



**HAL**  
open science

# Mineralization Enhancement of Pharmaceutical Contaminants by Radical-Based Oxidation Promoted by Oxide-Bound Metal Ions

Mahamadou Kamagate, Mathieu Pasturel, Marcello Brigante, Khalil Hanna

► **To cite this version:**

Mahamadou Kamagate, Mathieu Pasturel, Marcello Brigante, Khalil Hanna. Mineralization Enhancement of Pharmaceutical Contaminants by Radical-Based Oxidation Promoted by Oxide-Bound Metal Ions. *Environmental Science and Technology*, 2020, 54 (1), pp.476-485. 10.1021/acs.est.9b04542 . hal-02442225

**HAL Id: hal-02442225**

**<https://hal-univ-rennes1.archives-ouvertes.fr/hal-02442225>**

Submitted on 13 Feb 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

3

4             Mahamadou Kamagate<sup>1,2</sup>, Mathieu Pasturel<sup>3</sup>, Marcello Brigante<sup>4</sup>, Khalil Hanna<sup>\*1,5</sup>

5

6     <sup>1</sup>Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, UMR CNRS 6226, 11 Allée  
7     de Beaulieu, F-35708 Rennes Cedex 7, France.

8     <sup>2</sup>Université de Man, BP 20 Man, Côte d'Ivoire.

9     <sup>3</sup>Univ Rennes, Université de Rennes 1, UMR CNRS 6226, Avenue General Leclerc, F-35708  
10     Rennes Cedex 7, France.

11     <sup>4</sup>Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de Clermont-  
12     Ferrand, F-63000 Clermont-Ferrand, France.

13

14     <sup>5</sup> Institut Universitaire de France (IUF), MESRI, 1 rue Descartes, 75231 Paris Cedex.

15

16     \*Corresponding author: [khalil.hanna@ensc-rennes.fr](mailto:khalil.hanna@ensc-rennes.fr) / +332 23 23 80 27

17

18

19

20

21

22

23

24

Revised manuscript to *Environmental Science & Technology*

25

December, 2019

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 ( $\alpha$ -FeOOH) or manganese (Mn) oxide, and their  
33 impact on the subsequent mineralization of target compounds using  $\text{H}_2\text{O}_2$  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  $\text{Mn}^{\text{II}}$   
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<sup>1-2</sup>.  
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<sup>II</sup> or Mn<sup>II</sup>) and oxidative transformation of the molecule into oxidized products<sup>3-5</sup>.  
52 These interactions are mainly affected by solution pH, oxide surface properties, and structural  
53 characteristics of target compound<sup>6-13</sup>.

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 technologies<sup>11-13</sup>, 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 products<sup>5-10</sup>. Although they could modify the contaminant  
61 structure, they are not able to achieve total mineralization, *i.e.*, their complete conversion to  
62 CO<sub>2</sub> 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 (H<sub>2</sub>O<sub>2</sub>) or persulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>)<sup>14-16</sup>, and then the formation of strongly reactive  
65 transient species such as the hydroxyl radical, •OH (2.8 V), or the sulfate radical, SO<sub>4</sub>•<sup>-</sup> (2.5-  
66 3.1 V)<sup>17-18</sup>.

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 ( $\alpha$ -FeOOH) and manganese oxide ( $\text{MnO}_2$ ), 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  $\mu\text{g}$   
77 per L <sup>19-20</sup>. 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  $\text{H}_2\text{O}_2$  or  $\text{Na}_2\text{S}_2\text{O}_8$  and degradation/mineralization of target  
81 compounds were then investigated in presence of  $\text{MnO}_2$  or  $\alpha$ -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  $\text{Mn}^{\text{IV}}$  and  $\text{Mn}^{\text{III}}$  in the overall reaction, Mn-oxides  
87 with lower valence states as in manganite ( $\gamma$ - $\text{Mn}^{\text{III}}\text{OOH}$ ) were investigated, and the role  
88 played by mineral-bound  $\text{Mn}^{\text{II}}$  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 (H<sub>2</sub>O<sub>2</sub>, 35% w/w) and sodium persulfate (PS)  
96 (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> > 99.5% purity) were also provided by Sigma-Aldrich. Sulfuric acid, Sodium  
97 hydroxide, Manganese (II) nitrate tetrahydrate (Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O), 2-propanol (2-Pr, C<sub>3</sub>H<sub>8</sub>O),  
98 *t*-butanol (*t*-but, C<sub>4</sub>H<sub>10</sub>O) were obtained from Sigma–Aldrich. Solutions were prepared with  
99 high-purity water obtained from a Millipore Milli-Q system.

100 Goethite ( $\alpha$ -FeOOH), manganite ( $\gamma$ -MnOOH) and manganese oxide (MnO<sub>2</sub>) particles  
101 were synthesized as described in previous studies <sup>21-23</sup>. 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  $\alpha$ -FeOOH,  $\gamma$ -  
104 MnOOH and MnO<sub>2</sub> were 85 ± 1, 64 ± 1 and 371 ± 5 m<sup>2</sup> g<sup>-1</sup>, respectively. The point of zero  
105 charge (PZC) determined from potentiometric titration of MnO<sub>2</sub> 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 KMnO<sub>4</sub> standard solution. <sup>24</sup> AOS  
108 of the MnO<sub>2</sub> 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  $\mu$ 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  $\mu\text{m}$ ). 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  $\mu\text{M}$ , FLU initial concentration = 24  
119  $\mu\text{M}$  with  $\alpha\text{-FeOOH}$  and  $\text{MnO}_2$  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  $\text{CO}_2$  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  $\text{Mn}^{\text{II}}$  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  $\mu\text{m}$ ) 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  $\text{mL min}^{-1}$  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 $\mu\text{m}$ ). 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.<sup>25</sup>  
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  $\text{H}_2\text{O}_2$  and PS solutions in the  
145 presence of different concentrations of fluoroquinolone. Aliquots of chemical solutions (FLU,  
146 NOR,  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{H}_2\text{O}_2$ , 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 ( $\text{SCN}^-$ ) 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.<sup>25</sup> 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 ( $\text{mgC L}^{-1}$ ) 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  $\text{mW cm}^{-2}$  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 ( $20 \pm 2$  °C) along the experiment.

171 Two different experiments were conducted at room temperature. In the first series of  
172 experiments, FLU or NOR, oxidants ( $\text{H}_2\text{O}_2$  or  $\text{S}_2\text{O}_8^{2-}$ ) and oxides ( $\alpha\text{-FeOOH}$  or  $\text{MnO}_2$ ) 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  $\text{MnO}_2$  were added to 500 mL of  
177 contaminant solution and the pH was kept constant ( $6.5 \pm 0.1$ ) using NaOH or  $\text{H}_2\text{SO}_4$ . 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**

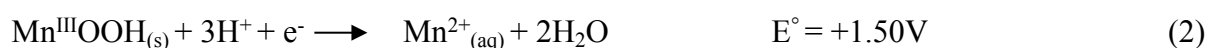
184

### 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  $\text{MnO}_2$ ) 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.*,  $\sim 40$  % of FLU was sorbed onto  $10 \text{ m}^2 \text{ L}^{-1}$  of  $\alpha\text{-$

190 FeOOH or MnO<sub>2</sub>, 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<sup>-1</sup>) obtained by linear  
 194 regression of  $-\ln([FLU]_{aq}/[FLU]_0)$  versus time were found close for  $\alpha$ -FeOOH (0.15 min<sup>-1</sup>)  
 195 and MnO<sub>2</sub> (0.17 min<sup>-1</sup>).

196 Both adsorption and oxidation appear to be involved in the removal of NOR in presence  
 197 of  $\alpha$ -FeOOH or MnO<sub>2</sub> (See [NOR]<sub>tot</sub> and [NOR]<sub>aq</sub> in Fig. S3), which is in agreement with  
 198 previous works <sup>6,26</sup>. This oxidation reaction was more pronounced for MnO<sub>2</sub> likely due to its  
 199 higher redox potential, *i.e.*, Mn<sup>III</sup>/Mn<sup>II</sup> being more electron acceptor than Fe<sup>III</sup>/Fe<sup>II</sup> <sup>3-5</sup>:

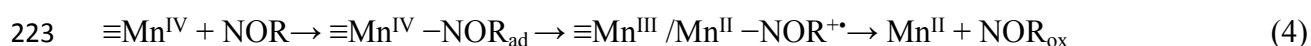


200  
 201 The disappearance kinetics of compounds undergoing adsorption/transformation process on  
 202 metal oxides cannot be described by simple equations that include classical exponential  
 203 functions (*e.g.*, pseudo-first order model). Instead, we calculated an initial rate constant ( $k_{in}$  in  
 204 min<sup>-1</sup>) 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<sup>-1</sup> for  $\alpha$ -FeOOH and 0.32 min<sup>-1</sup> for  
 206 MnO<sub>2</sub>. 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 MnO<sub>2</sub>/NOR system, an increase in dissolved Mn<sup>II</sup> concentration was observed over  
 210 time, confirming that NOR has been oxidized by MnO<sub>2</sub> 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  $\text{Mn}^{\text{II}}$  ions to  $\text{MnO}_2$   
213 surfaces at pH 6.5 (see below for more details). In case of goethite, dissolved  $\text{Fe}^{\text{II}}$  ion was  
214 below detection limit (i.e.  $0.2 \mu\text{M}$ ), probably because of the low amount of generated  $\text{Fe}^{\text{II}}$  (low  
215 oxidation extent, Fig. S3), and strong binding of  $\text{Fe}^{\text{II}}$  to  $\text{FeOOH}$  surfaces at pH 6.5 and  
216 subsequent oxidation of adsorbed  $\text{Fe}^{\text{II}}$  <sup>10</sup>.

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  $\text{MnO}_2$ , one  
219 electron is transferred from ligand to the surface-bound  $\text{Mn}^{\text{IV}}$  to yield radical intermediate and  
220  $\text{Mn}^{\text{III}}$  that can be further reduced to give  $\text{Mn}^{\text{II}}$ . Subsequently, the formed radical intermediate  
221 ( $\text{NOR}^\circ$ ) 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) <sup>10,21,27</sup>, 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  $\text{FeOOH}$   
230 or  $\text{MnO}_2$ . This phenomenon has been proposed in previous work<sup>6</sup> 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 moiety<sup>6</sup>, further supports this hypothesis.  
234 Indeed, two main byproducts were detected by LC/MS/MS analysis conducted on NOR  
235 solution reacted with  $\text{MnO}_2$  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)<sup>14, 28</sup>. 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 ( $\bullet OH$ )<sup>9, 29-30</sup>. However, a recent work has identified singlet  
268 oxygen ( $^1O_2$ ) as the primary species during PS activation by pyrolusite ( $\beta$ - $MnO_2$ ), which can  
269 be generated by direct oxidation or recombination of superoxide ions and radicals from a  
270 metastable manganese intermediate at neutral pH<sup>31</sup>. 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  $1.9 \times 10^9$   $M^{-1} s^{-1}$  and  $k_{SO_4^{\bullet-},2-Pr} = 4-7.42 \times 10^7$   $M^{-1} s^{-1}$ <sup>32-33</sup>, 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  $M^{-1} s^{-1}$ )<sup>32-34</sup>. 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).

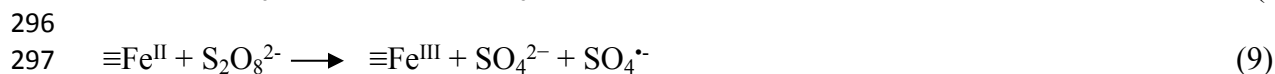
289 At pH 6.5, reaction of  $\text{SO}_4^{\cdot-}$  with  $\text{HO}^{\cdot}$  in order to generate  $\cdot\text{OH}$  must be of less extent,

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

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

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

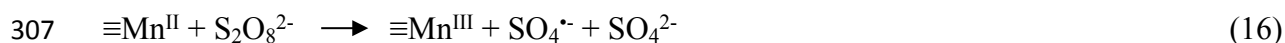
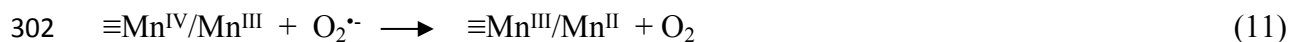
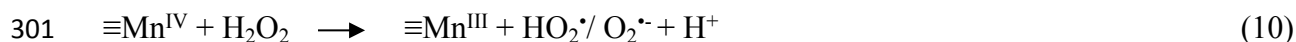
293 reaction chain, which lead to the production of radical species <sup>14, 15, 36</sup>:



298

299 Likewise, Mn could also initiate  $\text{H}_2\text{O}_2$  or PS decomposition to generate radical species

300 following equations <sup>29, 37, 38, 39</sup> :



308

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

310 those of the  $\text{Fe}^{\text{III}}$ (hydr)oxides (band gaps in Pyrolusite is 1.0 eV vs 2.5 eV for goethite)<sup>40</sup>, the

311 photoreductive dissolution of  $\text{Mn}^{\text{IV}}$ -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  $\text{MnO}_2$ , *i.e.*,  $\text{Mn}^{\text{IV}}$  can be photochemically reduced to  $\text{Mn}^{\text{III}}$  with or without further  
314 reduction into  $\text{Mn}^{\text{II}}$  <sup>43-45</sup>. Waite et al., <sup>43</sup> have reported that the 365-nm light irradiation  $\text{MnO}_2$   
315 can produce  $\text{Mn}^{\text{II}}$ , while other authors reported that photo-generation of  $\text{Mn}^{\text{III}}$  occurs under  
316 400-nm light irradiation of  $\text{MnO}_2$ , with no further reduction into  $\text{Mn}^{\text{II}}$  <sup>44</sup>. Furthermore,  
317 creation of photoexcited precursor species, which exhibits more facile electron transfer than  
318 occurs thermally, may take place under irradiation<sup>40-45</sup>.

319 In the present work,  $\text{Mn}^{\text{II}}$  aqueous concentration did not exceed 2  $\mu\text{M}$  even after 10h  
320 of irradiation of  $\text{MnO}_2$  suspension in  $\text{N}_2$  purging solution at pH 6.5, most likely due to strong  
321 binding of  $\text{Mn}^{2+}$  to  $\text{MnO}_2$  surfaces at pH 6.5. Consistently, environmental concentrations of  
322  $\text{Mn}^{2+}$  under oxic conditions are found generally very low, particularly in absence of dissolved  
323 organic matter<sup>41-43</sup>.

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  $\text{Mn}(\text{II})$ ) <sup>35-37</sup>. The UVA irradiation may  
327 promote the photo-assisted reduction of  $\text{Fe}^{\text{III}}$  to  $\text{Fe}^{\text{II}}$  or  $\text{Mn}^{\text{IV}}$  to  $\text{Mn}^{\text{III}}$  and/or  $\text{Mn}^{\text{II}}$ , which  
328 subsequently reacts with  $\text{H}_2\text{O}_2$  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 ( $\text{H}_2\text{O}_2$  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/MnO<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub>/Goethite, PS/Goethite, H<sub>2</sub>O<sub>2</sub>/MnO<sub>2</sub> and PS/MnO<sub>2</sub> 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/MnO<sub>2</sub> system (Fig. 3).

349 As the electron transfer reaction between NOR and MnO<sub>2</sub> 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/MnO<sub>2</sub> and PS/UVA/MnO<sub>2</sub> 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<sup>II</sup> 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 MnO<sub>2</sub> (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  $\text{MnO}_2$  after 1h and 24 h of reaction (called here  $\text{NOR}_{\text{ox}}$ ). 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  $\text{MnO}_2$  (*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  $\text{MnO}_2$  by NOR may lead to generate reduced Mn ions and thus  
373  $\text{Mn}^{\text{II}}$  or  $\text{Mn}^{\text{III}}$  -rich  $\text{MnO}_2$  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  $\text{Mn}^{2+}$  generated  
375 from the redox reaction  $\text{MnO}_2/\text{NOR}$  cannot be determined. However, adsorption isotherm  
376 determined at pH 6.5 indicated a great affinity of  $\text{Mn}^{2+}$  to  $\text{MnO}_2$  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  $\text{MnO}_2$  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.<sup>46-47</sup>

383

384 To assess the contribution of  $\text{Mn}^{\text{II}}$  in the advanced oxidation reaction (*i.e.* the second  
385 stage), we added  $\text{Mn}^{2+}$  (24  $\mu\text{M}$  to be equivalent to the stoichiometric amount of NOR) in  
386  $\text{MnO}_2$  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  $\text{Mn}^{\text{II}}$  concentration to 48  $\mu\text{M}$  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  $\text{MnO}_2$  or by adding  $\text{Mn}^{\text{II}}$  to the  
391  $\text{MnO}_2$  suspension. It is worth noting that  $\text{Mn}^{\text{II}}$  ions in homogeneous solution are not active for  
392 PS activation and NOR degradation (Fig. S15), and the mineralization is only achieved when  
393  $\text{Mn}^{\text{II}}$  was added to  $\text{MnO}_2$  suspension. As it is generally reported for  $\text{Fe}^{\text{II}}$  <sup>48</sup>, this higher  
394 reactivity of surface-bound  $\text{Mn}^{\text{II}}$  compared to aqueous  $\text{Mn}^{\text{II}}$  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  $\text{MnO}_2$   
403 system, Mn oxides with lower valence states ( $\text{Mn}^{\text{III}}$ ) as in manganite ( $\gamma\text{-Mn}^{\text{III}}\text{OOH}$ ) were  
404 investigated. 37 % and complete mineralization were obtained with PS/ $\text{MnOOH}$  and  
405 PS/ $\text{MnOOH}/\text{UVA}$  processes, respectively (Fig. 5), compared to 30 and 65 % with PS/ $\text{MnO}_2$   
406 and PS/ $\text{MnO}_2/\text{UVA}$  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/ $\text{MnOOH}/\text{UVA}$  system, but only after 35 h of reaction time (Fig. 5).  
409 This implies that the photo-generation of  $\text{Mn}^{\text{II}}$  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  $\text{Mn}^{\text{II}}$  is key in catalyzing the  
412 oxidation reaction and enhancing the mineralization rate under UVA irradiation through a  
413 redox cycle.  $\text{Mn}^{\text{II}}$  species or photogenerated  $\text{Mn}^{\text{II}}$  species react first with oxidants to produce  
414 radicals through eqs. 13 and 16. Then,  $\text{Mn}^{\text{II}}$  species could be re-generated via photo-reduction  
415 of active sites on  $\text{MnO}_x$  or  $\text{MnOOH}$  surfaces, which in turn react with PS or  $\text{H}_2\text{O}_2$  to generate  
416  $\text{SO}_4^{\cdot-}$  or  $\cdot\text{OH}$ . The higher fluoroquinolone degradation in the presence of PS compared to  
417  $\text{H}_2\text{O}_2$  can be probably ascribed to the *i*) higher ability of  $\text{Mn}^{\text{II}}$  in PS activation compared to  
418  $\text{H}_2\text{O}_2$  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  $\text{Mn}^{\text{II}}$  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.  $\text{MnO}_x$  system exhibits more reactivity than  $\text{FeOOH}$  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  $\text{H}_2\text{O}_2$  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  $\text{Mn}^{\text{II}}$  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  $\text{Mn}^{2+}$  generation, which in turn reacts with  $\text{H}_2\text{O}_2$  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  $\text{MnO}_2$  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  $\text{Mn}^{2+}$  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.

#### 457 **Acknowledgments**

458 We gratefully acknowledge the Région Bretagne and Institut Universitaire de France for  
459 providing financial support

460

461 **Supporting Information Available.** Solubility tests and speciation vs pH, additional kinetics  
462 data in sorption/desorption and formation of byproducts; adsorption of  $\text{Mn}^{2+}$  to  $\text{MnO}_2$ ;  
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

467 **References**

468

- 469 1. Cornell, R. M.; Schwertmann, U. *The Iron Oxides Structure, Properties, Reactions,*  
470 *Occurrences and Uses*; Wiley-VCH: Weinheim; Cambridge, **2003**.
- 471 2. Hochella, M. F.; Lower, S. K.; Maurice, P. A.; Penn, R. L.; Sahai, N.; Sparks, D. L.;  
472 Twining, B. S. Nanominerals, Mineral Nanoparticles, and Earth Systems. *Science* **2008**,  
473 *319* (5870), 1631–1635.
- 474 3. Stone, A. T. Reductive dissolution of manganese (III/IV) oxides by substituted phenols.  
475 *Environ. Sci. Technol.* **1987**, *21*, 979-988.
- 476 4. McBride, M. B. Adsorption and oxidation of phenolic compounds by iron and manganese  
477 oxides. *Environ. Toxicol. Chem.* **1987**, *51*(6), 1466–1472.
- 478 5. Feitosa-Felizzola, J.; Hanna, K.; Chiron, S. Adsorption and transformation of selected  
479 human-used macrolide antibacterial agents with iron(III) and manganese(IV) oxides.  
480 *Environ. Poll.* 2009, *157* (4), 1317-1322.
- 481 6. Zhang, H.; Huang, C.-H. Oxidative transformation of fluoroquinolone antibacterial agents  
482 and structurally related amines by manganese oxide. *Environ. Sci. Technol.* **2005**, *39*,  
483 4474- 4483.
- 484 7. Rubert, K. F.; Pedersen J.A. Kinetics of Oxytetracycline Reaction with a Hydrous  
485 Manganese Oxide. *Environ. Sci. Technol.* **2006**, *40* (23), 7216-7221.
- 486 8. Lin, K.; Liu, W.; Gan, J. Reaction of tetrabromobisphenol A (TBBPA) with manganese  
487 dioxide: Kinetics, products, and pathways. *Environ. Sci. Technol.* **2009**, *43* (12), 4480-  
488 4486.
- 489 9. Remucal, C. K.; Ginder-Vogel, M. A critical review of the reactivity of manganese oxides  
490 with organic contaminants. *Environ. Sci. Process. Impacts* **2014**, *16*, 1247–1266.

- 491 10. Martin, S.; Shchukarev, A.; Hanna, K.; Boily, J.-F., Kinetics and Mechanisms of  
492 Ciprofloxacin Oxidation on Hematite Surfaces. *Environ. Sci. Technol.* **2015**, *49*,  
493 12197–12205.
- 494 11. Salter-Blanc, A. J.; Bylaska, E. J.; Lyon, M. A.; Ness, S. C.; Tratnyek, P. G. Structure–  
495 Activity Relationships for Rates of Aromatic Amine Oxidation by Manganese Dioxide.  
496 *Environ. Sci. Technol.* **2016**, *50* (10), 5094-5102.
- 497 12. Balgooyen, S.; Alaimo, P. J.; Remucal, C. K.; Ginder-Vogel, M. Structural transformation  
498 of MnO<sub>2</sub> during the oxidation of Bisphenol A. *Environ. Sci. Technol.* **2017**, *51*, 6053-  
499 6062.
- 500 13. Huang, J.; Zhong, S.; Dai, Y.; Liu, C.-C.; Zhang, H. Effect of MnO<sub>2</sub> Phase Structure on the  
501 Oxidative Reactivity toward Bisphenol A Degradation. *Environ. Sci. Technol.* **2018**, *52*  
502 (19), 11309-11318.
- 503 14. Watts, R. J.; Sarasa, J.; Loge, F. J.; Teel, A. L. Oxidative and reductive pathways in  
504 manganese-catalyzed Fenton’s reactions. *J. Environ. Eng.* **2005**, *131*, 158-164.
- 505 15. Liu, H.; Bruton, T. A.; Doyle, F. M.; Sedlak, D. L. In Situ Chemical Oxidation of  
506 Contaminated Groundwater by Persulfate: Decomposition by Fe (III)- and Mn (IV)-  
507 Containing Oxides and Aquifer Materials. *Environ. Sci. Technol.* **2014**, *48*, 10330-10336.
- 508 16. Avetta, P.; Pensato, A.; Minella, M.; Malandrino, M.; Maurino, V.; Minero, C.; Hanna,  
509 K.; Vione, D. Activation of Persulfate by Irradiated Magnetite: Implications for the  
510 Degradation of Phenol under Heterogeneous Photo-Fenton-Like Conditions. *Environ. Sci.*  
511 *Technol.* **2015**, *49*, 1043-1050.
- 512 17. Neta, P.; Huie, R. E.; Ross, A. B. Rate constants for reactions of inorganic radicals in  
513 aqueous solution. *J. Phys. Chem. Ref. Data.* **1988**, *17*, 1027-1284.
- 514 18. Huie, R. E.; Clifton, C. L.; Neta, P. Electron transfer reaction rates and equilibria of the  
515 carbonate and sulfate radical anions. *Radiat. Phys. Chem.* **1991**, *38* (5), 477- 481.

- 516 19. Jia, A.; Wan, Y.; Xiao, Y.; Hu, J. Occurrence and Fate of Quinolone and Fluoroquinolone  
517 Antibiotics in a Municipal Sewage Treatment Plant. *Water Res.* **2012**, *46* (2), 387–394.
- 518 20. Zhang, T.; Li, B. Occurrence, Transformation, and Fate of Antibiotics in Municipal  
519 Wastewater Treatment Plants. *Crit. Rev. Env. Sci. Tec.* **2011**, *41* (11), 951–998.
- 520 21. Marsac, R.; Martin, S.; Boily, J.-F.; Hanna, K. Oxolinic Acid Binding at Goethite and  
521 Akaganéite Surfaces: Experimental Study and Modeling. *Environ. Sci. Technol.* **2016**, *50*  
522 (2), 660–668.
- 523 22. Murray, J. W. The surface chemistry of hydrous manganese dioxide. *J. Colloid Interface*  
524 *Sci.* **1974**, *46*, 357-371.
- 525 23. Yu, C.; Boily, J.-F.; Shchukarev, A.; Drake, H.; Song, Z.; Hogmalm, K.J., Åström, M.E. A  
526 cryogenic XPS study of Ce fixation on nanosized manganite and vernadite: Interfacial  
527 reactions and effects of fulvic acid complexation. *Chem. Geol.* **2018**, *483*, 304-311.
- 528 24. Zhao, H.; Zhu, M.; Li, W.; Elzinga, E. J., Villalobos, M., Liu, F.; Zhang, Feng, J.X.,  
529 Sparks, D. L. Redox Reactions between Mn(II) and Hexagonal Birnessite Change Its  
530 Layer Symmetry. *Environ. Sci. Technol.*, **2016**, *4*, 50-56.
- 531 25. Huang, W.; Bianco, W.; Brigante, M.; Mailhot, G. UVA-UVB activation of hydrogen  
532 peroxide and persulfate for advanced oxidation processes: Efficiency, mechanism and  
533 effect of various water constituents. *J. Haz. Mat.*, **2018**, *347*, 279-287.
- 534 26. Zhang, H.; Huang, CH. Adsorption and oxidation of fluoroquinolone antibacterial agents  
535 and structurally related amines with goethite, *Chemosphere* **2007**, *66* (8), 1502-1512.
- 536 27. Paul, T.; Liu, J.; Machesky, M.L.; Strathmann, T. Adsorption of zwitterionic  
537 fluoroquinolone antibacterials to goethite: A charge distribution-multisite complexation  
538 model. *J. Coll. Int. Sci.* **2014**, *428*, 63-72.



- 539 28. Furman, O.; Laine, D. F.; Blumenfeld, A.; Teel, A. L.; Shimizu, K.; Cheng, I. F.; Watts,  
540 R. J. Enhanced reactivity of superoxide in water – solid matrices. *Environ. Sci. Technol.*  
541 **2009**, 43, 1528-1533.
- 542 29. Liu, H.; Bruton, T. A.; Li, W.; Buren, J. V.; Prasse, C.; Doyle, F. M.; Sedlak D. L.  
543 Oxidation of Benzene by Persulfate in the Presence of Fe(III)- and Mn(IV)-Containing  
544 Oxides: Stoichiometric Efficiency and Transformation Products. *Environ. Sci. Technol.*  
545 **2016**, 50, 890-898.
- 546 30. Fang, G.; Chen, X.; Wu, W.; Liu, C.; Dionysiou, D. D.; Fan, T.; Wang, Y.; Zhu, C.; Zhou  
547 D. Mechanisms of Interaction between Persulfate and Soil Constituents: Activation, Free  
548 Radical Formation, Conversion, and Identification. *Environ. Sci. Technol.* **2018**, 52,  
549 14352–14361.
- 550 31. Zhu, S.; Li, X.; Kang J.; Duan, X.; Wang, S. Persulfate Activation on Crystallographic  
551 Manganese Oxides: Mechanism of Singlet Oxygen Evolution for Nonradical Selective  
552 Degradation of Aqueous Contaminants. *Environ. Sci. Technol.* **2018**, 53, 1, 307-315.
- 553 32. Neta, P.; Madhavan, V.; Zemel, H.; Fessenden, R.W. Rate constants and mechanism of  
554 reaction of  $\text{SO}_4^{\bullet-}$  with aromatic compounds. *J. Am. Chem. Soc.* **1977**, 99,163-164.
- 555 33. Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. Critical review of rate  
556 constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ( $\text{OH}$   
557 /  $\text{O}_2^{\bullet-}$ ) in aqueous solution. *J. Phys. Chem. Ref. Data* **1988**, 17, 513-886.
- 558 34. Gonzalez-Olmos, R.; Martin, M. J.; Georgi, A.; Kopinke, F.-D.; Oller, I.; Malato, S. Fe-  
559 zeolites as heterogeneous catalysts in solar Fenton-like reactions at neutral pH. *Appl.*  
560 *Catal. B: Environ.* **2012**, 125, 51-58.
- 561 35. Minella, M.; Marchetti, G.; De Laurentiis, E.; Malandrino, M.; Maurino, V.; Minero, C.;  
562 Vione, D.; Hanna, K. Photo-Fenton oxidation of phenol with magnetite as iron source.  
563 *Appl. Catal. B: Environ.* **2014**, 154, 102-109.

- 564 36. Kim, E. J.; Oh, D.; Lee, C. S.; Gong, J.; Kim, J. Manganese oxide nanorods as a robust  
565 Fenton-like catalyst at neutral pH: Crystal phase-dependent behavior. *Catal. Today* **2017**,  
566 282, 71-76.
- 567 37. Xu, Y.; Lin, H.; Li, Y.; Zhang H. The mechanism and efficiency of MnO<sub>2</sub> activated  
568 persulfate process coupled with electrolysis. *Sci. Total Environ.* **2017**, 609, 644-654.
- 569 38. Luther, G. W. III. The role of one- and two-electron transfer reactions in forming  
570 thermodynamically unstable intermediates as barriers in multi-electron redox reactions.  
571 *Aquat. Geochem.* **2010**, 16, 395-420.
- 572 39. Baral, S.; Lume-Pereira, C.; Janata, E. ; Henglein, A. Chemistry of colloidal manganese  
573 dioxide. 2. Reaction with superoxide anion (O<sub>2</sub><sup>-</sup>) and hydrogen peroxide (pulse radiolysis  
574 and stop flow studies). *J. Phys. Chem.* **1985**, 89, 5779-5783.
- 575 40. Sherman, D. M. Electronic structures of iron(III) and manganese(IV) (hydr)oxide  
576 minerals: Thermodynamics of photochemical reductive dissolution in aquatic  
577 environments. *Geochim. Cosmochim. Acta*, **2005**, 69, 13, 3249-3255.
- 578 41. Sunda, W. G.; Huntsman, S. A.; Harvey ,G. R. Photoreduction of manganese oxides in  
579 seawater and its geochemical and biological implications. *Nature*, **1983**, 301, 234-236.
- 580 42. Sunda, W. G.; Huntsman, S. A. Photoreduction of manganese oxides in seawater. *Mar.*  
581 *Chem.* **1994**, 46, 133-152.
- 582 43. Waite, T. D.; Wrlgley, I. C.; Szymczak R. Photoassisted Dissolution of a Colloidal  
583 Manganese Oxide in the Presence of Fulvic Acid. *Environ. Sci. Technol.* **1988**, 27 (7),  
584 778-785.
- 585 44. Marafatto, F. F.; Strader, M. L.; Gonzalez-Holguera, J.; Schwartzberg, A.; Gilbert, B.;  
586 Peña, J. Rate and mechanism of the photoreduction of birnessite (MnO<sub>2</sub>) nanosheets.  
587 *Proc. Nat. Acad. Sci.*, **2015**, 1-6.

- 588 45. Klausen, J.; Haderlein, S.B.; Schwarzenbach, R. P. Oxidation of substituted anilines by  
589 aqueous MnO<sub>2</sub>: Effect of Co-solutes on initial and quasi-steady-state kinetics. *Environ.*  
590 *Sci. Technol.* **1997**, 31, 2642- 2649.
- 591 46. Post, J.E. Manganese oxide minerals: Crystal structures and economic and environmental  
592 significance. *Proc. Natl. Acad. Sci.* **1999**, 96, 3447-3454.
- 593 47. Birkner, N.; Navrotsky, A. Rapidly reversible redox transformation in nanophase  
594 manganese oxides at room temperature triggered by changes in hydration. *Proc. Natl.*  
595 *Acad. Sci.* **2014**, 111, 6209-6214.
- 596 48. Alexandrov, V.; Rosso K.M. Ab initio modeling of Fe(II) adsorption and interfacial  
597 electron transfer at goethite ( $\alpha$ -FeOOH) surfaces, *Phys. Chem. Chem. Phys.*, **2015**,17,  
598 14518-14531.
- 599 49. An, T.; Yang, H.; Song, W.; Li, G.; Luo, H.; Cooper, W. J. Mechanistic considerations for  
600 the advanced oxidation treatment of fluoroquinolone pharmaceutical compounds using  
601 TiO<sub>2</sub> heterogeneous catalysis. *J. Phys. Chem. A* **2010**, 114, 2569-2575.

602

603

604

605

606

607

608  
609  
610  
611  
612  
613  
614  
615  
616

## 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		$1.31 \pm 0.30 \times 10^9$

617  
618

619  
620  
621  
622  
623  
624  
625  
626  
627  
628  
629  
630  
631  
632  
633  
634  
635  
636  
637  
638  
639  
640  
641

### Figure captions

**Figure 1:** Kinetics of NOR removal and  $\text{Mn}^{2+}$  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  $\text{NOR}_{\text{tot}}$  (empty symbols) and  $\text{TOC}_{\text{tot}}$  (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  $\text{NOR}_{\text{tot}}$  (empty symbols) and  $\text{TOC}_{\text{tot}}$  (full symbols) after 24 h of pre-equilibration time under dark and irradiation conditions at  $\text{pH } 6.5 \pm 0.1$ :  $[\text{NOR}]_0 = 24$

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

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

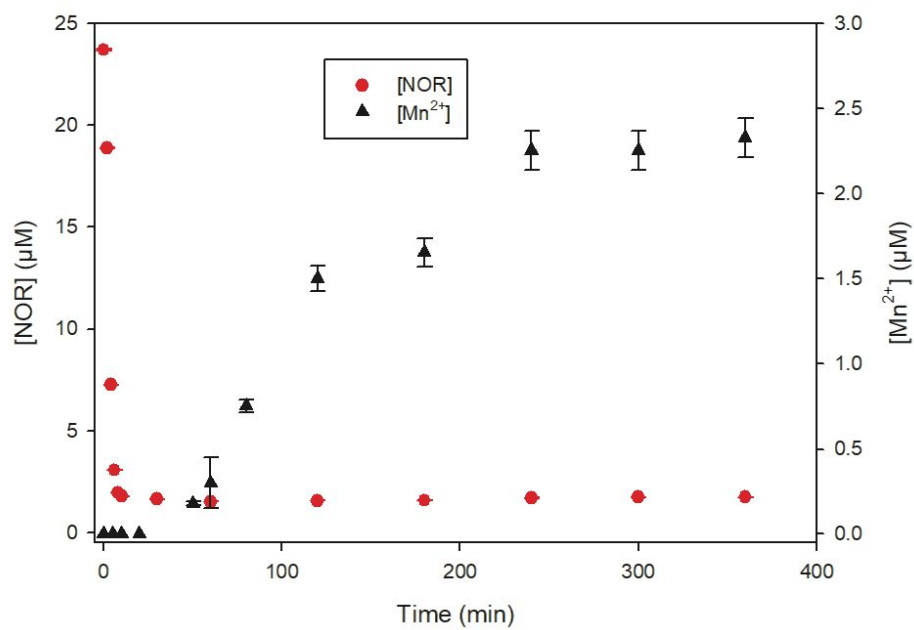
**Figure 4:** Removal kinetics of  $\text{NOR}_{\text{tot}}$  (empty symbols) and  $\text{TOC}_{\text{tot}}$  (full symbols) with  $\text{MnO}_2$  and  $\text{S}_2\text{O}_8^{2-}$  (PS) under dark and irradiation conditions at  $\text{pH } 6.5 \pm 0.1$ :  $[\text{NOR}]_0 = 24 \mu\text{M}$ ;

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

**Figure 5:** Removals kinetic of  $\text{NOR}_{\text{tot}}$  (empty symbols) and  $\text{TOC}_{\text{tot}}$  (full symbols) using  $\text{MnOOH}$  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.



642

643

**Figure 1**

644

645

646

647

648

649

650

651

652

653

654

655

656

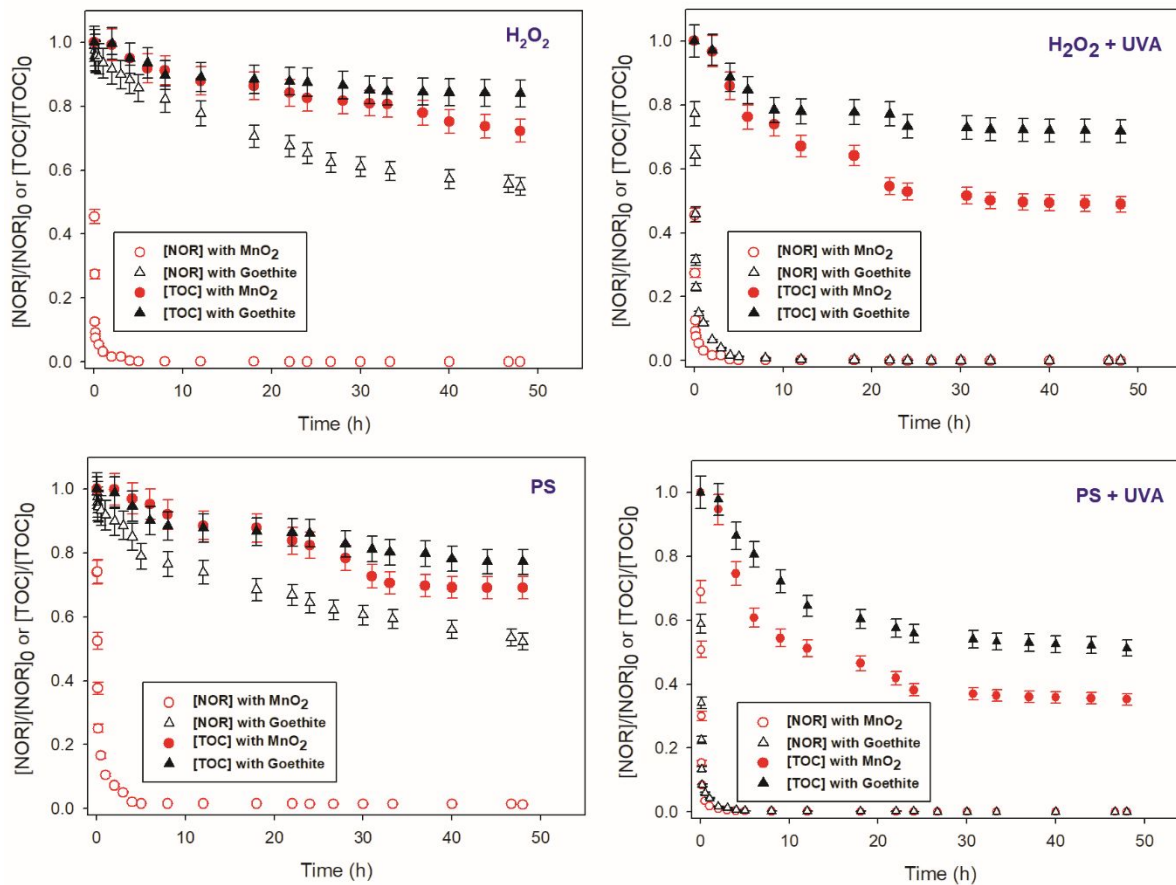
657

658

659

660

661



662

663

Figure 2

664

665

666

667

668

669

670

671

672

673

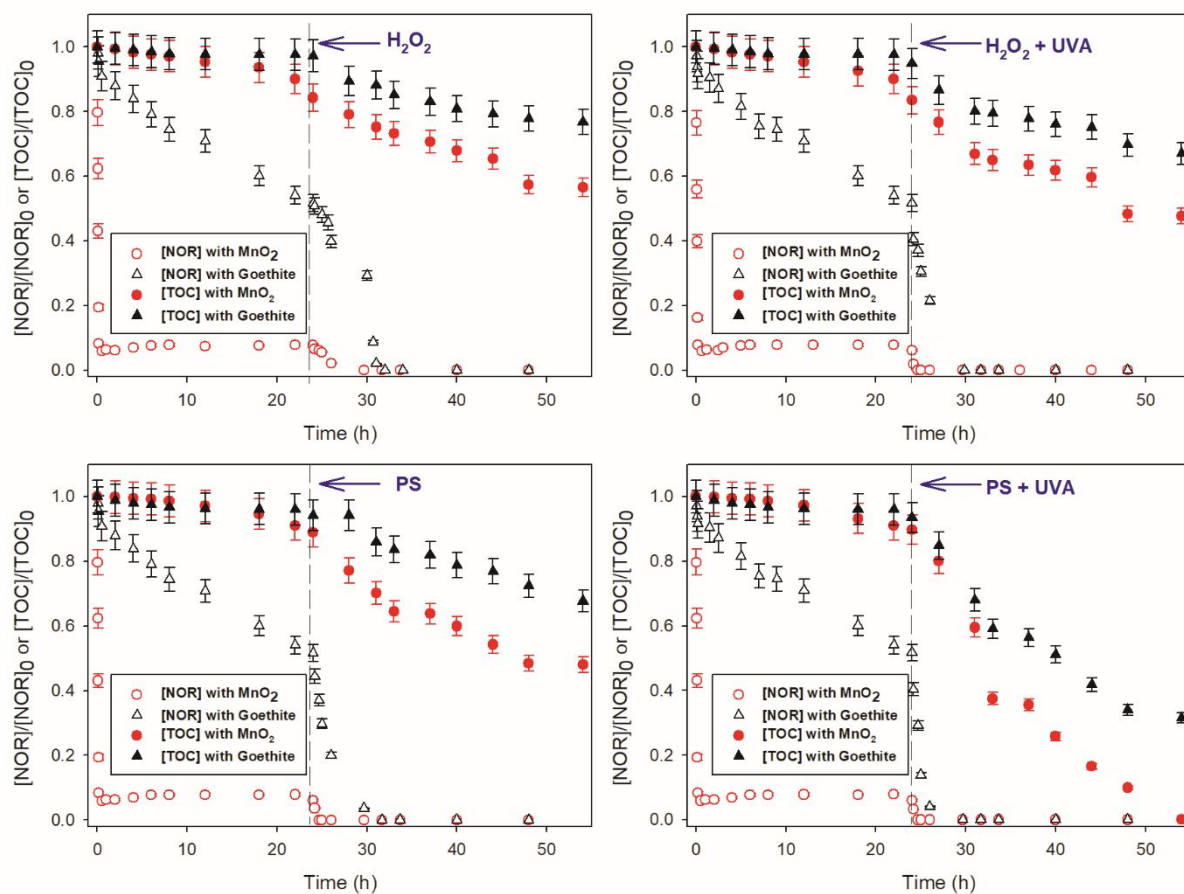
674

675

676

677

678



679

680

681

682

683

684

685

686

687

688

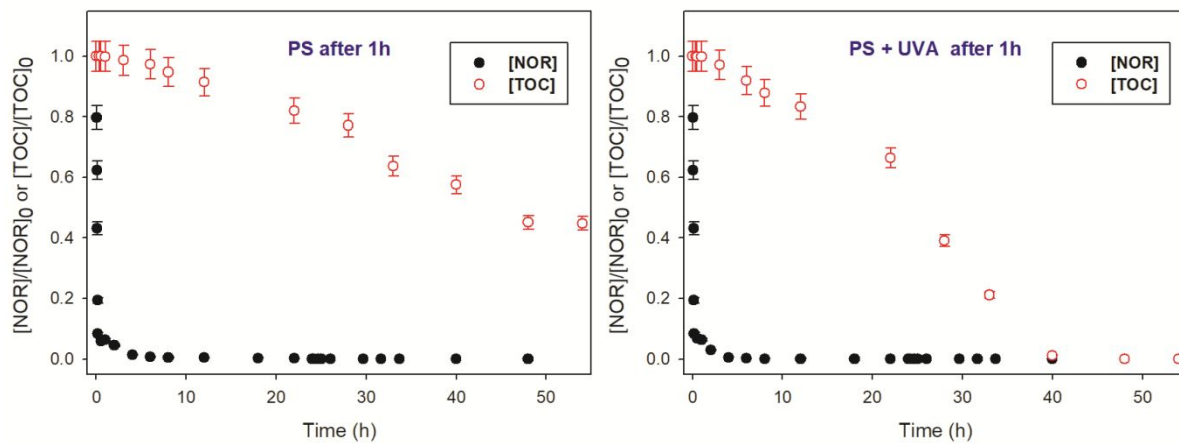
689

690

691

Figure 3



**Figure 4**

692

693

694

695

696

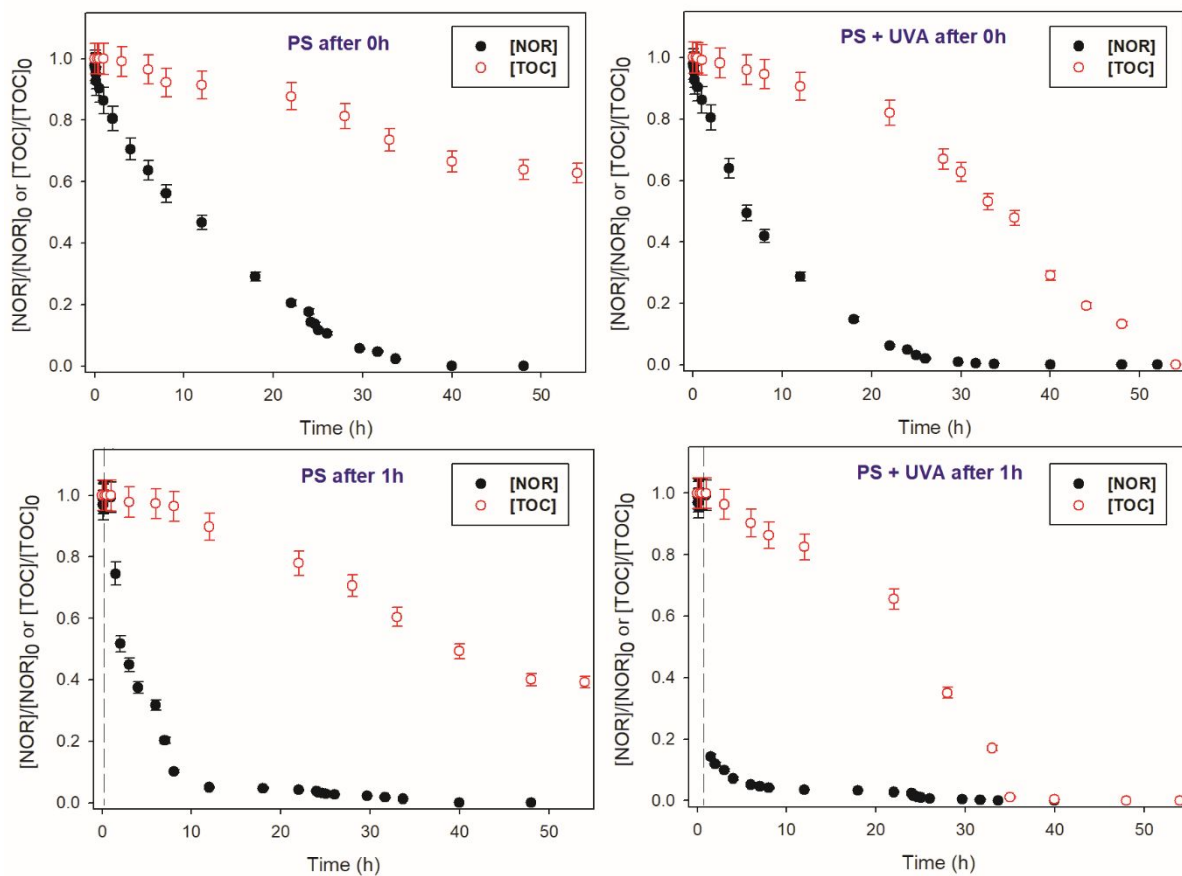
697

698

699

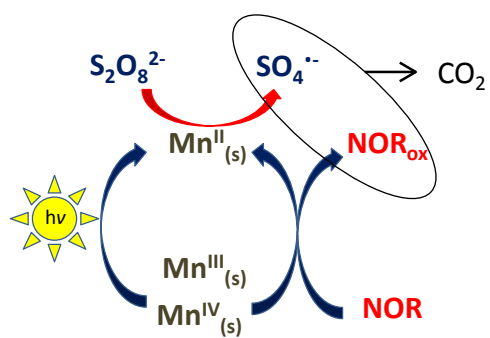
700

701

702  
703**Figure 5**

704

705

**Graphical Abstract**

706

707

708

709

710

711