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# Efficient removal of estrogenic compounds in water by MnIII-activated peroxymonosulfate: Mechanisms and application in sewage treatment plant water

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1 **Efficient removal of estrogenic compounds in water by Mn<sup>III</sup>-activated**  
2 **peroxymonosulfate: mechanisms and application in sewage treatment plant**  
3 **water**

4

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12

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16

17 **Abstract**

18 In this [paper](#), the degradation of three endocrine-disrupting chemicals (EDCs): bisphenol A  
19 (BPA), 17 $\beta$ -estradiol (E2) and 17 $\alpha$ -ethinylestradiol (EE2) by manganite ( $\gamma$ -MnOOH) activated  
20 peroxymonosulfate (PMS) was investigated. Preliminary optimisation experiments showed that  
21 complete degradation of the three EDCs was achieved after 30 min of reaction using 0.1 g L<sup>-1</sup>  
22 of  $\gamma$ -MnOOH and 2 mM of PMS. The degradation rate constants were determined to be 0.20,  
23 0.22 and 0.15 min<sup>-1</sup> for BPA, E2 and EE2, respectively. Combining radical scavenging  
24 approaches, Electron paramagnetic resonance (EPR) and X-ray photoelectron spectroscopy  
25 (XPS) analyses, we revealed for the first time that about 40 % of EDCs degradation can be  
26 attributed to heterogeneous electron transfer reaction involving freshly generated Mn(IV), and  
27 60 % to sulfate radical degradation pathway. The influence of various inorganic ions on the  $\gamma$ -  
28 MnOOH/PMS system indicated that removal efficiency was slightly affected by chloride and  
29 carbonate ions, while nitrate and nitrite ions had negligible impacts. The application of  $\gamma$ -  
30 MnOOH/PMS system in real sewage treatment plant water (STPW) showed that degradation  
31 rate constants of EDCs decreased to 0.035-0.048 min<sup>-1</sup> and complete degradation of the three  
32 EDCs after 45 min. This study provides new insights into the reactivity of combined  $\gamma$ -MnOOH  
33 and PMS, and opens new ways for the application of Mn-bearing species in wastewater  
34 treatment technologies.

35

36

37 **Keywords:** Manganite; Peroxymonosulfate; Metal-based oxidation; Sulfate radical; EDCs

## 38 **1. Introduction**

39 Endocrine-disrupting chemicals (EDCs) affect the normal functioning of endogenous hormones  
40 (Zhou et al., 2019). EDCs consist of various types of chemicals such as natural and synthetic  
41 hormones, plasticizers, pesticides, and flame retardants (C. Yang et al., 2020). With the  
42 development of industry and the pursuit of high-quality life of humans, the EDCs-containing  
43 products have been consumed in a large amount. Over the past 10 years, EDCs as a major  
44 concern of water quality have received extensive attention (Adeel et al., 2017; Havens et al.,  
45 2020; Vilela et al., 2018). The regularly detected amount of EDCs in surface and drinking  
46 waters are up to ng/L while higher concentrations in municipal wastewater, an important source  
47 of anthropogenic pollution release into the environment, were also reported (Adeel et al., 2017;  
48 Lei et al., 2020).

49 To decrease the concentration of EDCs in wastewater, different processes based on thermal and  
50 photochemical degradation were reported (Chaves et al., 2020; Gabet et al., 2021; Gmurek et  
51 al., 2017). Advanced oxidation processes (AOPs) are innovative technologies used to improve  
52 the degradation of the recalcitrant pollutants based on the formation of highly oxidative species  
53 (Gabet et al., 2021; Gmurek et al., 2017). Reactive oxygen and sulfur species (ROS and RSS)  
54 with high oxidation potentials such as hydroxyl ( $\text{HO}^\bullet$ ) and sulfate ( $\text{SO}_4^{\bullet-}$ ) radicals are generated  
55 through photochemical or electron transfer reaction (Gligorovski et al., 2015). Such radicals are  
56 capable of inducing hazardous pollutants degradation till complete mineralization in water.  
57 Among the different AOPs systems, transition metal-based activation of radical precursors  
58 represents a low-energy cost and efficient process (Wang and Wang, 2018; Xiong et al., 2020).  
59 Iron (Fe) is one of the most used metal in homogeneous and heterogeneous applications and the  
60 redox cycle between Fe(II) and Fe(III) provide a very efficient system for activation of radical  
61 precursors and abatement of organic pollutant concentration in waters (Kusic et al., 2011).

62 However, organic complexes such as aminopolycarboxylic are regularly used to improve the iron  
63 stability toward a large range of pH values (Abida et al., 2006; Huang et al., 2013).

64 Recently, other metals such as manganese (Mn) has been used for different water treatment  
65 applications. Mn is a promising metal due to its multiple oxidation states (+II, +III, +IV, +VII)  
66 and high oxidative and catalytic reactivity. Most of published reports have focused on  
67 manganese dioxide-based AOPs ( $\text{MnO}_2$ -AOPs), to remove pollutants, such as phenol and 2,4-  
68 dichlorophenol, using  $\text{MnO}_2$  activated peroxymonosulfate (PMS) or persulfate (PS) in water  
69 (Wang et al., 2015; Zhao et al., 2016). Huang et al. (2019) investigated the effects of properties  
70 of  $\text{MnO}_2$  such as crystal structure, morphology, and surface Mn oxidation states on PMS  
71 activation. They showed that the catalytic activity of  $\text{MnO}_2$  is positively corrected with the  
72 surface Mn(III) content (Huang et al., 2019).

73 Other studies have used Mn(III) oxides as a mean to activate oxidants (e.g. PMS and PS) and  
74 then remove organic contaminants, such as  $\alpha\text{-Mn}_2\text{O}_3$  (Saputra et al., 2014) and  $\text{MnOOH}$  (Xu et  
75 al., 2021). He et al. demonstrated that nanowires  $\text{MnOOH}$  have higher activity on PMS  
76 activation for 2,4-dichlorophenol oxidation as compared with multi-branches and nanorods  
77  $\text{MnOOH}$  (He et al., 2020). Moreover, (Li et al., 2016) showed that sulfate and hydroxyl  
78 radicals can be generated from manganite-activated PS under pH 11. Although the good ability  
79 of  $\text{Mn}^{\text{III}}$ -oxides for PS or PMS activation has been investigated the underlying mechanisms of  
80 activation and generation of reactive species remain elusive. In addition, most of available data  
81 on the  $\text{MnOOH}$ /PMS activation process has been obtained in ultrapure water and very little is  
82 known about the application of this process in real wastewater. Therefore, the ability of  $\gamma$ -  
83  $\text{MnOOH}$  for PMS activation under real-world conditions for wastewater treatment merits  
84 investigation.

85 In the present study, we investigated the degradation of three EDCs (Bisphenol A (BPA), 17 $\beta$ -  
86 estradiol (E2) and 17 $\alpha$ -ethinylestradiol (EE2)) using  $\gamma$ - $\text{MnOOH}$ -activated PMS process. We

87 have combined radical scavenging approaches, EPR and XPS analyses, to determine the  
88 different activation and removal mechanisms (i.e. radical and non-radical pathways). Moreover,  
89 the influence of key parameters such as the initial concentration of  $\gamma$ -MnOOH and PMS, and  
90 the impact of water inorganic constituents were also evaluated. Finally, the efficiency of the  
91 degradation system was evaluated in real sewage treatment plant water, collected from the “3  
92 rivières” urban treatment plant in Clermont-Ferrand, France.

93

## 94 **2. Material and Methods**

### 95 *2.1. Chemicals and reagents*

96 Bisphenol A (BPA, 99%), 17 $\beta$ -estradiol (E2, 98%), 17 $\alpha$ -ethynylestradiol (EE2, 98%),  
97 potassium peroxymonosulfate (PMS, purchased in the form of  $\text{KHSO}_5 \cdot 0.5\text{KHSO}_4 \cdot$   
98  $0.5\text{K}_2\text{SO}_4$ ), sodium nitrite ( $\text{NaNO}_2$ , 97%), sodium bicarbonate ( $\text{NaHCO}_3$ , 99.7%), and sodium  
99 chloride ( $\text{NaCl}$ , 99%) were purchased from Sigma-Aldrich Company, France. Sodium nitrate  
100 ( $\text{NaNO}_3$ , 99%) was bought from Fluka. Manganese (II) chloride ( $\text{MnCl}_2$ ) was purchased from  
101 Riedel-de Haen. HPLC grade acetonitrile solvent (ACN) was purchased from CARLO ERBA  
102 Reagents. Sodium hydroxide ( $\text{NaOH}$ , 99.9%) and perchloric acid ( $\text{HClO}_4$ , 72%) which were  
103 used to adjust solution pH were purchased from Sigma-Aldrich. Ethanol (96%, VWR  
104 Chemicals), *t*-Butyl alcohol (TBA), and furfuryl alcohol (FFA) from Sigma-Aldrich were  
105 employed as radical and singlet oxygen scavengers. Ultrapure water (Millipore, resistivity 18.2  
106  $\text{M}\Omega$  cm) was used in the preparation of all solutions. All chemicals were used as received  
107 without further purification.

108

### 109 *2.2. $\gamma$ -MnOOH synthesis and characterization*

110 Manganite ( $\gamma$ -MnOOH) particles were synthesized as described by Yu and co-workers (Yu et  
111 al., 2018). The nature of  $\gamma$ -MnOOH was confirmed by X-ray diffraction (XRD) and

112 Transmission Electron Microscopy- Selective Area Electron Diffraction (TEM-SAED) using  
113 an accelerating voltage of 200 kV (TEM Jeol JEM 2100 HR) (Fig. S1). TEM images of the as-  
114 prepared manganite display wire-like morphology with diameters of 20–40 nm, and the SAED  
115 pattern confirmed the nature of  $\gamma$ -MnOOH. For XPS analysis, 0.5 g/L of solid were put in  
116 contact with 5 mM of PMS with and without BPA (200  $\mu$ M). After 1 h of reaction, the solution  
117 was centrifuged and water was withdrawn and the remaining water completely removed under  
118 the N<sub>2</sub> stream. Then, the solid particles were collected and analyzed in a UHV chamber  
119 (pressure 10<sup>-7</sup> Pa) facilitated with an XPS system (hemispherical electron energy analyzer  
120 OMICRON EA125, Germany). Data analysis, curve fitting and quantification of the Mn XPS  
121 spectra were performed using CasaXPS software. The binding energy (BE) scale was  
122 referenced to the adventitious C1s peak at 284.8 eV. High-resolution XPS spectra were  
123 processed using Shirley background subtraction. After background subtraction, the spectra  
124 were smoothed and fitted by using of Gaussian-Lorentzian peak shape (70:30). For each  
125 sample, fitting parameters (FWHM, the full width at half maximum; H, the peak height; E, the  
126 peak position center) were adjusted to minimize the value of residual standard deviation (STD).

127

### 128 *2.3. Real water matrix*

129 The sewage treatment plant water (STPW) was collected from the urban treatment plant named  
130 “3 rivières” in Clermont-Ferrand, France in December 2019. Prior to use, the STP water was  
131 filtered using a syringe filter (CHROMAFIL<sup>®</sup> Xtra RC-45/25) and then use for experiments.  
132 The main physico-chemical parameters relevant to this study are reported in Table S1.

133

### 134 *2.4. Experimental procedure*

135 PMS was added to the solution containing selected EDCs and  $\gamma$ -MnOOH just before the  
136 reaction starts. All reactions were performed in a brown glass bottle (125 mL) at room

137 temperature ( $293 \pm 2$  K) and under stirring to ensure homogeneity. Unless otherwise stated,  
138 experiments were performed at pH  $6.5 \pm 0.2$ . For HPLC, 2 mL of solution were withdrawn at  
139 fixed interval times, filtered using 0.20  $\mu$ M PTFE filter and the reaction was immediately  
140 quenched with the addition of 20% methanol (HPLC grade, Sigma-Aldrich). Samples were  
141 kept at 277 K and analysis was performed within 4 hours. Furthermore, to identify the  
142 generated radicals, EtOH, TBA and FFA were added to the solution before PMS addition and a  
143 kinetic approach based on the second-order rate constants and pseudo-first order decay  
144 determination was used to assess the radical species involvement.

145

## 146 2.5. Analytical methods

147 BPA, E2 and EE2 quantification during reactions was performed by high performance liquid  
148 chromatography (HPLC) equipped with a diode array detector (Waters 2475, USA). The  
149 injection volume was 50  $\mu$ L and a flow rate of 1 mL min<sup>-1</sup> with a mobile phase consisting of a  
150 mixture of water and ACN (50/50, v/v) were used. An Agilent Eclipse XDB C18 of 250 mm  $\times$   
151 4.6 mm  $\times$  5  $\mu$ m column was adapted as the analytic column. Under these conditions, the  
152 detection wavelength and retention time were: for BPA (277 nm) at 5.4 min, for E2 (280 nm) at  
153 6.2 min, for EE2 (280 nm) at 7.3 min (Fig. S2). To investigate the mineralization, the total  
154 organic carbon (TOC) analysis (TOC-L CPH CN200, Shimadzu) was performed.

155 The pseudo-first order decay of selected pollutant ( $k'_p$ ) was determined from the slope of  
156  $\ln(C/C_0)$  vs reaction time as following:  $\ln \frac{C}{C_0} = k'_p \times t$ . Where  $C_0$  and  $C$  are the initial and  
157 remaining concentrations in solution and  $t$  is the reaction time.

158 PMS was quantified using the iodometric titration in which generated  $I_3^-$  was quantified at 348  
159 nm using a Cary 300 Varian Spectrophotometer (Wacławek et al., 2015). Calibration was  
160 performed using different PMS concentrations and data are presented in the supplementary  
161 Materials (Fig. S3). Briefly, 100  $\mu$ L of sample was withdrawn at different reaction times and



162 added to 5 mL of a solution containing KI (0.6 M) and  $\text{HCO}_3^-$  (0.06 M). The Abs of solution at  
163 348 nm was measured after 10 min of reaction and PMS concentration ( $C_{\text{PMS}}$ , (mM)) was  
164 determined as  $C_{\text{PMS}} = \frac{V_{\text{tot}}}{V_{\text{PMS}}} \times \frac{\text{Abs}_{348 \text{ nm}}}{0.5}$ . Where  $V_{\text{PMS}}$  and  $V_{\text{tot}}$  are the volume of sample (100  
165  $\mu\text{L}$ ) and total volume (5.1 mL), 0.5 was the slope of the linear correlation between the PMS  
166 concentration and value of Abs at 348 nm.

167 The Atomic absorption spectroscopy (AAS, PerkinElmer) was employed to determine the  
168 concentration of dissolved  $\text{Mn}^{2+}$  in the aqueous solution. The procedure involved the filtration  
169 of the samples through a 0.2  $\mu\text{m}$  PTFE filter and the addition of 2% nitric acid ( $\text{HNO}_3$ , 65%,  
170 Sigma-Aldrich) before detection.  $\text{Mn}^{2+}$  standard solution for AAS (TraceCERT<sup>®</sup>, 1000 mg  $\text{L}^{-1}$   
171 Mn in 2% nitric acid, Sigma-Aldrich) was used for making the calibration curve of  $\text{Mn}^{2+}$ . The  
172 detection wavelength was set at 279.48 nm.

173 The identification of reactive oxygen species was performed on the electron paramagnetic  
174 resonance spectroscopy (EPR, Burker) using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the  
175 spin trapping agents. Typically, 375  $\mu\text{L}$  of sample was withdrawn and immediately mixed with  
176 125  $\mu\text{L}$  of DMPO (100 mM), then the mixture was transferred into an EPR quartz capillary  
177 tube (0.5 mm, 100 mm) for measurement. The EPR spectrometer settings were as follows:  
178 modulation frequency,  $\sim 100$  kHz; microwave frequency,  $\sim 9.87$  GHz; microwave power,  $\sim 6.87$   
179 mW; center field,  $\sim 352.7$  mT; sweep width, 20 mT; sweep time, 30 s; sample g-factors, 2.0;  
180 modulation amplitude, 1.0 G.

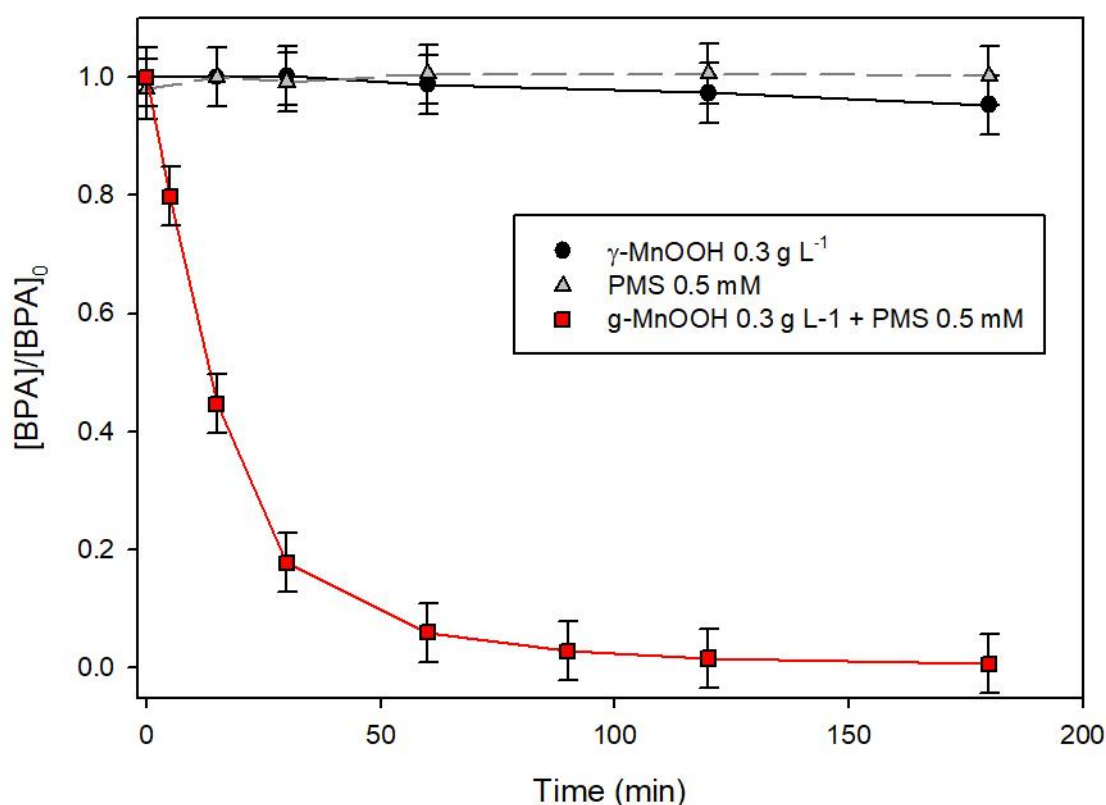
181

### 182 **3. Results and discussion**

#### 183 *3.1. Effect of $\gamma\text{-MnOOH}$ and PMS dosage*

184 Preliminary experiments showed that no significant degradation was observed with PMS or  $\gamma$ -  
185  $\text{MnOOH}$ , while efficient removal was reached when both  $\gamma\text{-MnOOH}$  and PMS were used  
186 simultaneously (Fig. 1). **In this system, BPA was completely removed after 2 h with an initial**

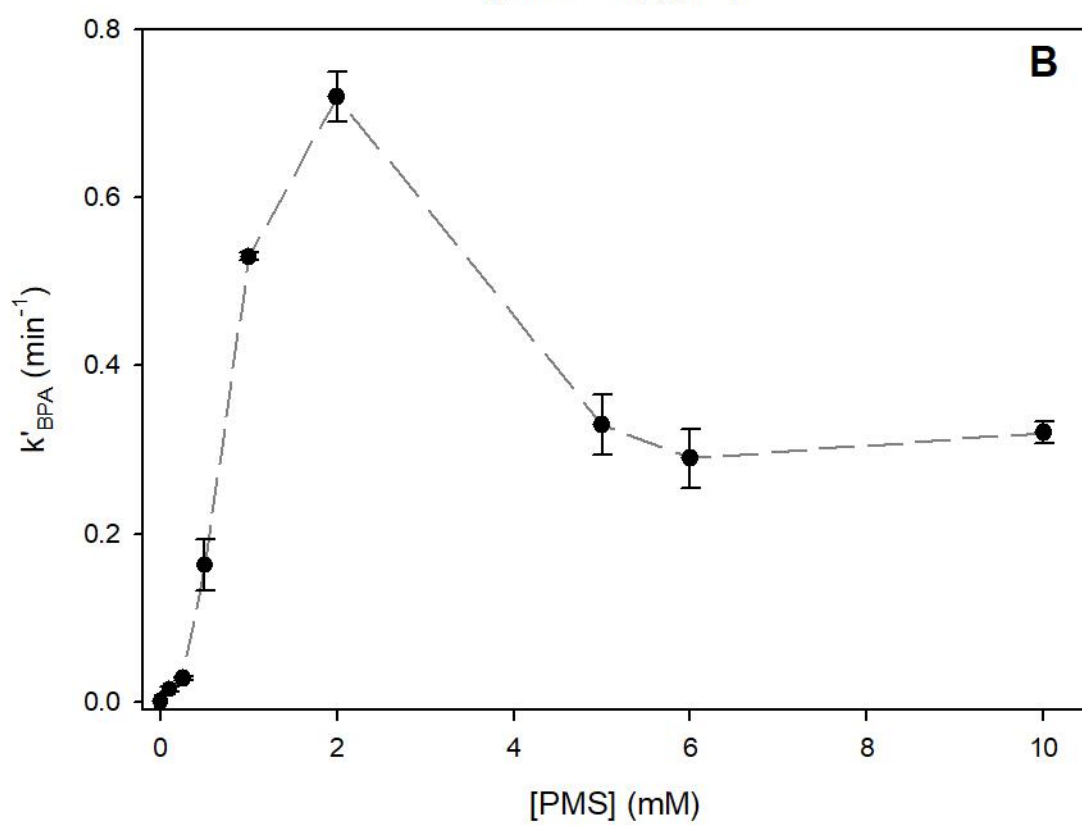
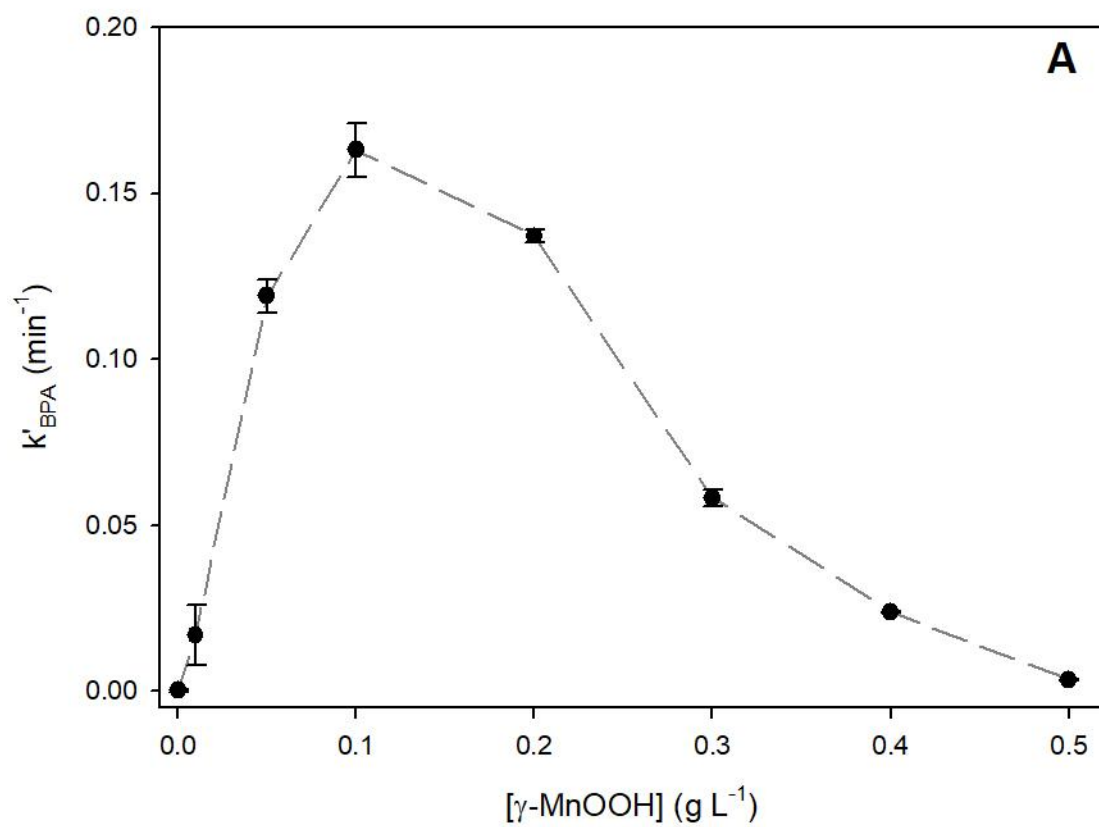
187 pseudo-first order degradation rate ( $k'_{BPA}$ ) of  $0.058 \pm 0.001 \text{ min}^{-1}$  showing that reactive  
188 species (such as  $\text{SO}_4^{\cdot-}$  and  $\text{HO}^{\cdot}$ ) may be generated through the reaction between  $\gamma\text{-MnOOH}$  and  
189 PMS in solution. Moreover, the adsorption of BPA on  $\gamma\text{-MnOOH}$  was negligible ( $< 3 \%$ ) after  
190 3h of reaction.  
191



192  
193 **Fig. 1.** Degradation of BPA ( $25 \mu\text{M}$ ) in the presence of  $\gamma\text{-MnOOH}$  ( $0.3 \text{ g L}^{-1}$ ) and PMS ( $0.5$   
194  $\text{mM}$ ) at pH 6.5.

195  
196 When various concentrations of  $\gamma\text{-MnOOH}$  were used in the presence of  $0.5 \text{ mM}$  PMS (Fig.  
197 2A), a different trend can be observed. Increasing the  $\gamma\text{-MnOOH}$  concentration up to  $0.1 \text{ g L}^{-1}$ ,  
198 faster degradation of BPA was determined and the corresponding kinetic rate constant of BPA  
199 degradation ( $k'_{BPA}$ ) increased up to  $0.163 \pm 0.001 \text{ min}^{-1}$ . At higher  $\gamma\text{-MnOOH}$  concentrations,  
200 the BPA degradation decreased and almost no degradation was observed using  $0.5 \text{ g L}^{-1}$  of  $\gamma\text{-}$

201 MnOOH. Similar trend was observed when different PMS concentrations were used in the  
202 presence of 0.1 g L<sup>-1</sup> of  $\gamma$ -MnOOH (Fig. 2B). From 0 to 2 mM,  $k'_{BPA}$  increased almost linearly  
203 to  $0.719 \pm 0.007 \text{ min}^{-1}$ , while higher PMS concentrations inhibited the degradation. This  
204 behavior suggests that Mn(III)-oxide and PMS would scavenge the generated reactive species  
205 when they are used at high concentrations. This behaviour suggests that Mn(III)-oxide and PMS  
206 would scavenge the generated reactive species when they are used at high concentrations. This effect  
207 can be attributed to the quenching of excessive  $\gamma$ -MnOOH and PMS on the active species(Wang et al.,  
208 2017; Zhang et al., 2021). Thus, an optimal concentration of  $\gamma$ -MnOOH (0.1 g/L) and PMS (2  
209 mM) was adopted for the followed study.



211 **Fig. 2.** Pseudo-first order degradation rate of BPA using different  $\gamma$ -MnOOH concentrations in  
212 the presence of 0.5 mM of PMS (A) and in the presence of  $\gamma$ -MnOOH (0.1 g L<sup>-1</sup>) and different  
213 PMS concentrations (B). Error bars are determined from the  $\sigma$ -level uncertainty of the data fit  
214 used to obtain  $k'_{BPA}$ .

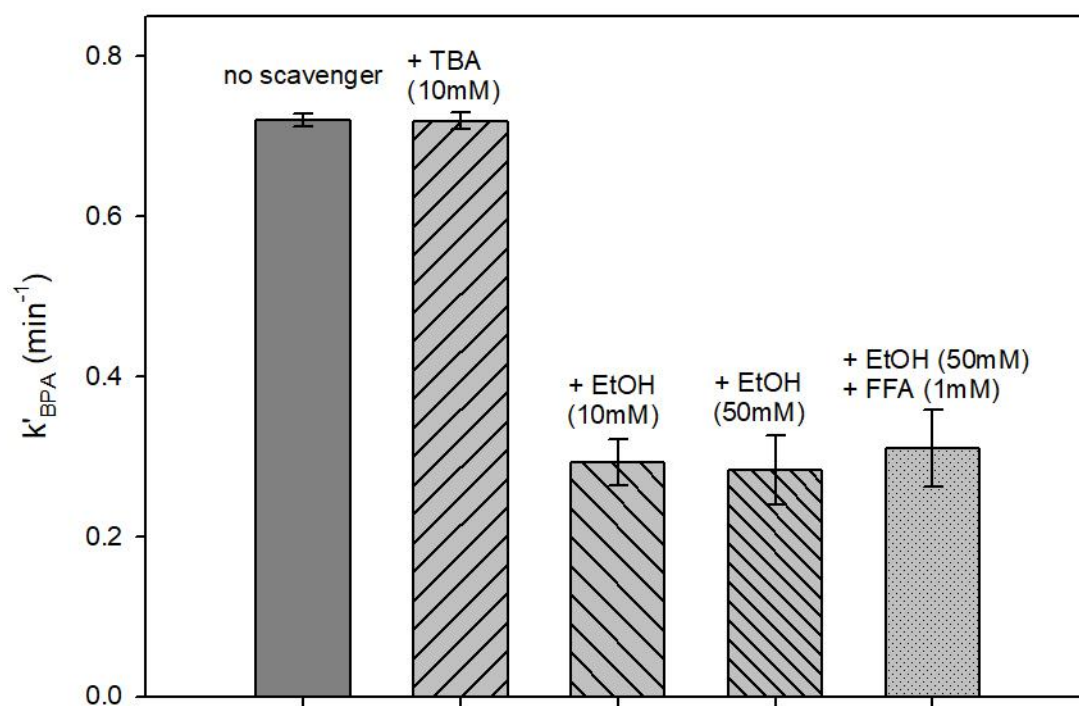
215

### 216 3.2. Activation pathway and reactive species formation

217 In order to verify the generation of reactive species resulted from the activation of  $\gamma$ -MnOOH,  
218 the leaching of dissolved Mn<sup>2+</sup> in  $\gamma$ -MnOOH/PMS system was measured, and the homogenous  
219 activation of PMS by Mn<sup>2+</sup> was evaluated. The total amount of leached and adsorbed Mn<sup>2+</sup> was  
220 determined at around 34  $\mu$ M after 30 min of reaction. However, a high amount of dissolved  
221 Mn<sup>2+</sup> (100  $\mu$ M) can only remove about 20% of target compound in 1 h reaction (Fig. S4).  
222 Therefore, the removal of BPA was mainly attributed to the heterogeneous activation of PMS  
223 by  $\gamma$ -MnOOH.

224 To identify the reactive species generated in the  $\gamma$ -MnOOH/PMS system, chemical scavenging  
225 tests and EPR experiments were conducted. Firstly, the generation of reactive oxidant species  
226 was investigated using different chemical quenchers. TBA was used as the HO<sup>•</sup> scavenger due  
227 to its higher selectivity toward HO<sup>•</sup> ( $k_{TBA,HO^{\bullet}} = 6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) compared to SO<sub>4</sub><sup>•-</sup> ( $k_{TBA,SO_4^{\bullet-}} = 8.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ) (Yuan et al., 2019). Theoretically, the addition of 10 mM of TBA can  
228 suppress 96% of BPA degradation considering the reaction rate constants of TBA, PMS and  
229 BPA with HO<sup>•</sup> ( $k_{PMS,HO^{\bullet}} = 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{BPA,HO^{\bullet}} = 8.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) (Table S2) (W.  
230 Huang et al., 2018; Maruthamuthu and Neta, 1977). However, the  $k'_{BPA}$  was not inhibited  
231 when 10 mM of TBA were added to the solution, indicating that no HO<sup>•</sup> was generated in the  
232 system (Fig. 3). Comparatively, using 10 mM of EtOH can efficiently quench both HO<sup>•</sup> and  
233 SO<sub>4</sub><sup>•-</sup> radicals ( $k_{EtOH,HO^{\bullet}} = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{EtOH,SO_4^{\bullet-}} = 4.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) (Buxton et al.,  
234 1988; Clifton and Huie, 1989). The  $k'_{BPA}$  decreases to 40 % of the initial value (0.719 min<sup>-1</sup>)  
235

236 showing that  $\text{SO}_4^{\bullet-}$  are generated and contributed to the BPA degradation. Further increasing  
237 EtOH concentration up to 50 mM, the BPA degradation decreased to 39 %. The generation of  
238 reactive radicals were also confirmed by the EPR experiments using DMPO as the complexing  
239 agents. Fig. S5 shows one clear seven-peaks signal was formed in the  $\gamma\text{-MnOOH/PMS}$  system.  
240 This multiplet peaks signal is recognized as the 5,5-dimethyl-2-oxo-pyrroline-1-oxyl  
241 (DMPOX) which can be generated by the overoxidizing of DMPO by reactive species such as  
242  $\text{HSO}_5^-$ ,  $\text{HO}^{\bullet}$  and  $\text{SO}_4^{\bullet-}$  radicals. Since no  $\text{HO}^{\bullet}$  was generated in the reaction, and  $\text{HSO}_5^-$  has  
243 low reactivity to oxidize DMPO (X. Yang et al., 2020), the formation of DMPOX can be  
244 reasonably attributed to the reactivity of DMPO with  $\text{SO}_4^{\bullet-}$  radicals.  
245 Furthermore, under the adopted experimental conditions we can estimate that, considering only  
246  $\text{SO}_4^{\bullet-}$  involved during the degradation system, quenching of 78.5 and 94.8% of BPA  
247 degradation should be expected with the addition of 10 and 50 mM of EtOH (Table S2).  
248 However, this difference has not been observed in our experiments, which suggest the  
249 occurrence of other reactive species un-quenchable by the organic scavengers. Thus, one non-  
250 radical mechanism was assumed to be responsible for the degradation of the rest part of BPA.  
251 He et al. reported the generation of singlet oxygen ( $^1\text{O}_2$ ) in the system of  $\gamma\text{-MnOOH/PMS}$  (He  
252 et al., 2020). To verify if  $^1\text{O}_2$  was generated, the degradation of BPA was followed in the  
253 presence of 1 mM FFA as  $^1\text{O}_2$  quencher ( $k_{\text{FFA},^1\text{O}_2} = 1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) in addition to 50 mM of  
254 EtOH (Haag et al., 1984). Since FFA has high reactivity with  $\text{HO}^{\bullet}$  ( $k_{\text{FFA}, \text{HO}^{\bullet}} = 1.5 \times 10^{10} \text{ M}^{-1}$   
255  $\text{ s}^{-1}$ ) (Yang et al., 2018), the simultaneous addition of FFA and EtOH was planned to consume  
256 all the possible  $\text{HO}^{\bullet}$  radicals using EtOH, and then verify the inhibition of BPA degradation  
257 caused by FFA addition was only attributed to the generation of  $^1\text{O}_2$ . As reported in Fig. 3,  
258 almost no effect was observed with the addition of FFA indicating that  $^1\text{O}_2$  was not generated.



259

260

261 **Fig. 3.** BPA degradation ( $k'_{\text{BPA}}$ ) in the system  $\gamma\text{-MnOOH } 0.1 \text{ g L}^{-1} + \text{PMS } 2 \text{ mM}$  in the absence  
 262 and presence of different scavengers at pH 6.5. Error bars are determined from the  $\sigma$ -level  
 263 uncertainty of the data fit used to obtain  $k'_{\text{BPA}}$ .

264

265 To further shed light on the non-radical mechanism in the  $\gamma\text{-MnOOH/PMS}$  system, more  
 266 attention had been paid to the oxidation states of Mn species changing during the reaction.  
 267 Since the direct oxidation of the organic compounds by Mn(IV) through electron transfer  
 268 process has been widely reported (Huang et al., 2019; J. Huang et al., 2018), we can suppose  
 269 that higher valence state Mn species (e.g.  $\text{Mn}^{\text{IV}}$ ) can be formed, and thus contribute to the  
 270 degradation of BPA. In order to get more insights on the redox process involving Mn species,  
 271 XPS analysis of  $\gamma\text{-MnOOH}$  surfaces was performed during different reaction steps. The  
 272 chemical oxidation state of Mn in the external layers was determined using the Mn 3s multiplet  
 273 splitting method and the position and shape of the Mn  $2p_{3/2}$  spectra (Fig. 4) (Ardizzone et al.,

1998; Ilton et al., 2016). The peak position and relevant parameters from curve fitting of Mn 3s and Mn 2p<sub>3/2</sub> high resolution spectra are listed in Table 1. The average oxidation state (AOS) of samples was calculated from the % of each Mn species from the fitting of Mn 2p<sub>3/2</sub> spectra and from the binding energy difference of Mn 3s doublet splitting as following:  $AOS = 8.956 - 1.126 \times \Delta E$  [25,26]. Using the multiplets fitting of the Mn 2p<sub>3/2</sub> peaks, the percent contents of Mn(IV), Mn(III) and Mn(II) in the  $\gamma$ -MnOOH sample were 7%, 85% and 8%, respectively and AOS was 2.99. After reaction with PMS, the relative contents of Mn(IV), Mn(III) and Mn(II) changed and Mn(IV) percentage increased to 24.5 consistently with an increase of AOS up to 3.10. In the sample  $\gamma$ -MnOOH + PMS + BPA, Mn(II) percentage increased to 37% while Mn(IV) decreased to 9% with a decrease of AOS down to 2.72. AOS values were consistent with those determined from the fitting of Mn 3s multiplet splitting data (Table 1). The increase of Mn(IV) in the presence of PMS followed by a decrease when BPA was present in solution, suggests that freshly generated Mn(IV) may contribute to the degradation of BPA. Such a process, called metal-based oxidation, was previously indicated as relevant surface-mediated oxidation of organic pollutants in the presence of Mn(IV) oxides (Kamagate et al., 2020). Huang et al. demonstrated the efficient oxidation of BPA by MnO<sub>2</sub> with different structures such as  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -MnO<sub>2</sub> with and without PMS (Huang et al., 2019; J. Huang et al., 2018). Wang et al. reported the removal of BPA was due to a complex between amorphous MnO<sub>2</sub> and PMS (Wang et al., 2018).

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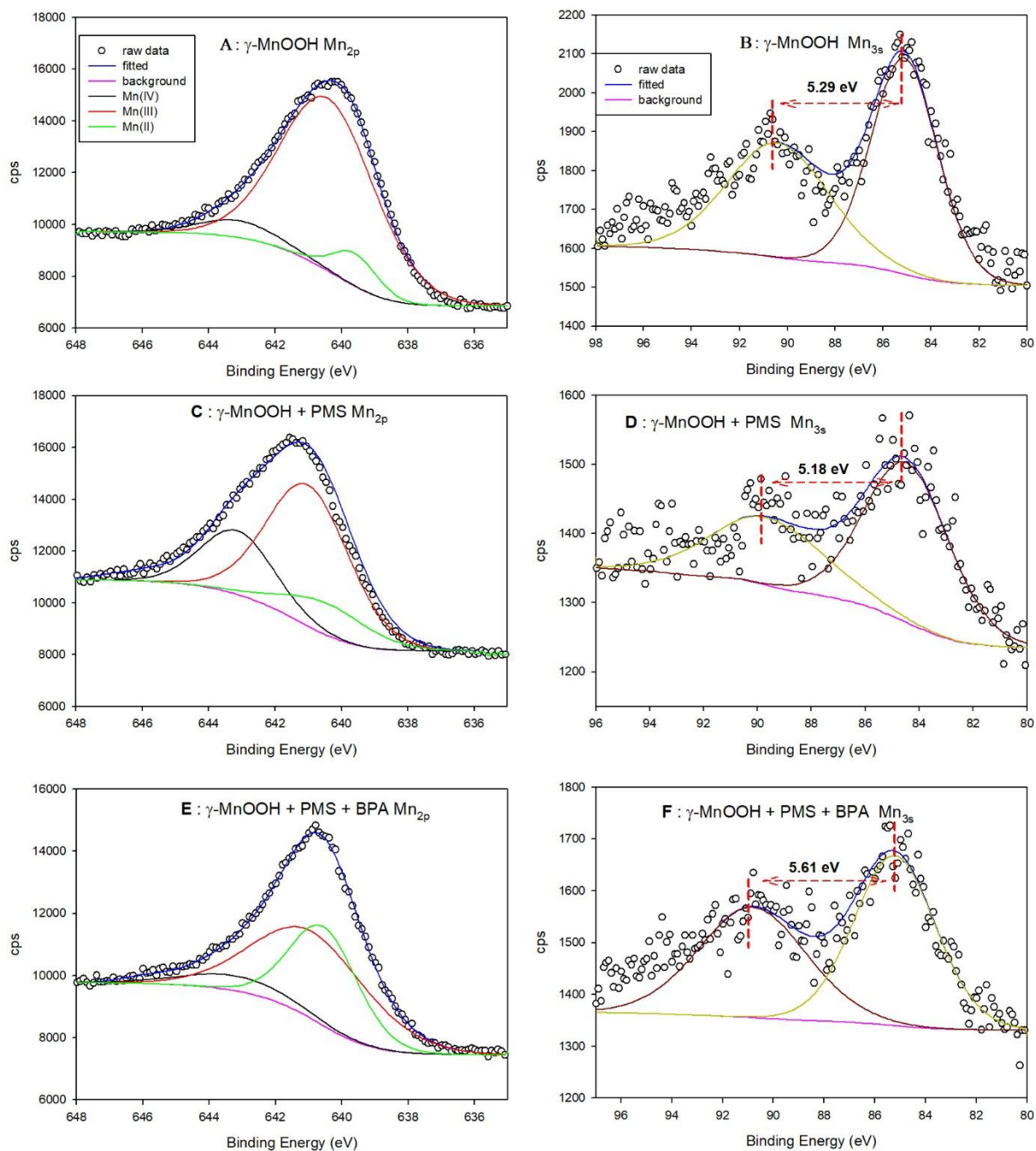
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302 **Fig. 4.** XPS Mn 2p and Mn 3s spectra of  $\gamma$ -MnOOH (A and B),  $\gamma$ -MnOOH + PMS (C and D)303 and  $\gamma$ -MnOOH + PMS + BPA (E and F) Initial conditions are [BPA] = 5  $\mu$ M, [ $\gamma$ -MnOOH] =304 0.1 g L<sup>-1</sup> and [PMS] = 2 mM at pH 6.5.

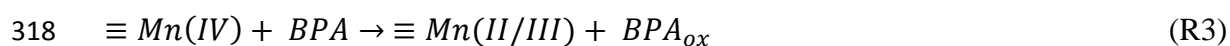
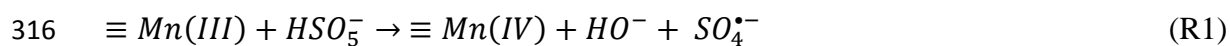
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306 **Table 1.** Parameters from curve fitting of Mn 3s and Mn 2p<sub>3/2</sub> XPS spectra and average  
 307 oxidation state.

Sample		$\gamma$ -MnOOH	$\gamma$ -MnOOH+PMS	$\gamma$ -MnOOH+PMS+BPA	
Mn 2p	Mn(II)	BE (eV)	639.60	639.64	640.54
		%	8	14	37
	Mn(III)	BE (eV)	640.41	641.00	640.88
		%	85	61	54
	Mn(IV)	BE (eV)	643.10	642.85	643.18
		%	7	25	9
		<b>AOS</b>	<b>2.99</b>	<b>3.10</b>	<b>2.72</b>
	Mn 3s	Multiplet Splitting (eV)	5.29	5.18	5.61
		<b>AOS</b>	<b>3.00</b>	<b>3.12</b>	<b>2.64</b>

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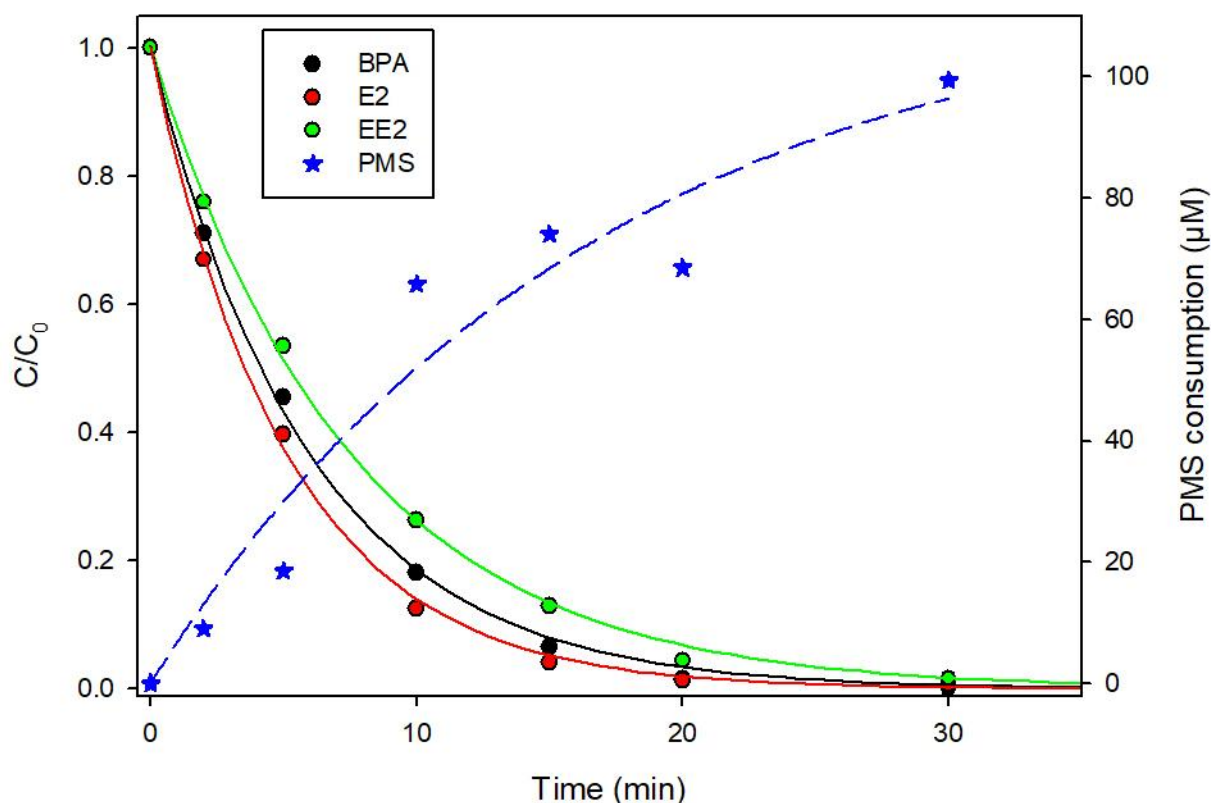
309 Collectively, quenching experiments and XPS analysis suggest that the first electron transfer  
 310 reaction occurring between  $\equiv\text{Mn(III)}$  and PMS on the surface of oxide led to the formation of  
 311  $\equiv\text{Mn(IV)}$  and  $\text{SO}_4^{\bullet-}$  (R1).  $\text{SO}_4^{\bullet-}$  can oxidize BPA (R4) (Table S2) while Mn(IV) can further  
 312 react with PMS leading to the formation of  $\equiv\text{Mn(III)}$  and  $\text{SO}_5^{\bullet-}$  (R2) or directly with BPA (R3).  
 313 The involvement of  $\text{SO}_5^{\bullet-}$  during the BPA degradation (R5) is reasonably considered less  
 314 relevant due to the typical second-order rate constants between  $\text{SO}_5^{\bullet-}$  and organic molecules  
 315 ( $10^4 - 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) (Huie and Neta, 1985).



321

### 322 3.3. Degradation and mineralization of BPA, E2 and EE2

323 Degradation and mineralization efficiencies of  $\gamma$ -MnOOH/PMS system were tested on BPA, E2  
324 and EE2 mixing solution at pH 6.5. In Fig. 5, the degradation of three EDCs (5  $\mu$ M each) and  
325 PMS (2 mM) consumption were followed during the reaction time in the presence of  $\gamma$ -  
326 MnOOH (0.1 g L<sup>-1</sup>). Despite no degradation in the presence of  $\gamma$ -MnOOH alone and less than  
327 10 % after 2 hours in the presence of PMS alone (Fig. S6), almost complete degradation of  
328 three pollutants can be observed after 30 min. Degradation of BPA, E2 and EE2 follows a  
329 mono-exponential decay and after 30 min of reaction, ~ 100  $\mu$ M of PMS were consumed. We  
330 can then estimate an efficiency of degradation system considering the stoichiometric efficiency  
331 value ( $\eta$ ) that is calculated as the ratio between degraded EDCs vs consumed PMS ( $\eta$   
332 =  $\frac{\Delta[EDCs]}{\Delta[PMS]}$ ). In the presence of 0.1 g L<sup>-1</sup>  $\gamma$ -MnOOH and 2 mM of PMS a value of  $\eta = 15\%$  was  
333 determined at pH 6.5.



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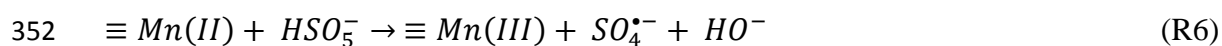
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337 **Fig. 5.** Degradation of BPA, E2 and EE2 in the system  $\gamma$ -MnOOH/PMS. The solid lines show  
 338 the fit of data using a mono-exponential decay function. Blue points show the PMS  
 339 consumption during the reaction. Initial conditions are [BPA] = [E2] = [EE2] = 5  $\mu\text{M}$ , [ $\gamma$ -  
 340 MnOOH] = 0.1  $\text{g L}^{-1}$  and [PMS] = 2 mM at pH 6.5.

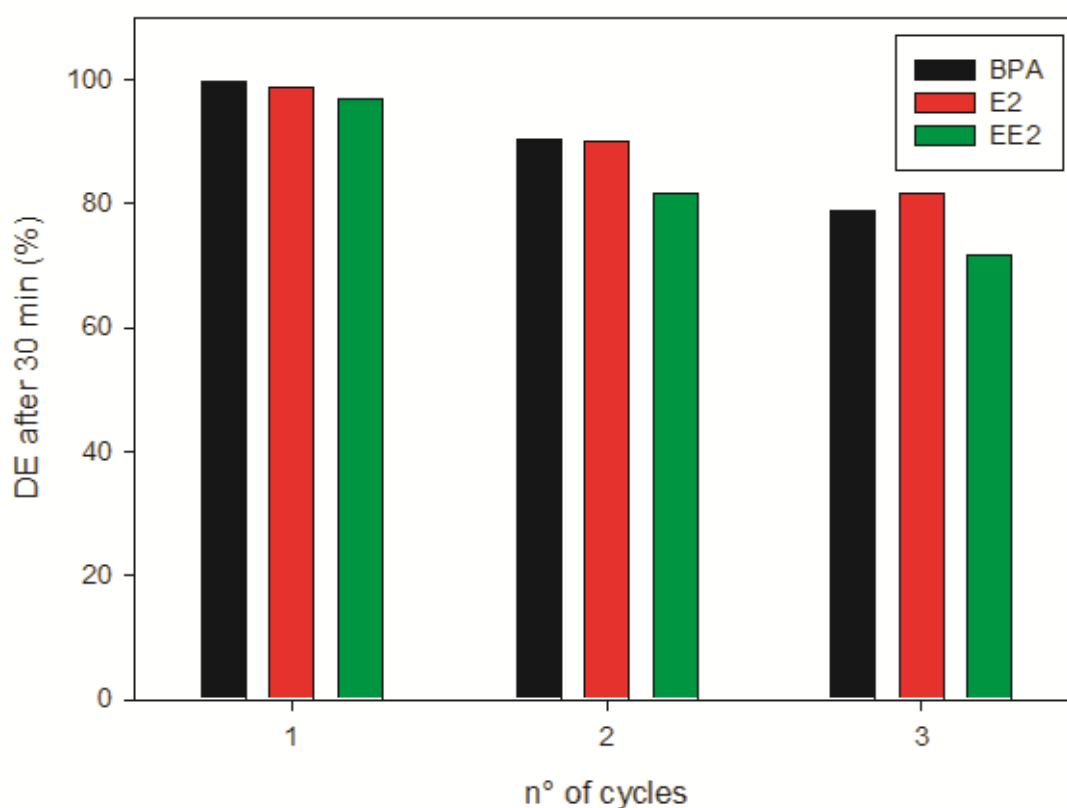
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342 The reuse of  $\gamma$ -MnOOH is an important parameter with regard to the possible application in  
 343 water treatment processes. For this purpose, the degradation efficiency (DE) for each EDCs  
 344 after 30 min of reaction was tested for 3 cycles. For the recycling experiments, the solution  
 345 containing mainly soluble products (PMS and EDCs degradation products) was completely  
 346 removed from the reactor and a fresh solution containing PMS and EDCs at initial  
 347 concentration was added again into the reactor containing  $\gamma$ -MnOOH. As shown in Fig. 6, after

348 three cycles of reuse, a reduction of EDCs degradation efficiency of about 20 % was observed  
349 indicating a good reusability of the oxidative system for EDCs removal. This effect can be  
350 explained considering the generation of  $\equiv Mn(II)$  (R3) and slower formation of  $\equiv Mn(III)$   
351 through PMS reactivation (R6) (Gao et al., 2021).



353



354

355 **Fig. 6.** Reusability of  $\gamma$ -MnOOH over 3 cycles. Experimental conditions are:  $[\gamma\text{-MnOOH}] = 0.1$   
356  $\text{g L}^{-1}$ ,  $[\text{PMS}] = 2 \text{ mM}$ ,  $[\text{BPA}] = [\text{E2}] = [\text{EE2}] = 5 \mu\text{M}$  and  $\text{pH} = 6.5$ .

357

### 358 3.4. Effect of inorganic ions

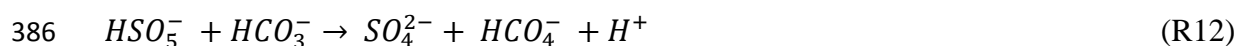
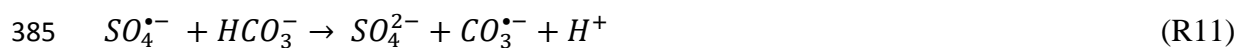
359 Inorganic anions are commonly detected in natural waters and they could affect the radical-  
360 mediated degradation efficiency of organic pollutants. In the  $\gamma$ -MnOOH / PMS system, the  
361 effect of chloride ( $\text{Cl}^-$ ), bicarbonate ( $\text{HCO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ) anions was

362 investigated and BPA, E2, and EE2 degradations were followed using 0.1 g L<sup>-1</sup> of  $\gamma$ -MnOOH  
363 and 2 mM of PMS.

364 As illustrated in Fig. 7A, increasing the concentration of Cl<sup>-</sup> from 0 to 5 mM, the BPA, E2, and  
365 EE2 degradation rates slightly increased indicating a positive effect of Cl<sup>-</sup> on the oxidation  
366 system. The results are in agreement with previous studies which indicated that improvement of  
367 organic pollutants degradation efficiency in the presence of Cl<sup>-</sup> was attributed to the generation  
368 of reactive chlorine species such as Cl<sup>•</sup> and HOCl (R7 to R9) (Wang and Wang, 2021). In fact,  
369 despite a different reactivity constant between Cl<sup>•</sup> and Cl<sub>2</sub><sup>•-</sup> with organic compounds ( $k_{Cl^{\bullet}} = 10^9$   
370  $- 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{Cl_2^{\bullet-}} = 10^7-10^8 \text{ M}^{-1} \text{ s}^{-1}$ ), their lower reactivity was partially counterbalanced by  
371 direct activation occurring in the presence of PMS leading to the formation of oxidant species  
372 such as HOCl as observed at high Cl<sup>-</sup> concentration in absence of  $\gamma$ -MnOOH (R9) (Fig. S6)  
373 (Lente et al., 2009).



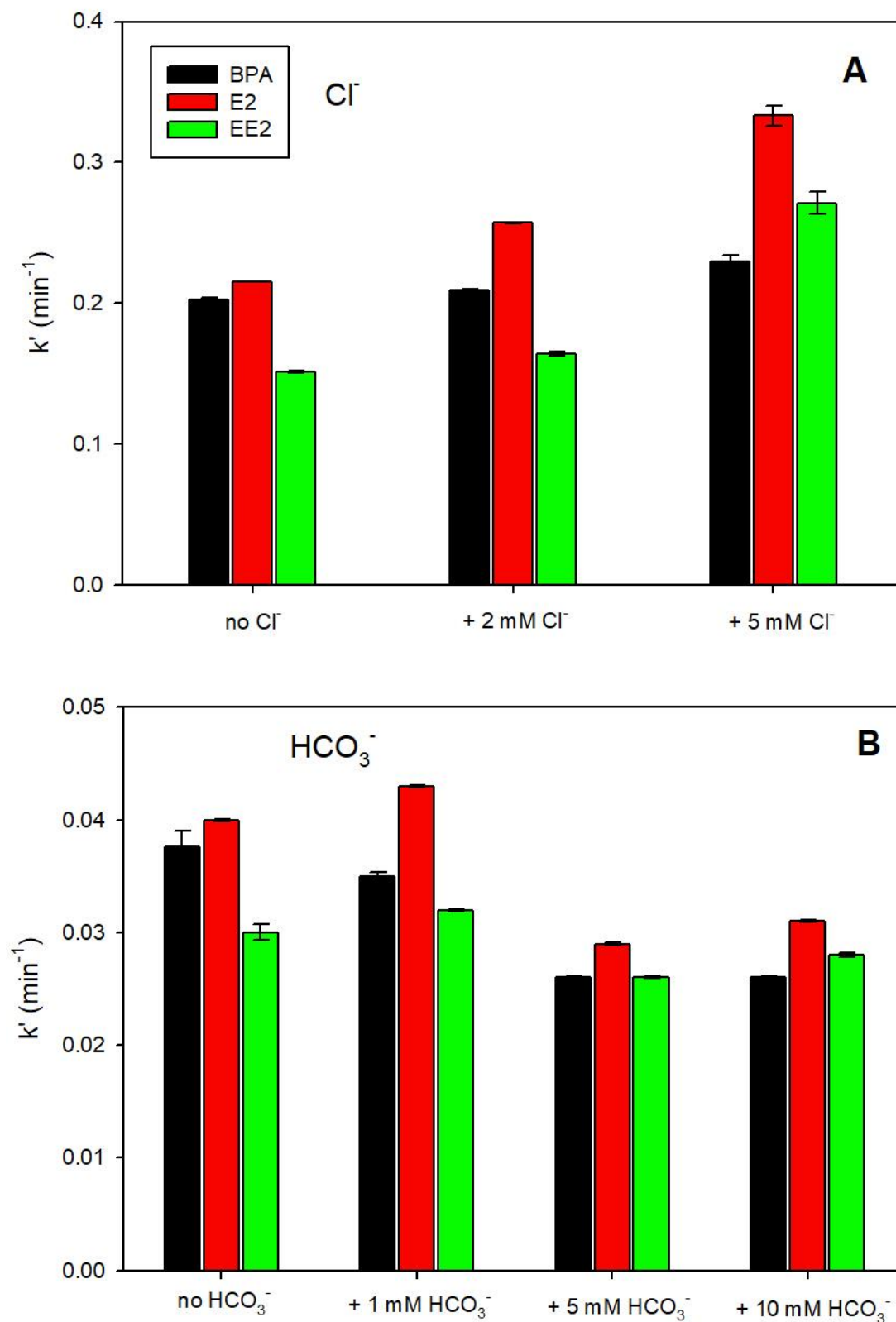
377 Bicarbonate ions (HCO<sub>3</sub><sup>-</sup>) are generally considered as interfering species during oxidative  
378 processes based on radical species generation due to their reactivity with radicals and  
379 generation of less oxidative species such as CO<sub>3</sub><sup>•-</sup> (Buxton et al., 1988; Clifton and Huie, 1989).  
380 However, a negligible impact on the EDCs degradation was observed with the addition of  
381 HCO<sub>3</sub><sup>-</sup> (Fig. 7B). Such effect can be explained considering that the inhibition effect on the  
382 sulfate radical reactivity (R10-R11) is counterbalanced by the direct activation of HCO<sub>3</sub><sup>-</sup> by  
383 PMS leading to the formation of HCO<sub>4</sub><sup>-</sup> as reported in Fig. S7 (R12) (Wang and Wang, 2021).



387 The effect of nitrogen anions ( $\text{NO}_2^-$  and  $\text{NO}_3^-$ ) on BPA, E2 and EE2 degradation were  
388 investigated, individually. As shown in Fig. S8, no effect of both  $\text{NO}_2^-$  and  $\text{NO}_3^-$  on the  
389 degradation of the three EDCs was observed.

390

391



392  
 393 **Fig. 7.** Effect of chloride ions (Cl<sup>-</sup>) (A) and bicarbonate ions (HCO<sub>3</sub><sup>-</sup>) (B) on the degradation of  
 394 BPA, E2, and EE2 using  $\gamma$ -MnOOH/PMS system. Experimental conditions are: [ $\gamma$ -MnOOH] =  
 395 0.1 g L<sup>-1</sup>, [PMS] = 2 mM, [BPA] = [E2] = [EE2] = 5  $\mu$ M, pH = 6.5 (for Cl<sup>-</sup>) and pH = 8.0 (for

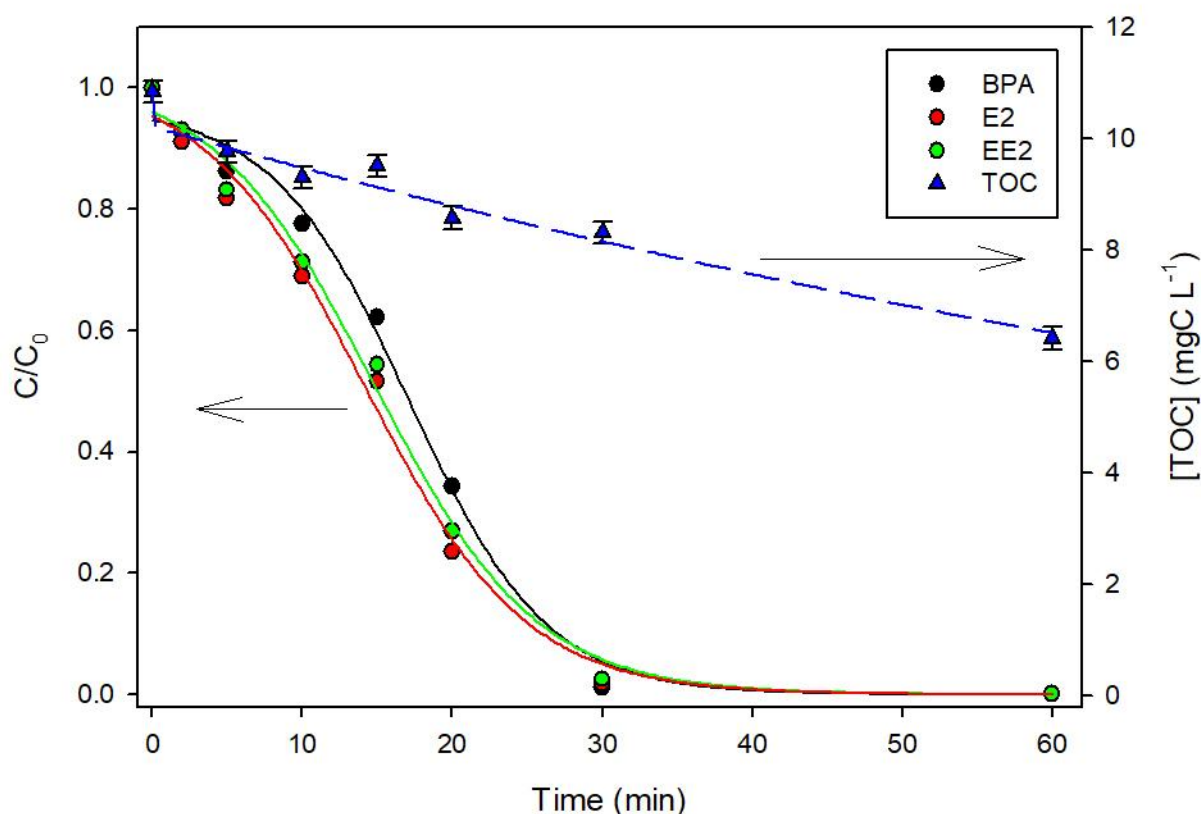


396  $\text{HCO}_3^-$ ). Error bars are determined from the  $\sigma$ -level uncertainty of the data fit used to obtain  $k'$   
397 of estrogens.

398

### 399 *3.5. Efficiency in the real water matrix*

400 To evaluate the efficiency of  $\gamma$ -MnOOH/PMS system in realistic conditions, the treatment of  
401 three EDCs in filtered sewage treatment plant water (STPW) was conducted. The initial TOC  
402 was determined to be  $10.8 \text{ mgC L}^{-1}$  (in which  $2.8 \text{ mgC L}^{-1}$  come from the addition of 3 EDCs).  
403 As expected, the removal rates and efficiencies of EDCs and TOC in STP water were slower in  
404 comparison with results in milli-Q water (Fig. 8). This effect can be attributed to the organic  
405 matter and inorganic anions present in STP water, which can compete with degradation EDCs  
406 during the  $\gamma$ -MnOOH/PMS process. It is interesting to notice that EDCs initial degradation in  
407 STP water is lower during the first 15 min and rapidly increases to almost complete removal  
408 after 35-40 min. 18 % of TOC removal was also observed after 30 min of reaction and TOC  
409 removal continues after EDCs degradation with a rate of  $0.067 \pm 0.007 \text{ mgC min}^{-1}$ .



410

411 **Fig. 8.** BPA, E2 and EE2 degradation by  $\gamma$ -MnOOH/PMS system in STPW and TOC removal.

412 Experimental conditions are:  $[\gamma\text{-MnOOH}] = 0.1 \text{ g L}^{-1}$ ,  $[\text{PMS}] = 2 \text{ mM}$ ,  $[\text{BPA}] = [\text{E2}] = [\text{EE2}] =$   
 413  $5 \mu\text{M}$ , and  $\text{pH} = 6.5$ . Error bars on TOC analysis was  $0.2 \text{ mgC L}^{-1}$ .

414

#### 415 **4. Conclusion**

416 In this work, the degradation of three estrogens: BPA, E2 and EE2 was performed using  
 417 manganite ( $\gamma\text{-MnOOH}$ ) in the presence of peroxymonosulfate ions (PMS). The rapid  
 418 degradation in water was attributed to the generation of sulfate radical and the direct oxidation  
 419 mediated by Mn(IV). In fact, about 60% of estrogens degradation was attributed to the  
 420 generation of sulfate radical, while  $\sim 40\%$  to the direct oxidation mediated by Mn(IV). The  
 421 effect of inorganic ions at environmentally relevant concentrations showed only limited  
 422 inhibition effect on EDCs degradation in ultrapure water and real sewage treatment plant water,  
 423 indicating that the  $\gamma\text{-MnOOH/PMS}$  system can be applied for real wastewater treatment. The

424 Mn(III)/(IV) cycle represents the main reaction step leading to the formation of sulfate radical  
425 but also mediated Mn(IV) species have high oxidation ability toward the removal of selected  
426 pollutants. These results have strong implications for the development of Mn-mediated  
427 oxidation processes in wastewater remediation technologies.

428

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