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

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Abstract

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

1. Introduction

Fe- and Mn- oxyhydroxides, commonly found in the Earth's near-surface environment, are generally the dominant sorbents and redox-active compounds in the environment¹⁻². Interactions of these oxides with organic compounds may involve the adsorption associated or not with a heterogeneous redox reaction. The latter, which is typically attributed to sequential one electron-transfer reactions, results in reductive dissolution of the oxide into reduced ions (e.g. Fe^{II} or Mn^{II}) and oxidative transformation of the molecule into oxidized products³⁻⁵. These interactions are mainly affected by solution pH, oxide surface properties, and structural characteristics of target compound⁶⁻¹³.

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

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

adsorption and/or heterogeneous redox reactions) of two kinds of fluoroquinolone antibiotics with goethite (α -FeOOH) and manganese oxide (MnO_2), which are the most common redox-active minerals in terrestrial and marine environments. The formation of byproducts and reduced metal ions during the first stage of reaction was also monitored. Flumequine (FLU) and norfloxacin (NOR) were selected because of their growing use in human and veterinary medicine and continuous release into the environment, resulting in their large presence in surface waters, groundwaters and sediments at concentrations levels ranging from ng to μg per L¹⁹⁻²⁰. Fluoroquinolones such as NOR are electron donor–acceptor compounds with the piperazinyl group serving as the electron donor and 4-oxoquinoline-3-carboxylic acid as the electron acceptor in the neutral and zwitterion forms.

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

2. Materials and methods

2.1. Chemicals

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

Goethite (α-FeOOH), manganite (γ-MnOOH) and manganese oxide (MnO₂) particles were synthesized as described in previous studies²¹⁻²³. The nature of goethite and manganite was confirmed by X-ray diffraction (XRD) (Fig. S1). The diffractogram of manganese oxide corresponds to that of pyrolusite (Fig S1). The B.E.T. specific surface area of α-FeOOH, γ-MnOOH and MnO₂ were 85 ± 1, 64 ± 1 and 371 ± 5 m² g⁻¹, respectively. The point of zero charge (PZC) determined from potentiometric titration of MnO₂ and MnOOH were 2.4 and 6.3, respectively, whereas that of goethite was 9.1. Mn average oxidation state (AOS) of pyrolusite was measured by a back-titration method using a KMnO₄ standard solution.²⁴ AOS of the MnO₂ used in this study was determined as 3.95.

2.2. Adsorption, redox and Laser Flash Photolysis experiments

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

chromatography (HPLC, Waters 600 controller with a C18 column (250 mm×4.6 mm i.d., 5 μ m). Solubility is relatively low at acidic pH for FLU (~80 μ M) and between pH 7 and 8 for NOR (~1200 μ M) (Fig. S2).

Adsorption and redox kinetics were then evaluated at pH = 6.5 $\pm$ 0.1, NaCl concentration = 10 mM, NOR initial concentration = 24 μ M, FLU initial concentration = 24 μ M with α -FeOOH and MnO₂ concentration = 10 m² L⁻¹. All batch experiments were performed under an atmosphere of N₂ (g) to purge dissolved CO₂ from the aqueous solutions. Because the adsorption of target compounds is negligible at pH higher than 10 (according to preliminary adsorption tests), desorption tests were conducted at pH = 11 as a means to check the mass balance. Amount of Mn^{II} released in the reaction solution was monitored by Atomic Absorption Spectrometer (Varian AA 140). Possible generation of dissolved ferrous ion was assessed by UV-visible spectrophotometry (Cary 50 probe, Varian) using the 1-10 phenanthroline method.

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

Oxidation by-products were analyzed with a water ultrapure HPLC-MS/MS (Acquity UPLC) system, equipped with a BEH C18 column (100 mm x 2.1mm, 1.7 μ m). The mobile phase consisted of acetonitrile containing 0.1 % of formic acid (eluant A) and mixture acetonitrile/water (*i.e.*, 10 % / 90 %) containing 0.1 % of formic acid (eluant B) with gradient 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 thiocianate 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 (pK_a 6.3) and at pH 3.5, 7.5 and 11 for NOR (pK_a 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

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

Two different experiments were conducted at room temperature. In the first series of experiments, FLU or NOR, oxidants (H₂O₂ or S₂O₈²⁻) and oxides (α -FeOOH or MnO₂) were mixed simultaneously few minutes before UVA irradiation. In the second experimental series, suspensions containing antibiotics and goethite or manganese oxide were stirred in the dark for a certain time (1, 24, or 48 h) before adding oxidant and/or starting UVA irradiation.

In both experiments, 0.059 g of goethite or 0.0135 g of MnO₂ were added to 500 mL of contaminant solution and the pH was kept constant (6.5 ± 0.1) using NaOH or H₂SO₄. At each time interval, an aliquot of solution was collected to determine the aqueous concentration of FLU or NOR by HPLC/UV. Total Organic Carbon (TOC) was determined using a TOC-meter (Shimadzu TOC-VCSH). All experiments were conducted in triplicates and showed a good reproducibility within 5 % of relative standard deviation.

Results and discussion

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

Sorption kinetics of FLU onto 10 m² L⁻¹ of oxide (α -FeOOH or MnO₂) with 10 mM NaCl at pH = 6.5 ± 0.1 conducted over a 6-day period showed that a steady-state was achieved within approximately 20 h of reaction time (Fig. S3). Mass balance showed that FLU was removed only by adsorption (*i.e.*, ~ 40 % of FLU was sorbed onto 10 m² L⁻¹ of α -

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

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

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

Although both FLU and NOR may form similar surface complexes with metal surfaces (i.e. metal-bonded complexes with surface sites and/or directly hydrogen-bonded complexes with surface hydroxo groups) ^{10,21,27}, oxidative transformation was only observed for NOR. Since FLU does not contain a piperazine ring, we may suppose that the piperazine moiety, the electron donor group, should play a critical role in the molecular transformation with FeOOH or MnO_2 . This phenomenon has been proposed in previous work ⁶ to explain why four fluoroquinolones all containing a piperazine moiety exhibited a very similar oxidation rate. The nature of primary oxidation byproducts identified in the present work as a result of dealkylation and hydroxylation at the piperazine moiety ⁶, further supports this hypothesis. Indeed, two main byproducts were detected by LC/MS/MS analysis conducted on NOR solution reacted with MnO_2 for 22h (Fig. S4). The first ($m/z = 251$, $M - 69$) is supposed to form through N-dealkylation of the piperazine ring with a final aniline functional group, while

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

3.2. Assessment of radical-based oxidation in presence of H_2O_2 or PS under UVA irradiation

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

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

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

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

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

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

because of the low concentration of HO^- in solution at this pH value and the low reaction rate,

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

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

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

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

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

Because the conduction bands of Mn^{IV} (hydr)oxides are at much lower energies than those of the Fe^{III} (hydr)oxides (band gaps in Pyrolusite is 1.0 eV vs 2.5 eV for goethite)⁴⁰, the photoreductive dissolution of Mn^{IV} -oxides is more energetically feasible. However, two one-electron transfer steps or a single two-electron step may be operative during photo-assisted

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

3. Environmental implications

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

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

Oxide-bound Mn^{II} is essential in catalyzing oxidation reaction and then producing greater amounts of radical species through a photo-assisted redox cycle. Light enhanced the rate of 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 then oxidize/mineralize target compounds. This shows the greater ability of MnO_2 as compared to iron oxides, in inducing electron transfer reactions with antibiotics, and then triggering their subsequent radical-based degradation. These results provide a novel strategy towards the application of redox active minerals in a dynamic two-step treatment process, where the redox byproducts generated *in-situ* during the first stage strongly contribute in achieving total removal of TOC. Because of the great affinity of manganese ions for Mn -oxide surfaces at neutral pH, the Mn^{2+} leaching from the oxide surface is very limited, and much below the wastewater discharge limits. Therefore, the developed system will be of scientific significance in both Mn -based oxidation reactions and practical wastewater 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/>.

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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		$1.31 \pm 0.30 \times 10^9$

Figure captions

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

$[\text{NOR}]_0 = 24 \mu\text{M}$; $[\text{MnO}_2] = 0.027 \text{ g L}^{-1}$ ($10 \text{ m}^2 \text{ L}^{-1}$).

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 $\text{pH } 6.5 \pm 0.1$: $[\text{NOR}]_0 = 24 \mu\text{M}$; $[\text{H}_2\text{O}_2]_0 = [\text{S}_2\text{O}_8^{2-}]_0 = 0.5 \text{ mM}$; $[\text{goethite}]_0 = 0.118 \text{ g L}^{-1}$ ($10 \text{ m}^2 \text{ L}^{-1}$); $[\text{MnO}_2]_0 = 0.027 \text{ g L}^{-1}$ ($10 \text{ m}^2 \text{ L}^{-1}$). The arrow indicates the moment where oxidant addition and/or UVA irradiation take place.

Figure 4: Removal kinetics of 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.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

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