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1 **Alteration of Birnessite Reactivity in Dynamic Anoxic/Oxic**

2 **Environments**

3
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19

20 **Abstract**

21 Although the oxidative capacity of manganese oxides has been widely investigated,
22 potential changes of the surface reactivity in dynamic anoxic/oxic environments have
23 been often overlooked. In this study, we showed that the reactivity of layer structured
24 manganese oxide (birnessite) was highly sensitive to variable redox conditions within
25 environmentally relevant ranges of pH (4.0 – 8.0), ionic strength (0 to 100 mM NaCl)
26 and Mn(II)/MnO₂ molar ratio (0 - 0.58) using ofloxacin (OFL), a typical antibiotic, as
27 a target contaminant. In oxic conditions, OFL removal was enhanced relative to anoxic
28 environments under alkaline conditions. Surface-catalyzed oxidation of Mn(II) enabled
29 the formation of more reactive Mn(III) sites for OFL oxidation. However, an increase
30 in Mn(II)/MnO₂ molar ratio suppressed MnO₂ reactivity, probably because of
31 competitive binding between Mn(II) and OFL and/or modification in MnO₂ surface
32 charge. Monovalent cations (*e.g.*, Na⁺) may compensate the charge deficiency caused
33 by the presence of Mn(III), and affect the aggregation of MnO₂ particles, particularly
34 under oxic conditions. An enhancement in the removal efficiency of OFL was then
35 confirmed in the dynamic two-step anoxic/oxic process, which emulates oscillating
36 redox conditions in environmental settings. These findings call for a thorough
37 examination of the reactivity changes at environmental mineral surfaces (*e.g.*, MnO₂)
38 in natural systems that may be subjected to alternation between anaerobic and
39 oxygenated conditions.

40 **Keywords:** manganese oxide; redox; antibiotics; oxidation; removal.

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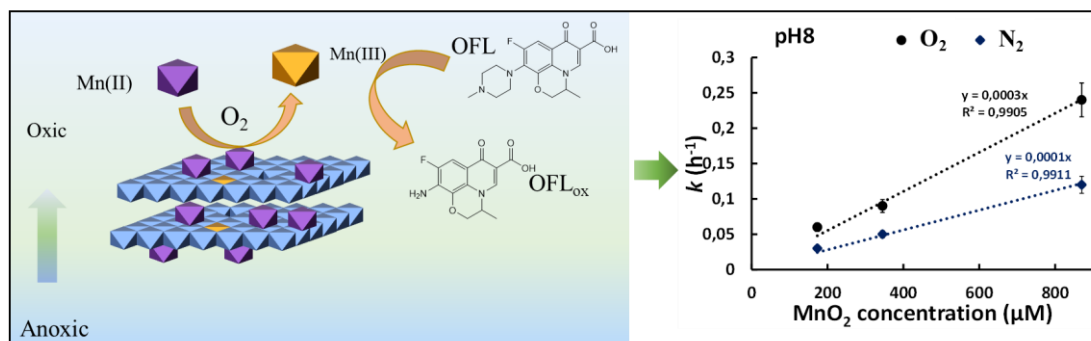
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42

Surface-catalyzed oxidation of Mn(II) by dissolved oxygen controls the reactivity of

43

nanostructured birnessite.



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46 **1. Introduction**

47 Manganese dioxides (MnO_2) are ubiquitous in a wide range of aquatic and terrestrial
48 environments (Post, 1999). They are widely used in various energy and environmental
49 applications, because of their specific nanoscale properties, high surface areas, low cost,
50 strong oxidation and sorption abilities (Post, 1999; Remucal and Ginder-Vogel, 2014).
51 The layer structured manganese oxide (*e.g.*, birnessite) is structurally similar to
52 biogenically precipitated natural manganese oxides, and thus the common natural
53 occurring MnO_2 in surficial environments. It basically consists of randomly stacked
54 edge-sharing MnO_6 octahedra and has a large excess of negative charges because of the
55 Mn(IV) vacancies and substitution of Mn(II)/(III) for Mn(IV) (Elzinga, 2011). As a
56 result, MnO_2 exhibits a high affinity for cation sorption, but also a non-negligible anion
57 adsorption capacity. Another important feature of MnO_2 is the ease of switching the
58 oxidation state, which imparts a good catalytic activity (Post, 1999; Remucal and
59 Ginder-Vogel, 2014).

60 In oxic environments, it has been reported that MnO_2 surfaces can catalyze the
61 oxidation of Mn(II) by dissolved oxygen to generate Mn(III)/(IV) (Yang et al., 2018;
62 Zhao et al., 2016), while homogeneous oxidation of Mn(II) by oxygen is considered
63 kinetically sluggish (Davies and James, 1989; Diem et al., 1984; Lan et al., 2017; Nico
64 et al., 2002; Wilson, 1980). Surface oxygen ligands bound to inner-sphere adsorbed
65 Mn(II) may accelerate the electron transfer between Mn(II) and O_2 (Junta and Hochella,
66 1994; Lan et al., 2017; Luther, 2005; Namgung et al., 2020), leading to higher Mn(II)
67 removal under oxic conditions compare to anoxic conditions at circumneutral to

68 alkaline pH (Elzinga, 2011; Lefkowitz et al., 2013; Li et al., 2020). The accumulated
69 Mn(III) can incorporate into Mn octahedral layers and induce the transformation of
70 MnO₂ (Hinkle et al., 2017; Wang et al., 2018a).

71 Although the influence of phase transformation on the reactivity of birnessite has been
72 already investigated (Lefkowitz and Elzinga, 2015; Wang et al., 2018a; Wang et al.,
73 2019), very little knowledge exists about the impact of oxygen on the removal of
74 organic compounds interacted with MnO₂ surfaces. Furthermore, MnO₂ may co-exist
75 with dissolved Mn(II) and emerging contaminants in natural systems which may be
76 subjected to alternation between anaerobic and oxic conditions, such as water-sediment
77 interfaces, water table fluctuations, groundwater recharge (Jeong et al., 2010; Wu et al.,
78 2020; Zhao et al., 2021). However, little is known about the potential changes in the
79 surface reactivity of MnO₂ in environmental settings under alternating redox conditions.
80 This work has examined for the first time how a shift of redox conditions from anoxic
81 into oxic may alter the reactivity of birnessite.

82 Ofloxacin (OFL) was chosen here as a target contaminant in order to explore the
83 changes in MnO₂ reactivity under dynamic anoxic/oxic conditions. OFL is widely used
84 in human and veterinary medicine, and frequently detected in surface water,
85 groundwater, soils and municipal wastewater systems, with concentration ranging from
86 ng/L to µg/L (Zhang and Huang, 2005). Removal kinetics of OFL in the presence of
87 acid birnessite were performed at pH ranging from 4.0 to 8.0, representing the common
88 pH conditions of suboxic environments (Elzinga, 2016; Wang et al., 2018a). The
89 oxidation byproducts of OFL were determined using an ultra performance liquid

90 chromatography-tandem mass spectrometry (UPLC-MS/MS). The oxidative capacity
91 of MnO₂ was further monitored for variable Mn(II)/MnO₂ molar ratios and ionic
92 strengths under environmentally relevant conditions. In addition, X-ray diffraction
93 (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy
94 (SEM) were used to identify the changes in Mn valence states and mineral phase
95 transformation. This work calls for more consideration of alteration of the oxidative
96 capacity of birnessite in redox transition zone in groundwater systems.

97

98 **2. Materials and Methods**

99 **2.1. Materials and Chemicals**

100 All chemicals employed in this study were purchased from Sigma-Aldrich of analytical
101 grade and used without further purification. Ultrapure water (specific resistivity, 18.2
102 MΩ cm⁻¹, Milli-Q, Millipore) was used for all solutions and suspensions.

103 Acid birnessite was synthesized by reacting KMnO₄ and HCl as described in previous
104 studies (Li et al., 2020; Mckenzie, 1971; Pokharel et al., 2020). The purity of mineral
105 phase was confirmed with XRD and SEM (Figure S1). The specific surface area (SSA)
106 measured by Brunauer-Emmett-Teller (BET)-N₂ adsorption was 85.0 ± 3.0 m² g⁻¹ and
107 the isoelectric point (pH_{IEP}) was around 2.0, respectively (Figure S2). Analysis of XPS
108 data showed that the average oxidation state of the pristine material was 3.87, with 88.3 %
109 Mn(IV), 10.7 % Mn(III) and 1.0 % Mn(II) (Figure S3).

110 **2.2. Batch experiments**

111 All batch experiments were carried out in 500 mL polyethylene bottles, containing

112 varying concentrations of acid birnessite. The solutions were spiked with aliquots of
113 1.0 mM OFL and 0.05 M MnCl_2 stock solution to achieve initial concentration of 10
114 μM OFL and variable target Mn(II) concentrations ranging from 0 to 200 μM . The ionic
115 strength was fixed using NaCl at various concentrations. The pH of the suspensions
116 was adjusted to the desired values over the reaction time using an auto pH titrator with
117 addition of small volumes of HCl (0.1 M) or NaOH (0.1 M) solutions and maintained
118 at pH 4.0, 6.0 and 8.0 throughout the experiments. No pH buffers were used, to prevent
119 any impact on the birnessite reactivity. The stirring speed of the mixture was maintained
120 at 350 rpm. Batch experiments were carried out under ambient air atmosphere or by
121 bubbling oxygen gas (oxic conditions), or by bubbling nitrogen gas (anoxic conditions).
122 A two-step anoxic/oxic dynamic process was investigated as follows: after a period of
123 anoxic conditions where the bottle was under N_2 , an oxic environment was
124 subsequently created by removing the cap of the bottle or by bubbling O_2 . The same
125 kinetic behavior was observed when either the suspension was stirred under open
126 atmosphere (ambient air) or with bubbling O_2 (data not shown). In the open system,
127 CO_2 from the atmosphere will generate carbonates in solution at high pH values, but
128 this effect on the reactivity can be excluded according to a previous study (Li et al.,
129 2020).

130 Aliquots of solution were periodically withdrawn and filtered through a 0.20 μm
131 membrane filter for analysis of OFL concentration, whereas other aliquots without
132 filtration were immediately mixed with 0.1 M ascorbic acid to quench the reaction. At
133 the end of experiments, the remaining suspensions were centrifuged at 4500 rpm for 20

134 min and settled particles were freeze-dried, and then stored at 4 °C for further solid
135 analysis. In another experimental series involving mixing with 1.0 mM sodium
136 pyrophosphate, a volume of about 3.0 mL sample was periodically withdrawn from the
137 mixed solution, filtered and analyzed immediately by UV–Vis spectrophotometry in
138 the range of 200-600 nm wavelength. Batch experiments were conducted in triplicates
139 and the standard deviation was calculated for each experimental series.

140 **2.3. Analytical methods**

141 The concentration of OFL in the samples was analyzed via High Performance Liquid
142 Chromatography analysis with UV–Vis detection (HPLC-UV) equipped with a
143 reversed-phase C18 column (250 mm × 4.6 mm i.d., 5 μm) and a UV–Vis detector
144 (Waters 2489) at a wavelength of 287 nm. The mobile phase consisted of
145 acetonitrile/water (15/85 v/v,) containing 0.1% formic acid at a flow rate of 0.6 mL/min.
146 Filtered suspensions were digested with 2% nitric acid and dissolved Mn(II)
147 concentrations were determined by Atomic Absorption Spectroscopy (AAS, AA140,
148 Varian, Shimadzu) with a detection limit of 0.02 μM.

149 The oxidation byproducts of OFL were identified using an ultra performance liquid
150 chromatography-tandem mass spectrometry (UPLC-MS/MS) system. An electrospray
151 interface was used for the MS measurements in positive ionisation mode and full scan
152 acquisition.

153 XPS spectra were recorded on an XPS system PHI 5000 VersaProbe II (ULVAC-PHI
154 Inc.) equipped with a scanning microprobe X-ray source (monochromatic Al K α , $h\nu =$
155 1486.7 eV). An electron flood gun generating low energy electrons (1.1 eV) and low

156 energy argon ions (6 eV) by a floating ion gun were applied for charge compensation
157 at isolating samples (dual beam technique). Survey scans were recorded with an X-ray
158 source power of 31 W, X-ray spot size diameter 200 μm , and pass energy of the analyzer
159 of 187.85 eV. Narrow scans of the elemental lines were recorded at 23.5 eV pass energy,
160 which yields an energy resolution of 0.69 eV FWHM at the Ag 3d_{5/2} elemental line of
161 pure silver. Calibration of the binding energy scale of the spectrometer was performed
162 using well-established binding energies of elemental lines of pure metals
163 (monochromatic Al K α : Cu 2p_{3/2} at 932.62 eV, Au 4f_{7/2} at 83.96 eV) (Seah et al., 1998).
164 The error in binding energies of elemental lines is estimated to ± 0.1 eV for conductors
165 and ± 0.2 eV for isolating samples. High-resolution XPS spectra were calibrated by the
166 carbon deposit C1s binding energy at 284.8 eV and further analyzed by CasaXPS
167 software. After Shirley background subtractions, all peaks were fitted using 70:30
168 Gaussian: Lorentzian sum function.

169 A FEI Quanta 650 FEG environmental scanning electron microscope (now Thermo
170 Fisher Scientific Inc.) was applied to image the sample surfaces.

171 XRD data were collected by using a D8 Advance (Bruker) diffractometer with Cu K α
172 radiation over the range of 10–80° 2 θ at a step size of 0.02° and phases were determined
173 according to the PDF database in Jade 6 software.

174

175 **3. Results and Discussion**

176 **3.1. Effect of oxygen and pH on the initial removal rate of OFL by MnO₂**

177 Removal kinetics of OFL were investigated under anoxic and oxic conditions as a

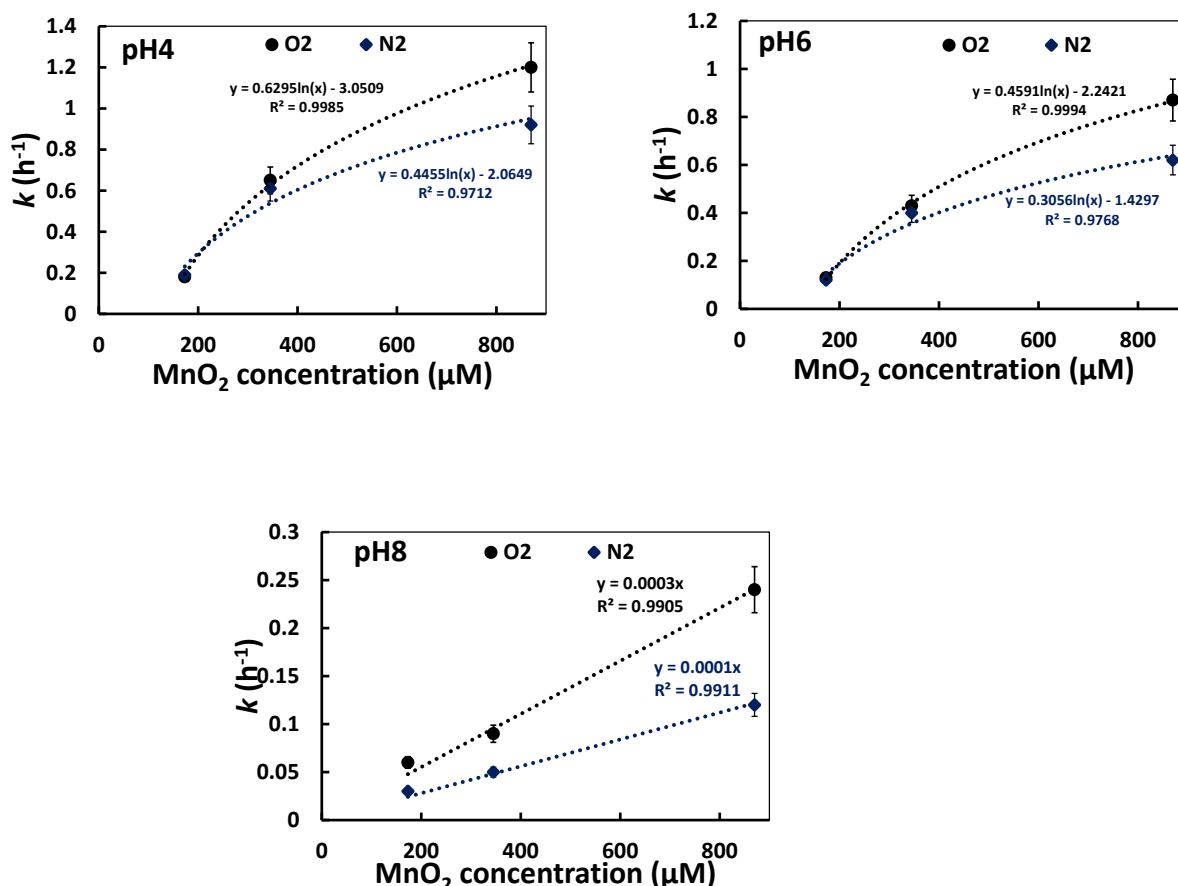
178 function of MnO₂ concentration (173-870 μM or 15 -75.6 mg/L) at three pH values (4.0,
179 6.0, 8.0 (± 0.1)) over 8 hours of reaction time (Figure S4). The entire kinetic curve could
180 not be properly described by simple equations that include classical exponential
181 functions (*e.g.*, first- or second- order model), probably due to the complexity of
182 involved reactions including accumulation and competition of reaction products (*e.g.*
183 OFL byproducts, Mn(II) ions, etc.) and/or a gradual change of the reactivity of surface
184 sites. For the sake of simplicity and to overcome possible interference caused by the
185 accumulated byproducts, we have determined the rate constant over the first stage of
186 reaction (*i.e.*, 1h). The initial rate constants k (h⁻¹) calculated by linear regression of ln
187 [OFL]/[OFL]₀ versus time, were plotted against MnO₂ concentration in Figure 1. The
188 correlation coefficients (R²) of linear regression ($\ln C/C_0 = -kt$) were more than 0.90
189 for all experiments.

190 The rate constants exhibited the same order, pH 4.0 > pH 6.0 > pH 8.0, regardless of
191 MnO₂ concentration. This is consistent with previous reports (Li et al., 2020; Zhang
192 and Huang, 2005; Zhang et al., 2008), which showed that acidic conditions enabled
193 higher quinolones removal in the presence of MnO₂. This can be ascribed to more
194 favorable interactions between the less negatively charged surface (pH_{IEP} of MnO₂ ~
195 2.0) and OFL (pK_a 6.08 and 8.25, Figure S5) at acidic pH values. Furthermore, the
196 decrease in redox potential of MnO₂ from 0.99 V to 0.76 V when the pH increased from
197 4.0 to 8.0 would also explain the enhanced reactivity under acidic conditions, as
198 previously reported (Li et al., 2020).

199 Mass balance showed that adsorption and oxidation are involved in the removal of OFL

200 in the presence of MnO₂, even though the adsorption appears to be relatively weak for
201 our experimental conditions (*e.g.*, less than 1.5 μmol m⁻², at pH 6.0; less than 0.1 μmol
202 m⁻², at pH 8.0). Based on previous investigations for fluoroquinolones (Kamagate et al.,
203 2019; Martin et al., 2015; Zhou et al., 2019), OFL may form metal-bonded complexes
204 with surface sites and/or directly hydrogen-bonded complexes with surface hydroxo
205 groups involving both carboxylate and keto groups. However, accurate quantification
206 of the adsorption is not straightforward, because binding of redox-active compounds to
207 birnessite is followed by an electron transfer process resulting in the concomitant
208 oxidation of sorbed compound and reduction of surface-bound metal. LC/MS analysis
209 showed that OFL oxidation passes through partial or full N-dealkylation of the
210 piperazine ring, as two predominant products of *m/z* = 336 (M-26) and *m/z* = 279 (M-
211 69) have been detected (See Figure S6 for more details). Indeed, the piperazine ring of
212 OFL can be oxidized through two one-electron transfers from the N atom of piperazine
213 ring to Mn(IV), and then N-dealkylation and/or C-hydroxylation causes ring opening,
214 as typically observed for similar compounds (Zhang and Huang, 2005). Additionally,
215 trace amounts of M+16, M-44 (decarboxylation), M-101 and M+30 were detected, as
216 previously reported for the Mn-based oxidation of OFL (Li et al., 2021; Zhang and
217 Huang, 2005).

218



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222

223 **Figure 1.** Initial removal rate constants of OFL *versus* MnO₂ concentration at three pH values 4.0,
 224 6.0, 8.0 (± 0.1). 173, 345, 870 μM (15, 30, 75.6 mg/L) MnO₂; 10 μM OFL; 10 mM NaCl; under
 225 anoxic (N₂) and oxic (O₂) conditions. Dashed lines are the best correlation obtained between *k* and
 226 MnO₂ amount. Correlation coefficients (R²) are indicators of the strength of the linear or non-linear
 227 relationship.

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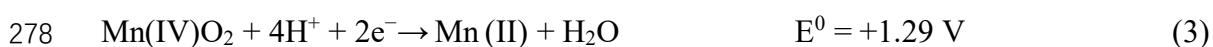
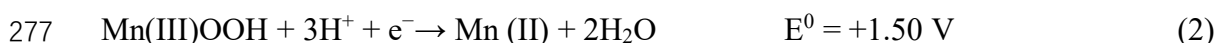
229 The effect of oxygen on the removal efficiency of OFL was only observed at high MnO₂
 230 concentration (870 μM) or at pH 8.0 ± 0.1 for the full range of MnO₂ concentration
 231 (Figure 1). In both conditions, the apparent pseudo-first-order rate constant *k* (h⁻¹)
 232 increased with increasing MnO₂ concentration. It is worth noting that a linear
 233 dependence of reactivity on MnO₂ amount was only observed at pH 8.0, while a
 234 logarithmic relationship was observed at pH 4.0 and 6.0 (Figure 1). Contribution of
 235 Fenton-like reaction through, for instance hydroxyl radical formation, in OFL removal

236 is excluded, since the addition of ethanol, used as a hydroxyl radical scavenger, has no
237 effect on the OFL removal (Figure S7). Furthermore, we found that the impact of
238 oxygen on birnessite reactivity at pH 8.0 is not specific to OFL, since similar behavior
239 has been observed with another antibiotic compound, pipemidic acid (see Figure S8).
240 It is generally known that the reaction of MnO₂ with redox-active compounds is
241 complex and involves several reaction pathways that occur simultaneously. The redox
242 byproducts generated through reductive dissolution of MnO₂ or OFL oxidation, can
243 bind onto the MnO₂ surfaces, and alter the initial surface reactivity (*i.e.*, passivation).
244 Generally, the generated Mn(II) is sorbed onto the MnO₂ surface and then oxidized.
245 Mn(IV) is reduced, and the resulting product is Mn(III), which is commonly called the
246 comproportionation reaction (Wang et al., 2019; Zhao et al., 2016). In addition, the
247 adsorbed Mn(II) on vacant sites can be oxidized by O₂ at high pH to yield Mn(III).
248 Because higher MnO₂ concentration enables more OFL oxidation (higher *k*, Figure 1),
249 more reductive dissolution or Mn(II) production is expected. Dissolved Mn(II) was
250 below the detection limit (< 0.02 μM for AAS) in all investigated conditions,
251 confirming that generated Mn(II) by reductive dissolution of MnO₂ was completely
252 removed by binding to MnO₂. Competitive binding between OFL and Mn(II) at MnO₂
253 edge sites, and/or adsorption of OFL oxidation byproducts at the MnO₂ surface may
254 also explain the passivation of the Mn-oxide surface. All these reactions are pH-
255 dependent, as well as the passivation of MnO₂ surfaces. This may explain why the
256 relationship between the oxidation rate constant of OFL and MnO₂ content is not linear
257 over the whole pH range investigated (Figure 1). Furthermore, higher surface-oxidation

258 rates of Mn(II) at alkaline pH values (Lefkowitz et al., 2013; Namgung et al., 2014)
259 may explain the pronounced impact of oxygen on birnessite reactivity at pH 8.0 (Figure
260 1).

261 Collectively, these results suggest that enhanced removal efficiency of OFL under oxic
262 conditions at high MnO₂ concentration or high pH is due to the Mn(III) generated
263 through Mn(II) surface-catalyzed oxidation by oxygen. This is, however, in
264 disagreement with a recent work which reported that oxygen inhibited phenol
265 degradation by δ -MnO₂ because the generated Mn(III)-phases at the MnO₂ surface may
266 block reactive sites and cause particle aggregation, thereby lowering the surface
267 reactivity (Hu et al., 2019). This discrepancy with the present work may be explained
268 by the difference in experimental conditions including target contaminant
269 characteristics and its affinity to MnO₂ surfaces, and target compound/MnO₂ molar
270 ratio.

271 On the other hand, previous works have reported that the Mn(III) oxides or Mn(III)
272 complexes can rapidly oxidize a variety of organic compounds (Chen et al., 2013;
273 Huang et al., 2018; Klewicki and Morgan, 1999; Nico and Zamoski, 2001). Mn(III) is a
274 strong oxidant for one electron transfer reaction (Hu et al., 2017; Sun et al., 2021),
275 compared to two electron transfer reaction involving Mn(IV).



279

280 In a heterogeneous system, the greater reactivity of Mn(III)-bearing phases has been
281 explained by longer and weaker Mn(III)-O bonds facilitating the electron transfer with
282 sorbing compounds (*e.g.*, phenol) (Huang et al., 2018; Ukrainczyk and McBride, 1992).
283 It seems that direct coordination of Mn(III) with target compounds ensures to facilitate
284 electron transfer without change in the Mn spin state, while the outer sphere electron
285 transfer in surface Mn(IV) requires a change in the Mn spin state, in turn making the
286 electron transfer process more difficult (Huang et al., 2018; Ukrainczyk and McBride,
287 1992). Indeed, Mn(III) was reported to be as a high spin d^4 ion with much lower ligand
288 field stabilization energy and faster ligand exchange rates comparing with Mn(IV)
289 (Nico and Zasoski, 2000). In contrast, other reports showed that Mn(III) sites are less
290 reactive with respect to target contaminants. For example, lower As(III) oxidation have
291 been attributed to the lower affinity of Mn(III) sites for As(III) adsorption, and slower
292 electron transfer rates with adsorbed As(III) (Lafferty et al., 2010a; Lafferty et al.,
293 2010b; Zhu et al., 2009). Moreover, the surface functional groups on Mn(III) sites are
294 more labile than functional groups on Mn(IV) sites (Zhu et al., 2009), and therefore
295 strong adsorption via ligand exchange processes on Mn(III) sites than on Mn(IV) sites
296 is expected. Finally, different types of Mn sites, *e.g.*, Mn(III, IV) in sheets, Mn(III, IV)
297 at edges, and Mn(III) in interlayers, likely have varying reactivity (Manceau et al., 1997;
298 Simanova and Peña, 2015; Yu et al., 2012). The interlayer Mn(III) was suggested to be
299 the dominant oxidizing site, and the abundance of Mn(III) with respect to total Mn may
300 be key in promoting the reactivity of birnessite (Peng et al., 2017). From a kinetic point
301 of view, Mn(III) at the edges seems to contribute at short reaction times, while Mn(III,
302 IV) in the MnO₂ sheets is important at longer times (Simanova and Peña, 2015; Wang
303 et al., 2018b). Despite this conflicting information about the role of structural Mn(III)
304 in promoting MnO₂ reactivity, we may conclude that multiple factors may control the

305 contribution of Mn(III) in enhancing the removal capacity of birnessite. This may
306 include the ratio of Mn(III) to Mn(IV), mineral phase transformation along the redox
307 reaction, and properties of target contaminants and its interaction with Mn sites. To gain
308 more insights into the underlying passivation mechanisms, the effects of Mn(II)/MnO₂
309 ratio on the removal kinetics of OFL were investigated under oxic and anoxic
310 conditions in the following section.

311

312 **3.2. Combined effects of Mn(II) and O₂ under a wide range of ionic strength**

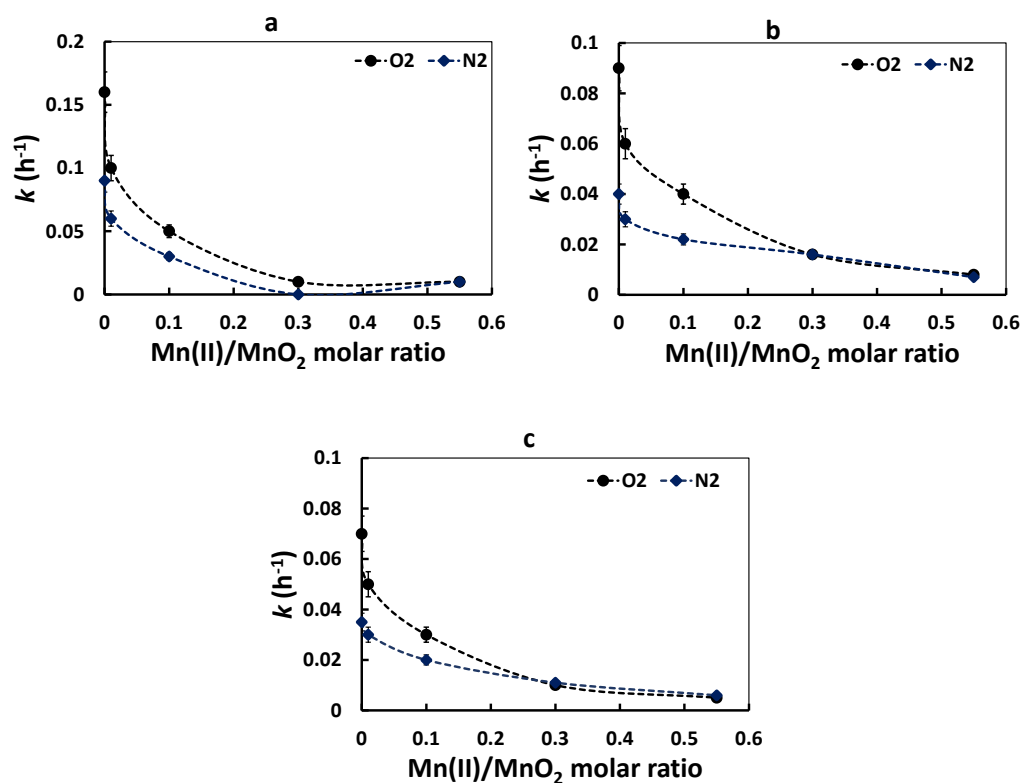
313 As an attempt to confirm the impact of surface-catalyzed oxidation of Mn(II) by O₂ on
314 the reactivity of MnO₂, OFL removal kinetics were investigated with different
315 Mn(II)/MnO₂ molar ratios at pH 8.0 (Figure 2). As expected, the initial rate constants
316 of OFL sharply decreased with increasing Mn(II) under both investigated conditions.
317 As previously reported (Chen et al., 2010; Li et al., 2020; Remucal and Ginder-Vogel,
318 2014), dissolved Mn(II) strongly adsorbed on the negatively charged birnessite surfaces,
319 resulting in competition between OFL and Mn(II) binding to the reactive surface sites
320 of MnO₂. This Mn(II) binding is much more important at alkaline pH values (Lefkowitz
321 et al., 2013). The adsorbed Mn(II) on vacant sites at high pH is oxidized to Mn(III)
322 through surface-catalyzed oxidation of Mn(II) enabling more Mn(III) in the vacancies
323 (Zhu et al., 2010). This explains why the dissolved Mn(II) concentration was found
324 here below the AAS detection limit, even for the highest Mn(II) amount (200 μM).
325 Time-dependent UV-Vis measurements for birnessite suspensions containing 200 μM
326 Mn(II), suggested more generated Mn(III) in the presence of oxygen relative to anoxic
327 conditions (Figure S9). Indeed, the intensity of adsorption bands at 258 nm for the
328 potential Mn(III)-PP complex ($\lambda_1 = 480 \text{ nm}$, $\varepsilon_1 = 65 \text{ M}^{-1}$; $\lambda_2 = 258 \text{ nm}$, $\varepsilon_2 = 6750 \text{ M}^{-1}$)
329 (Hu et al., 2017) was found to be higher under oxic conditions.

330 It should be noted that the greater reactivity of birnessite under oxic conditions relative
331 to anoxic systems is only observed at lower Mn(II)/MnO₂ molar ratio (≤ 0.1). At higher
332 ratio, strong competition between Mn(II) and OFL may act as a counterweight to the
333 Mn(III) contribution, thereby reducing the overall reactivity of MnO₂.

334

335 When removal kinetics was investigated at higher ionic strength (10 or 100 mM of
336 NaCl), a decrease in the initial rate constants of OFL was observed, mainly under oxic
337 conditions and at low Mn(II)/MnO₂ molar ratio (Figure 2). Increasing ionic strength
338 may increase the size of MnO₂ via oriented aggregations (Burrows et al., 2012; Yang
339 et al., 2019), thereby reducing the surface reactivity. This decrease in surface reactivity
340 has also been previously observed during aging of manganese oxides through
341 coalescence of particles (Stone and Morgan, 1984). Furthermore, Na⁺ ions may
342 compete with the cationic Mn(II) and/or zwitterionic form of OFL ($pK_{a,1} = 6.08$ and
343 $pK_{a,2} = 8.25$) for negatively charged adsorptive sites on MnO₂ ($pH_{IEP} \sim 2.0$). Na⁺ can
344 occupy the interlayers of birnessite, potentially competing with Mn(II) and/or
345 influencing the diffusion process of Mn(II) at reactive surface sites (Yang et al., 2019).
346 Previous work reported similar competitive binding due to the presence of monovalent
347 or divalent cations, resulting in decrease in the rate and magnitude of organic compound
348 transformation (Chen et al., 2010). Under oxic conditions, oxidation of Mn(II) into
349 Mn(III) and subsequent incorporation of Mn(III) into the layers may occur, resulting in
350 birnessite transformation from hexagonal to orthogonal layer symmetry (Zhao et al.,
351 2016). In this case, Na⁺ ions could compensate for the charge deficiency caused by the
352 presence of Mn(III), and subsequently act to stabilize Mn(III) in the layers (Drits et al.,
353 2007; Zhu et al., 2010). This may explain the pronounced effect of increasing NaCl
354 concentration on the MnO₂ surface reactivity in the presence of O₂.

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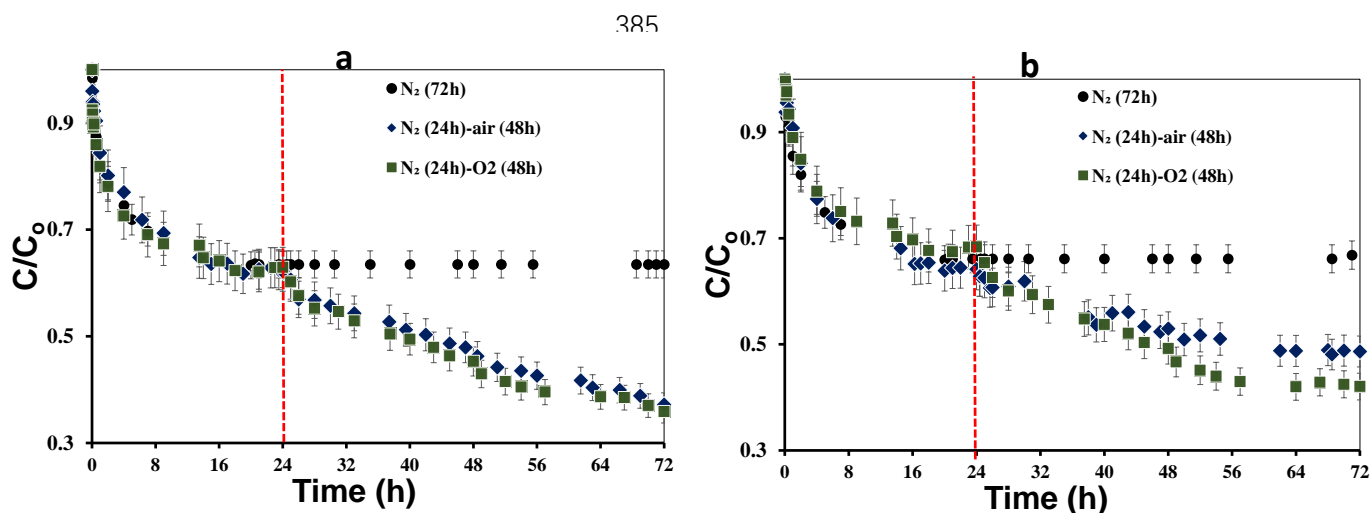
359

360 **Figure 2.** Initial removal rate constants of OFL as a function of Mn(II)/MnO₂ molar ratio under
361 anoxic or oxic conditions. pH 8.0 (\pm 0.1), 345 μ M (30 mg/L) acid birnessite. 0, 5, 50, 100, 200 μ M
362 Mn(II); 10 μ M OFL; (a) 0 mM NaCl, (b) 10 mM NaCl, (c) 100 mM NaCl. Dashed lines are only as
363 visual guide.

364

365 To check whether transition zones at oxic-anoxic interfaces may influence the reactivity
366 of birnessite, removal kinetics experiments were conducted for 24 h under N₂, with
367 subsequent ambient air conditions or bubbling O₂ for 48h (Figure 3). Under anoxic
368 conditions, a plateau was observed at around 16h, and then continued over 72 h. When
369 suspensions were exposed to ambient air or O₂ after a pre-equilibration period of 24h
370 under N₂, OFL was further removed up to 65% in suspension, which could be ascribed
371 to the Mn(III) generated through Mn(II) surface-catalyzed oxidation by oxygen. As
372 mentioned above, these newly generated Mn(III) are more reactive for OFL oxidation.
373 It should be noted that strong oxygenation of solution with bubbling O₂ has no greater
374 effect on the birnessite reactivity, as compared to the solution exposed to ambient air.

375 The same two-step anoxic/oxic process was repeated but in the presence of 5 μM Mn(II).
 376 This Mn(II) amount was chosen to cover the typical range of Mn concentration found
 377 in surface and groundwaters ($\sim 4 \mu\text{M}$) (Namgung et al., 2014). The presence of 5 μM
 378 Mn(II) did not significantly affect the removal rate whether under oxic or anoxic
 379 conditions. Only a slight inhibition was observed especially for longer reaction times ,
 380 likely because of competitive effects of Mn(II) and OFL for binding onto reactive sites.
 381 In all conditions, removal kinetic exhibited a plateau under N_2 , followed by a drop in
 382 the aqueous concentration of OFL when the reaction media was exposed to air or O_2
 383 (Figure 3).
 384



386 **Figure 3.** Removal kinetics of OFL in dynamic same two-step anoxic/oxic process: (a) 0 μM Mn(II);
 387 (b) 5 μM Mn(II). pH 8.0 (± 0.1); 10 μM OFL; 10 mM NaCl; 345 μM acid birnessite. The red vertical
 388 line indicates the beginning of oxygenation through exposure to ambient air or with bubbling O_2 .
 389

390 3.3. XRD and XPS investigations

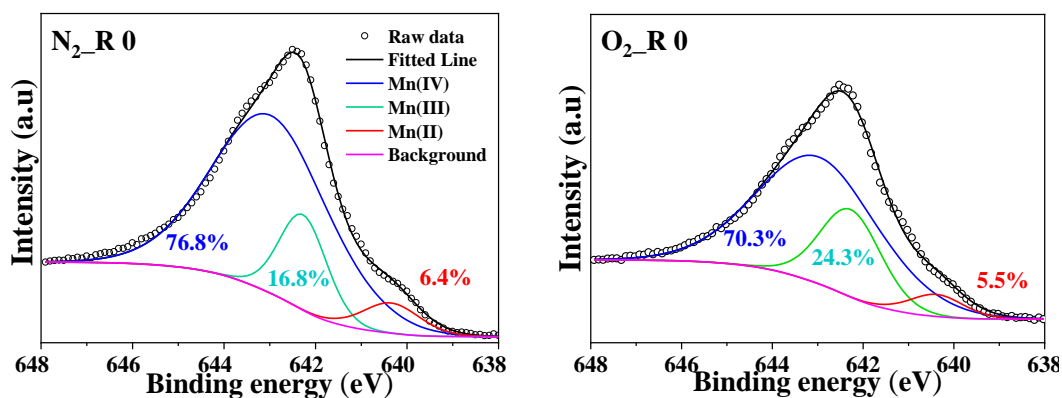
391 To evaluate the role of Mn speciation on reactivity changes and the passivation of the
 392 MnO_2 surface, XPS analysis of initial and reacted MnO_2 samples were performed under
 393 defined experimental conditions.

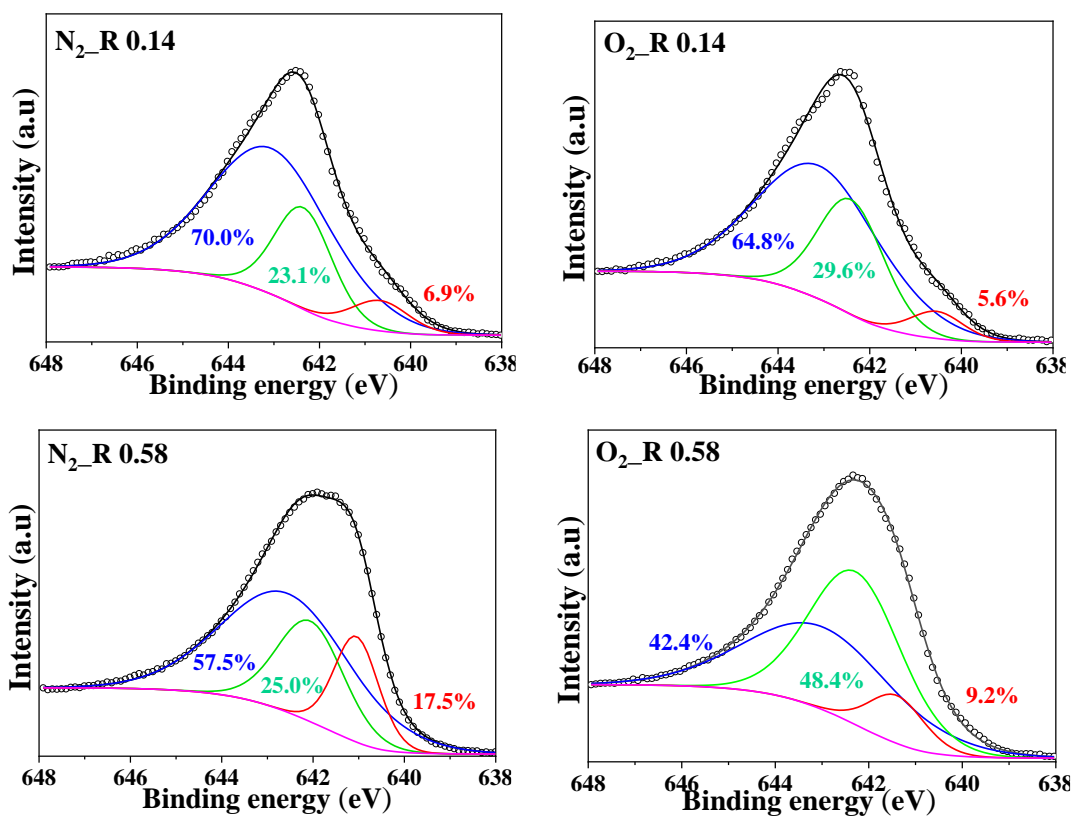
394 First, the total contents of major elements are reported in Table S1. In the absence of
 395 Mn(II), a decrease in Mn content in reacted samples was observed, likely resulting from

396 the presence of various adsorbing ligands at the surface (Table S1) (Shaikh et al., 2016).
397 Higher Na content under oxic conditions also proved the compensation effect of Na⁺ as
398 discussed above. Increasing Mn(II) concentrations from 50 μM to 200 μM enhanced
399 Mn percentage, likely because of the adsorption of Mn(II) onto the MnO₂ surfaces. K
400 content was below detection limit, likely due to the large adsorption amounts of Mn
401 exchanging with interlayer K⁺ ion.

402 Second, the high resolution spectra of Mn 2p_{3/2} was then fitted and the BE (binding
403 energy) positions of Mn(II), Mn(III), Mn(IV) ranged from 640.1 to 641.4 eV, from
404 642.1 to 642.4 eV and from 642.6 to 643.1 eV respectively, consistent with previously
405 reported values (Figure 4, Table S2) (Sun et al., 2019; Tang et al., 2013; Tang et al.,
406 2014). We have subsequently determined the average oxidation state (AOS) of all
407 samples, and found that the AOS (initial value 3.87) decreased for all reacted samples
408 (Table S2).

409 As expected, increasing the Mn(II) concentration from 0 μM to 200 μM enhanced the
410 amount of Mn(II) bond to MnO₂ surfaces (Figure 4). An increase in the percentage of
411 Mn(III) was also observed in the presence of oxygen relative to anoxic conditions,
412 while that of Mn(IV) decreased. As previously explained, Mn(II) can undergo surface-
413 catalyzed oxidation by molecular oxygen and/or comproportionation with structural
414 Mn(IV) forming Mn(III) sites. Both processes can enhance the Mn(III) content in MnO₂,
415 particularly under oxic conditions (Table S2).





417

418

419

420 **Figure 4.** Fitting of Mn $2p_{3/2}$ XPS high resolution spectra of the synthesized pristine acid birnessite
 421 and samples treated with Mn(II) and OFL under anoxic and oxic conditions. The R represents the
 422 Mn(II)/MnO₂ molar ratio. 345 μ M acid birnessite; 10 μ M OFL; 10 mM NaCl; 0, 50, 200 μ M Mn(II);
 423 48 h reaction time; pH 8.0 (\pm 0.1). The numbers inset are the percentage of Mn(II) (red), Mn(III)
 424 (green) and Mn(IV) (blue).

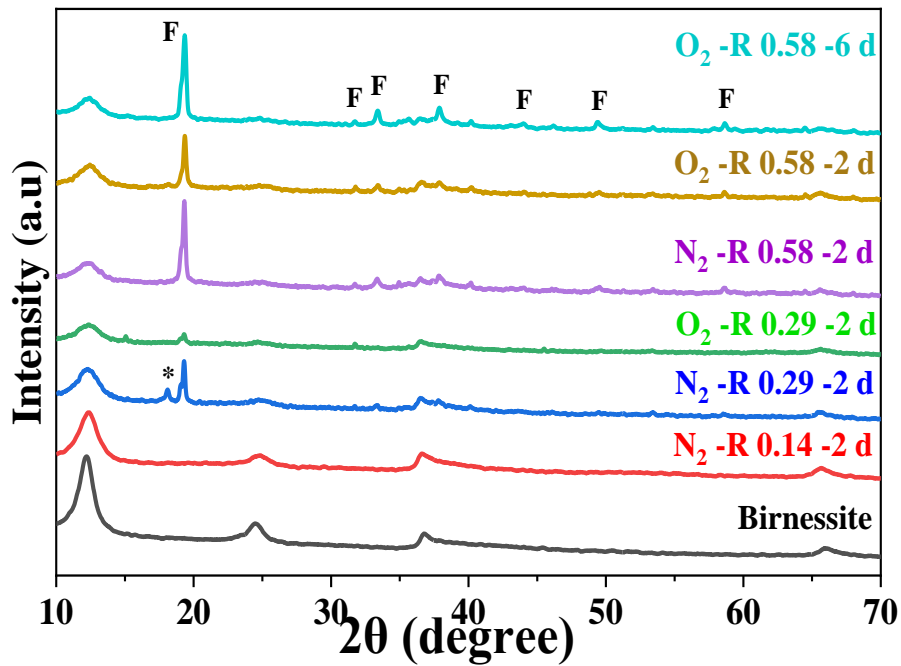
425

426 The high-resolution spectra of O1s were then evaluated to assess potential
 427 transformation of birnessite surfaces (Table S3 and Figure S10). The compositions of
 428 oxygen bonding types consisted of a main peak located at around 530.2 eV
 429 corresponding to lattice oxygen with metal (O_{latt}), a shoulder peak near 531.6 eV
 430 attributing to the adsorbed oxygen species on MnO₂ surface (O_{ads}) in the form of
 431 hydroxide oxygen (OH^-) and the weakest peak at higher binding energy assigning to
 432 the adsorbed oxygen in water molecule (O_{surf}) (Tang et al., 2013; Zhang et al., 2020).
 433 After reaction, the increased proportions of H₂O suggested that the surface became
 434 progressively hydroxylated and hydrated. It is worth noting that in the presence of
 435 200 μ M Mn(II), high contents in Mn(III) and OH^- under anoxic condition have been

436 considered as characteristic of intermediate reaction products Mn(III)-hydroxide, here
437 represented as MnOOH (Nesbitt et al., 1998). Moreover, the content of O_{latt} decreased
438 to 49 % (anoxic) and 65 % (oxic), which suggests that lattice oxygen may participate
439 in the oxidation of Mn(II) with the formation of oxygen vacancy (Cheng et al., 2019).
440 Once the O_{latt} is consumed, dissolved oxygen could compensate (Cheng et al., 2019),
441 which would explain the difference in O_{latt} content between anoxic and oxic
442 environments.

443 The produced Mn(III) may incorporate into the layer of birnessite and induce the
444 changes of mineral structure by converting birnessite into lower valence Mn phases
445 (Zhao et al., 2016). To check possible phase transformation, XRD analysis of MnO_2
446 samples under various Mn(II)/ MnO_2 molar ratios (R) and under anoxic and oxic
447 conditions was conducted (Figure 5). Samples reacted with OFL in the presence of
448 dissolved Mn(II) (50 μM , R = 0.14) showed no bulk transformation. However, XRD
449 data of samples with higher R (i.e. 0.29 or 0.58) showed different peaks, both under
450 anoxic and oxic conditions, which could suggest the presence of lower valence Mn
451 oxides, e.g. feitknechte ($\beta\text{-MnOOH}$) (Wang et al., 2018a; Lefkowitz et al., 2013). This
452 is consistent with SEM images where needle-shaped particles were observed amid
453 nanoflower-shaped particles of birnessite, especially at higher Mn(II) concentration and
454 under oxic conditions (Figure S11). These needle-shaped crystals can be attributed
455 either to the presence of manganite ($\gamma\text{-MnOOH}$) as previously reported by *e.g.* Larsen
456 et al., (1998), or more certainly according to XRD data, to feitknechte as previously
457 reported by Lefkowitz et al., (2013).

458



459

460 **Figure 5.** XRD patterns of the MnO₂ samples treated with Mn(II) and OFL under oxic and anoxic
 461 conditions. 345 μM acid birnessite; 10 μM OFL; 10 mM NaCl; 0, 50, 100, 200 μM Mn(II); 48 h or
 462 6 d reaction time; pH 8.0 (± 0.1). The R represents the Mn(II)/MnO₂ molar ratio. The **f** symbols
 463 indicate XRD peaks visible on the feitknechtite (β-MnOOH) sample in Lefkowitz et al., 2013; the
 464 * symbol has previously been attributed to hausmannite (Wang et al., 2018a) but in the absence of
 465 the main Bragg peaks of this phase, it would rather belong to an hydrated α-MnO₂ phase (Rossouw
 466 et al., 1992).

467

468 **Conclusions**

469 As a result of natural or anthropogenic activities, such as groundwater recharge,
 470 sediment dredging, water table fluctuations, etc., alternating redox conditions
 471 commonly occur in natural systems. Here, we have demonstrated for the first time that
 472 the oxygen can alter the redox reactivity of MnO₂ under environmentally-relevant
 473 conditions of Mn(II) dosage, pH and ionic strength. A decline in the oxidation rate
 474 constant with increasing pH was observed, likely because of the decrease in the redox
 475 potential of MnO₂ at higher pH and modification in surface interactions with the target
 476 compound. At high pH, the adsorbed Mn(II) on vacant sites can be oxidized by O₂ or
 477 Mn(IV) surrounding the vacant sites into Mn(III) (comproportionation reaction).

478 Therefore, OFL adsorbed at vacant sites can be oxidized by the newly generated Mn(III)
479 sites, which seems to be strong oxidizing species. However, excess dissolved Mn(II)
480 would compete with compounds for binding at reactive sites, thus decreasing the
481 removal capacity of birnessite. The decreased reactivity of MnO₂ with higher ionic
482 strength also suggested that the sorption of alkali cation (Na⁺) on the surface may
483 control the birnessite reactivity. Furthermore, sequential anoxic-oxic dynamic process
484 may significantly impact the fate of existing contaminants in the presence of birnessite.
485 Combining anoxic and oxic environments into one process may be relevant in many
486 subsurface environments, for instance, when anoxic aquifers and/or sediments come
487 into contact with oxygen. Further redox oscillation studies are needed to explore the
488 fate and mobility of contaminants and co-existing natural compounds (*e.g.*, dissolved
489 organic matter), in the presence of manganese oxides.

490

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496

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