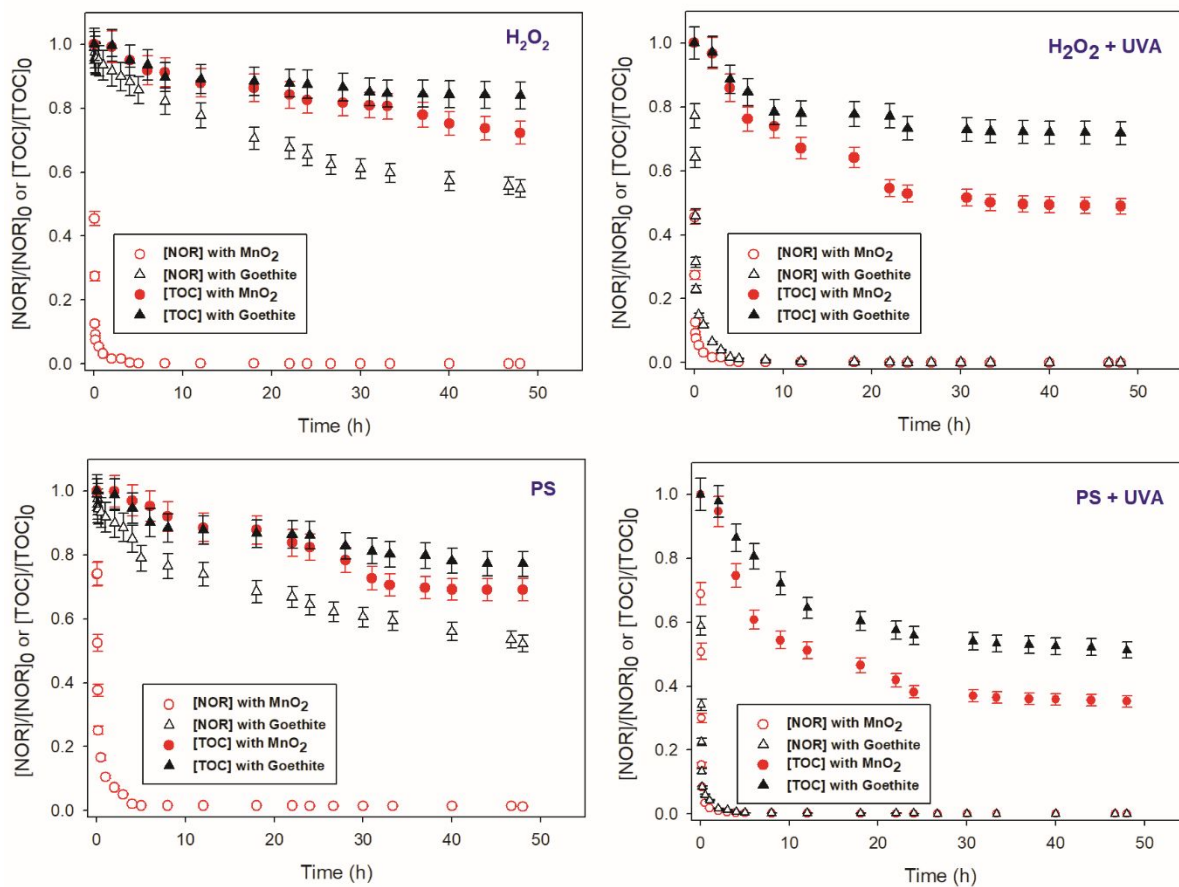
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Figure 2

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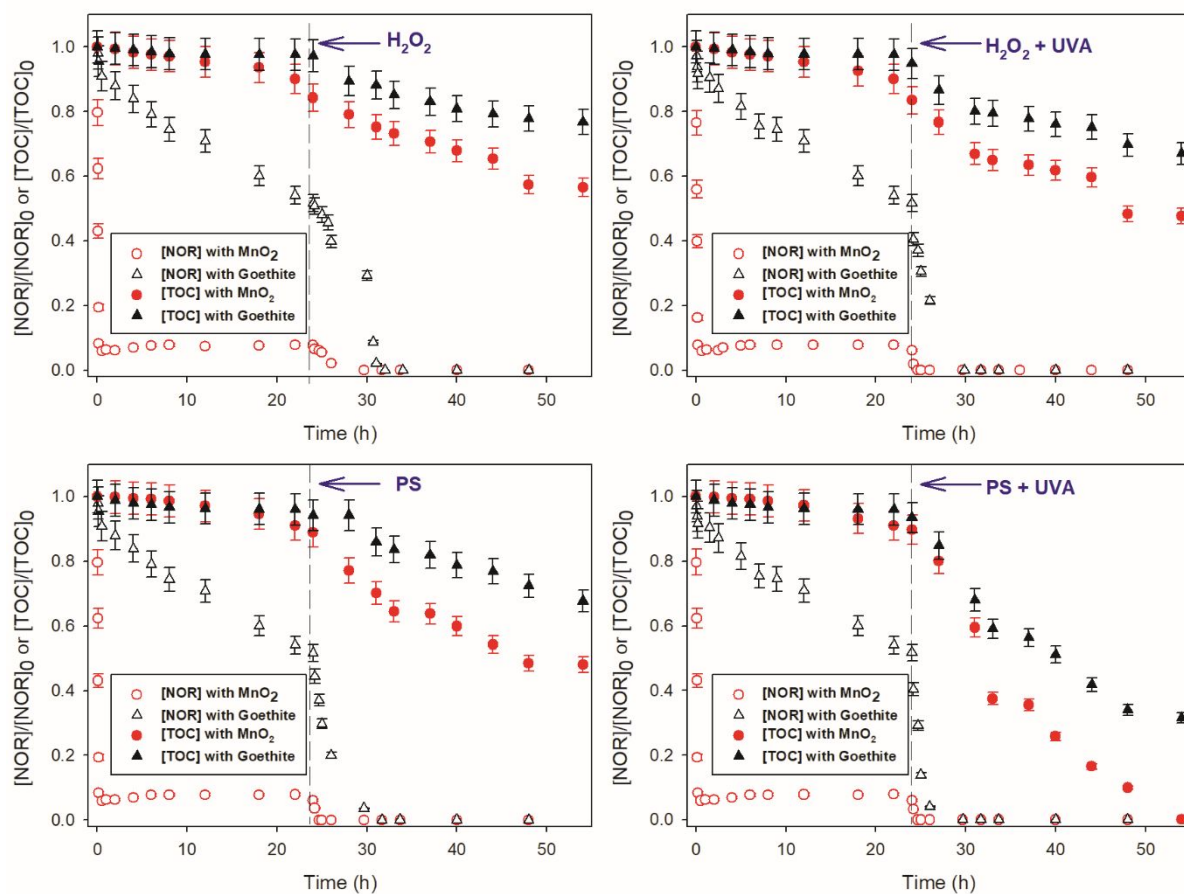
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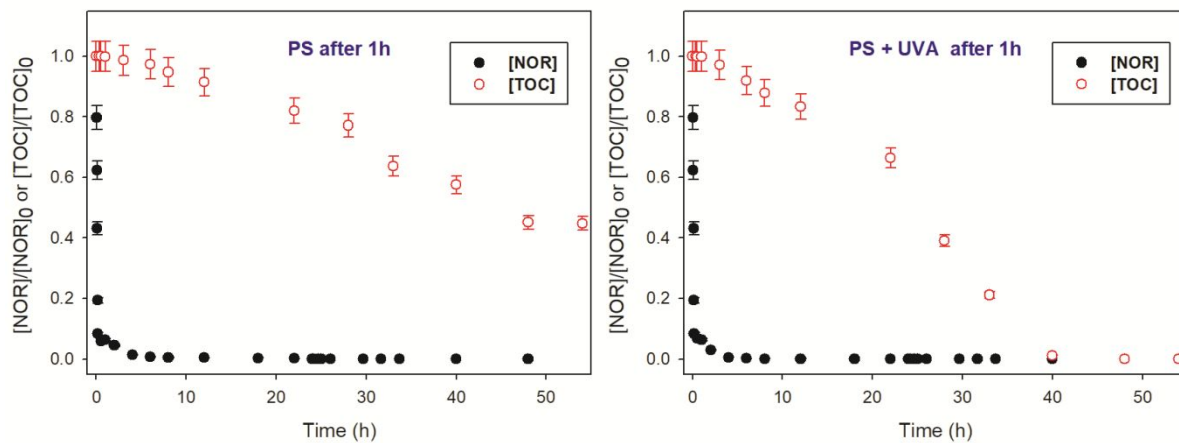
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Figure 3

**Figure 4**

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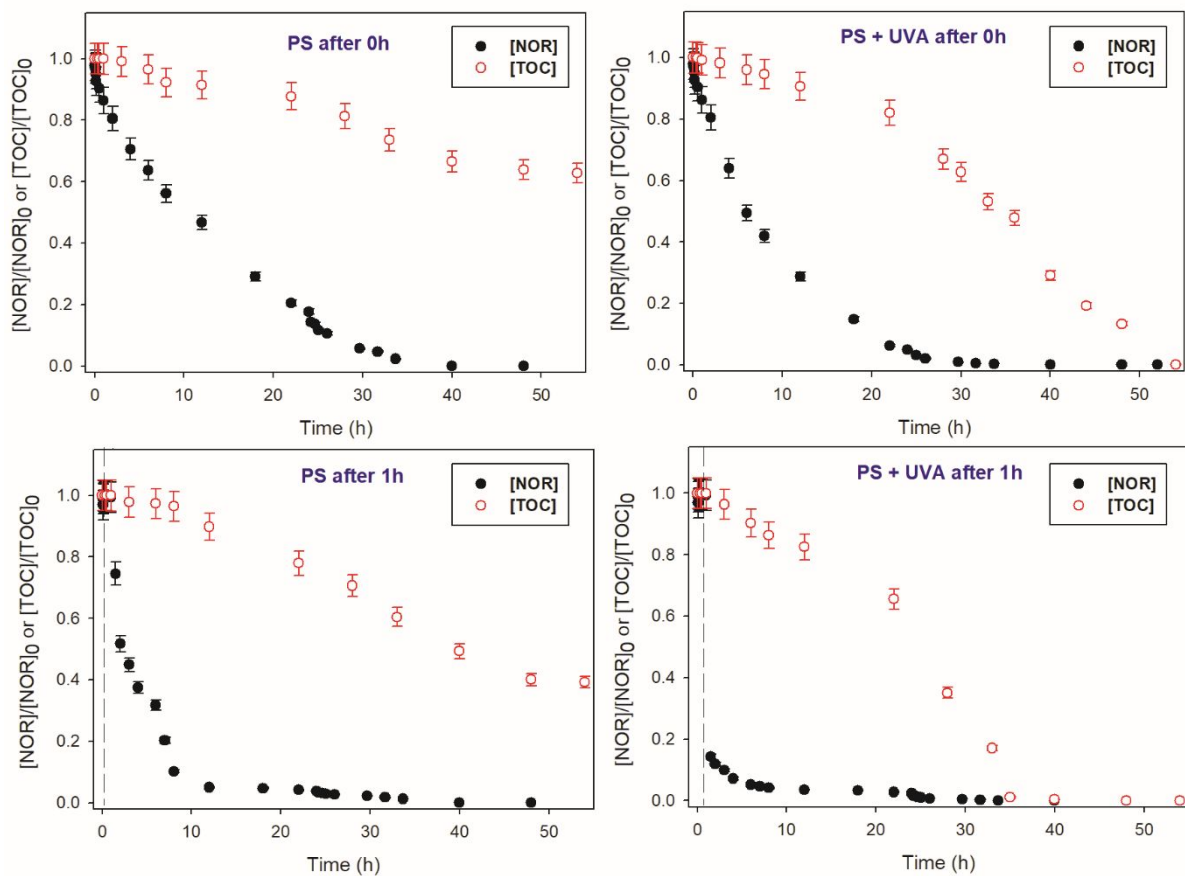
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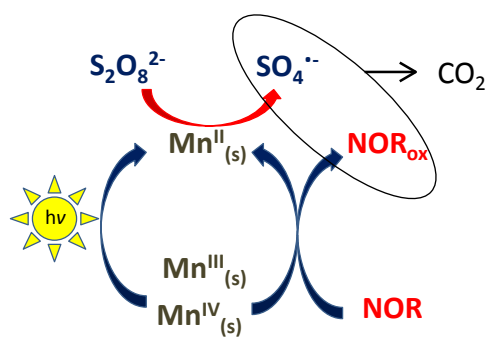
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703**Figure 5**

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Graphical Abstract

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