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1 **Efficient removal of estrogenic compounds in water by Mn^{III}-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 β -estradiol (E2) and 17 α -ethinylestradiol (EE2) by manganite (γ -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⁻¹
22 of γ -MnOOH and 2 mM of PMS. The degradation rate constants were determined to be 0.20,
23 0.22 and 0.15 min⁻¹ 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 γ -
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 γ -
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⁻¹ and complete degradation of the three
32 EDCs after 45 min. This study provides new insights into the reactivity of combined γ -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 (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 (MnO₂-AOPs), to remove pollutants, such as phenol and 2,4-
68 dichlorophenol, using MnO₂ 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 MnO₂ such as crystal structure, morphology, and surface Mn oxidation states on PMS
71 activation. They showed that the catalytic activity of MnO₂ 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 α -Mn₂O₃ (Saputra et al., 2014) and MnOOH (Xu et
75 al., 2021). He et al. demonstrated that nanowires MnOOH have higher activity on PMS
76 activation for 2,4-dichlorophenol oxidation as compared with multi-branches and nanorods
77 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 Mn^{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 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 γ -
83 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 β -
86 estradiol (E2) and 17 α -ethinylestradiol (EE2)) using γ -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 γ -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 β -estradiol (E2, 98%), 17 α -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 (NaNO_2 , 97%), sodium bicarbonate (NaHCO_3 , 99.7%), and sodium
99 chloride (NaCl , 99%) were purchased from Sigma-Aldrich Company, France. Sodium nitrate
100 (NaNO_3 , 99%) was bought from Fluka. Manganese (II) chloride (MnCl_2) was purchased from
101 Riedel-de Haen. HPLC grade acetonitrile solvent (ACN) was purchased from CARLO ERBA
102 Reagents. Sodium hydroxide (NaOH , 99.9%) and perchloric acid (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. γ -MnOOH synthesis and characterization*

110 Manganite (γ -MnOOH) particles were synthesized as described by Yu and co-workers (Yu et
111 al., 2018). The nature of γ -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 γ -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 μ M). After 1 h of reaction, the solution
117 was centrifuged and water was withdrawn and the remaining water completely removed under
118 the N₂ stream. Then, the solid particles were collected and analyzed in a UHV chamber
119 (pressure 10⁻⁷ 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[®] 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 γ -MnOOH just before the
136 reaction starts. All reactions were performed in a brown glass bottle (125 mL) at room

137 temperature (293 ± 2 K) and under stirring to ensure homogeneity. Unless otherwise stated,
138 experiments were performed at pH 6.5 ± 0.2 . For HPLC, 2 mL of solution were withdrawn at
139 fixed interval times, filtered using 0.20 μ 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 μ L and a flow rate of 1 mL min⁻¹ 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 μ 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 μ L of sample was withdrawn at different reaction times and

162 added to 5 mL of a solution containing KI (0.6 M) and HCO_3^- (0.06 M). The Abs of solution at
163 348 nm was measured after 10 min of reaction and PMS concentration (C_{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_{PMS} and V_{tot} are the volume of sample (100
165 μL) 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 Mn^{2+} in the aqueous solution. The procedure involved the filtration
169 of the samples through a 0.2 μm PTFE filter and the addition of 2% nitric acid (HNO_3 , 65%,
170 Sigma-Aldrich) before detection. Mn^{2+} standard solution for AAS (TraceCERT[®], 1000 mg L^{-1}
171 Mn in 2% nitric acid, Sigma-Aldrich) was used for making the calibration curve of 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, Burkert) using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the
175 spin trapping agents. Typically, 375 μL of sample was withdrawn and immediately mixed with
176 125 μL 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, ~ 100 kHz; microwave frequency, ~ 9.87 GHz; microwave power, ~ 6.87
179 mW; center field, ~ 352.7 mT; sweep width, 20 mT; sweep time, 30 s; sample g-factors, 2.0;
180 modulation amplitude, 1.0 G.

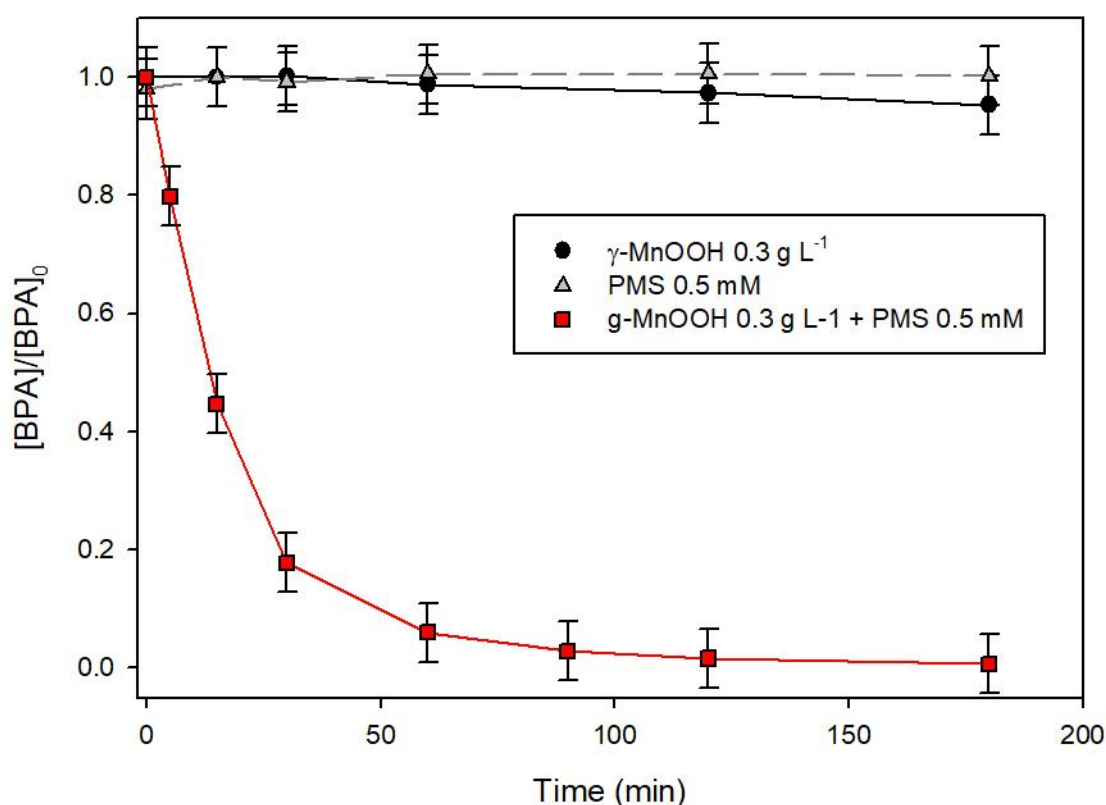
181

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 γ -
185 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**

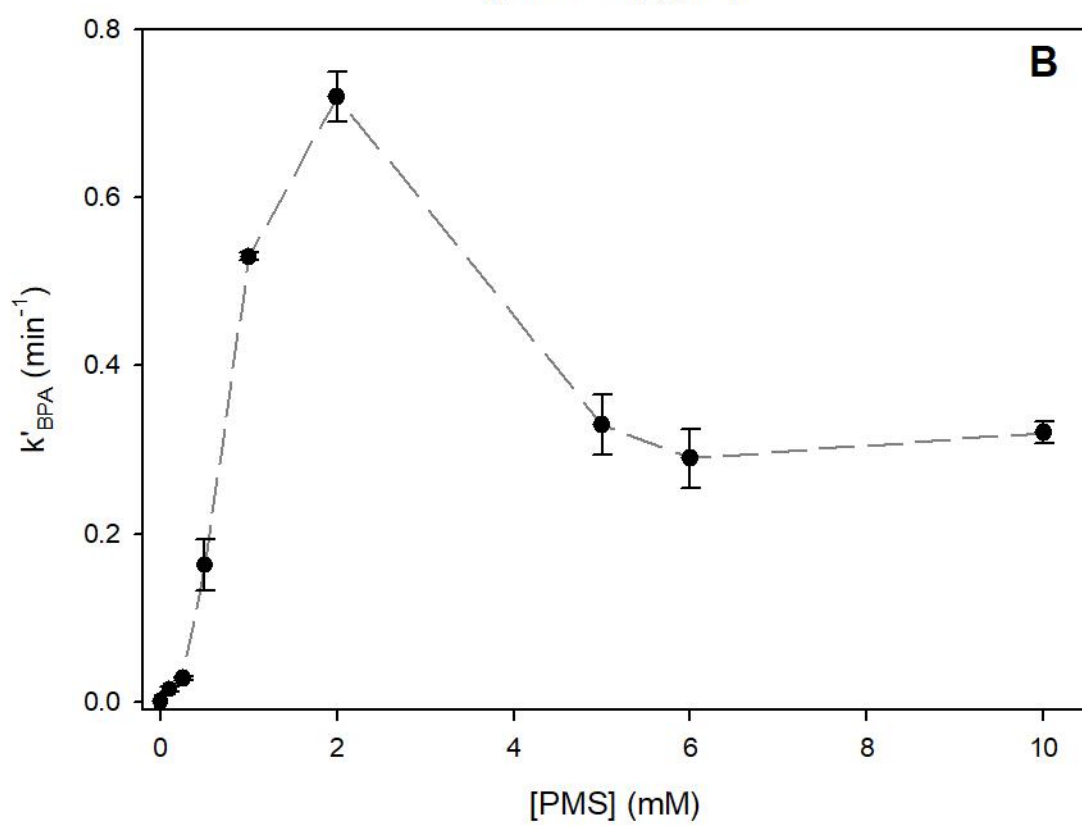
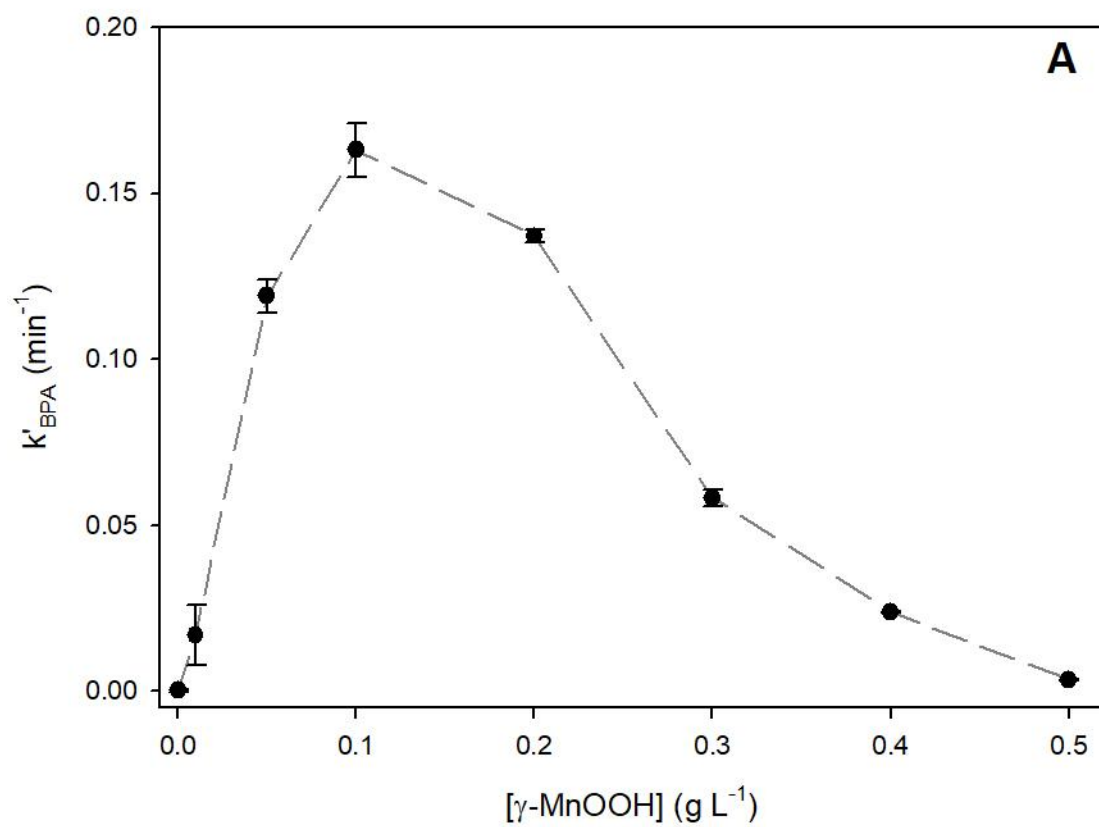
187 pseudo-first order degradation rate (k'_{BPA}) of $0.058 \pm 0.001 \text{ min}^{-1}$ showing that reactive
188 species (such as $\text{SO}_4^{\cdot-}$ and HO^{\cdot}) may be generated through the reaction between $\gamma\text{-MnOOH}$ and
189 PMS in solution. Moreover, the adsorption of BPA on $\gamma\text{-MnOOH}$ 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 g L^{-1}) and PMS (0.5
194 mM) at pH 6.5.

195
196 When various concentrations of $\gamma\text{-MnOOH}$ were used in the presence of 0.5 mM PMS (Fig.
197 2A), a different trend can be observed. Increasing the $\gamma\text{-MnOOH}$ concentration up to 0.1 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 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⁻¹ of γ -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 γ -MnOOH and PMS on the active species (Wang et al.,
208 2017; Zhang et al., 2021). Thus, an optimal concentration of γ -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 γ -MnOOH concentrations in
212 the presence of 0.5 mM of PMS (A) and in the presence of γ -MnOOH (0.1 g L⁻¹) and different
213 PMS concentrations (B). Error bars are determined from the σ -level uncertainty of the data fit
214 used to obtain k'_{BPA} .

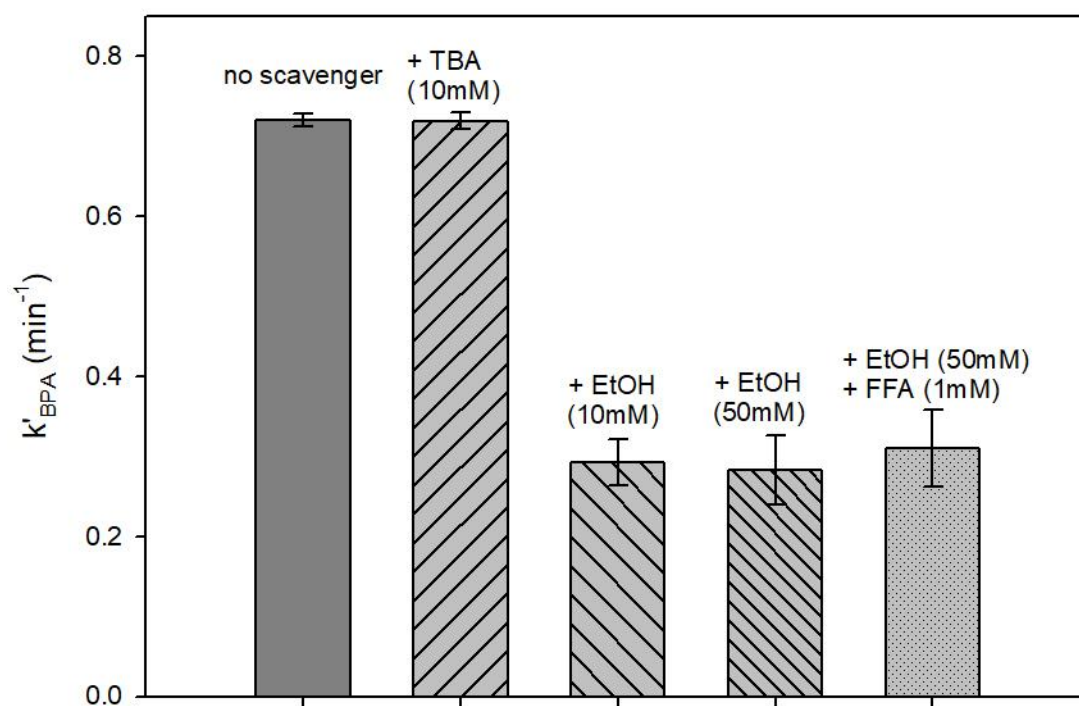
215

216 3.2. Activation pathway and reactive species formation

217 In order to verify the generation of reactive species resulted from the activation of γ -MnOOH,
218 the leaching of dissolved Mn²⁺ in γ -MnOOH/PMS system was measured, and the homogenous
219 activation of PMS by Mn²⁺ was evaluated. The total amount of leached and adsorbed Mn²⁺ was
220 determined at around 34 μ M after 30 min of reaction. However, a high amount of dissolved
221 Mn²⁺ (100 μ 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 γ -MnOOH.

224 To identify the reactive species generated in the γ -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[•] scavenger due
227 to its higher selectivity toward HO[•] ($k_{TBA,HO^{\bullet}} = 6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) compared to SO₄^{•-} ($k_{TBA,SO_4^{\bullet-}} = 8.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) (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[•] ($k_{PMS,HO^{\bullet}} = 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ 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[•] was generated in the
232 system (Fig. 3). Comparatively, using 10 mM of EtOH can efficiently quench both HO[•] and
233 SO₄^{•-} 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⁻¹)
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 HSO_5^- , HO^{\bullet} and $\text{SO}_4^{\bullet-}$ radicals. Since no HO^{\bullet} was generated in the reaction, and 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 HO^{\bullet} ($k_{\text{FFA}, \text{HO}^{\bullet}} = 1.5 \times 10^{10} \text{ M}^{-1}$
255 s^{-1}) (Yang et al., 2018), the simultaneous addition of FFA and EtOH was planned to consume
256 all the possible 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'_{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 σ -level
 263 uncertainty of the data fit used to obtain k'_{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. Mn^{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.,

274 1998; Ilton et al., 2016). The peak position and relevant parameters from curve fitting of Mn 3s
275 and Mn 2p_{3/2} high resolution spectra are listed in Table 1. The average oxidation state (AOS) of
276 samples was calculated from the % of each Mn species from the fitting of Mn 2p_{3/2} spectra and
277 from the binding energy difference of Mn 3s doublet splitting as following: $AOS = 8.956 -$
278 $1.126 \times \Delta E$ [25,26]. Using the multiplets fitting of the Mn 2p_{3/2} peaks, the percent contents of
279 Mn(IV), Mn(III) and Mn(II) in the γ -MnOOH sample were 7%, 85% and 8%, respectively and
280 AOS was 2.99. After reaction with PMS, the relative contents of Mn(IV), Mn(III) and Mn(II)
281 changed and Mn(IV) percentage increased to 24.5 consistently with an increase of AOS up to
282 3.10. In the sample γ -MnOOH + PMS + BPA, Mn(II) percentage increased to 37% while
283 Mn(IV) decreased to 9% with a decrease of AOS down to 2.72. AOS values were consistent
284 with those determined from the fitting of Mn 3s multiplet splitting data (Table 1). The increase
285 of Mn(IV) in the presence of PMS followed by a decrease when BPA was present in solution,
286 suggests that freshly generated Mn(IV) may contribute to the degradation of BPA. Such a
287 process, called metal-based oxidation, was previously indicated as relevant surface-mediated
288 oxidation of organic pollutants in the presence of Mn(IV) oxides (Kamagate et al., 2020).
289 Huang et al. demonstrated the efficient oxidation of BPA by MnO₂ with different structures
290 such as α -, β -, γ -, δ -MnO₂ with and without PMS (Huang et al., 2019; J. Huang et al., 2018).
291 Wang et al. reported the removal of BPA was due to a complex between amorphous MnO₂ and
292 PMS (Wang et al., 2018).

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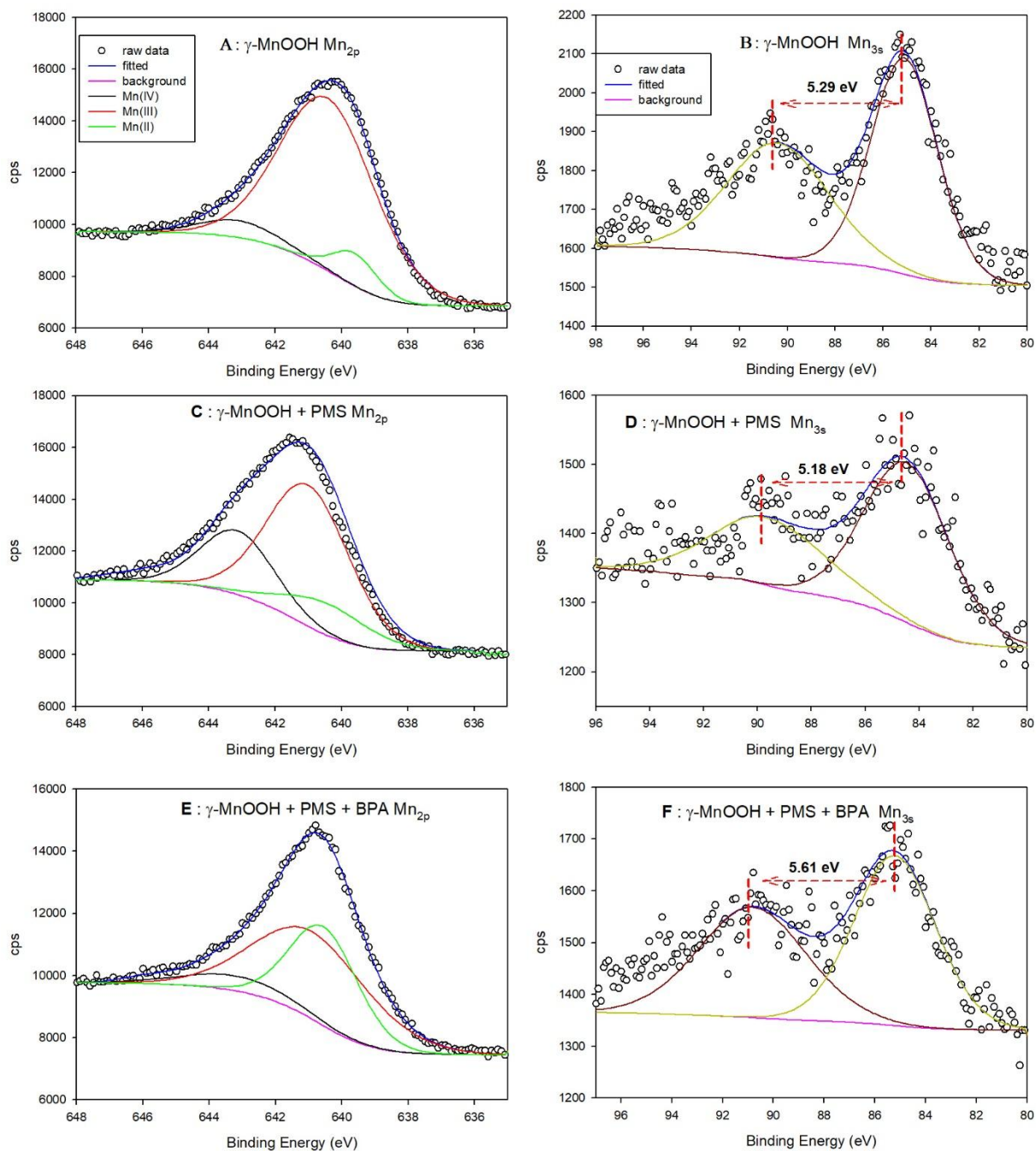
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302 **Fig. 4.** XPS Mn 2p and Mn 3s spectra of γ -MnOOH (A and B), γ -MnOOH + PMS (C and D)
 303 and γ -MnOOH + PMS + BPA (E and F) Initial conditions are [BPA] = 5 μ M, [γ -MnOOH] =
 304 0.1 g L⁻¹ and [PMS] = 2 mM at pH 6.5.

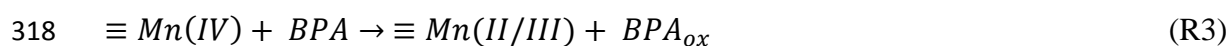
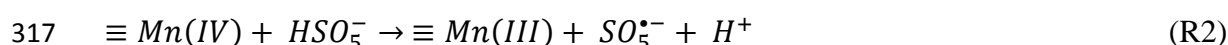
305

306 **Table 1.** Parameters from curve fitting of Mn 3s and Mn 2p_{3/2} XPS spectra and average
 307 oxidation state.

Sample		γ -MnOOH	γ -MnOOH+PMS	γ -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
		AOS	2.99	3.10	2.72
	Mn 3s	Multiplet Splitting (eV)	5.29	5.18	5.61
		AOS	3.00	3.12	2.64

308

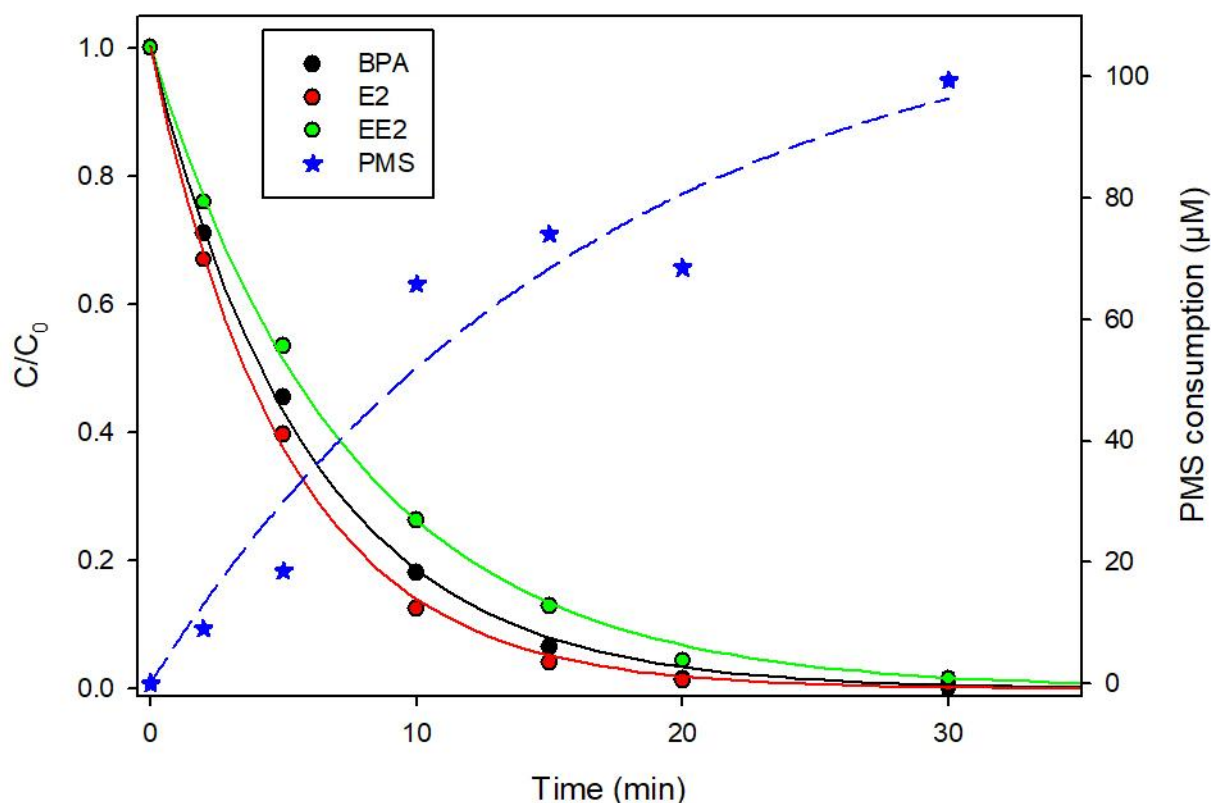
309 Collectively, quenching experiments and XPS analysis suggest that the first electron transfer
 310 reaction occurring between $\equiv\text{Mn(III)}$ and PMS on the surface of oxide led to the formation of
 311 $\equiv\text{Mn(IV)}$ and $\text{SO}_4^{\bullet-}$ (R1). $\text{SO}_4^{\bullet-}$ can oxidize 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 γ -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 μ M each) and
325 PMS (2 mM) consumption were followed during the reaction time in the presence of γ -
326 MnOOH (0.1 g L⁻¹). Despite no degradation in the presence of γ -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 μ M of PMS were consumed. We
330 can then estimate an efficiency of degradation system considering the stoichiometric efficiency
331 value (η) that is calculated as the ratio between degraded EDCs vs consumed PMS (η
332 = $\frac{\Delta[EDCs]}{\Delta[PMS]}$). In the presence of 0.1 g L⁻¹ γ -MnOOH and 2 mM of PMS a value of $\eta = 15\%$ was
333 determined at pH 6.5.



334

335

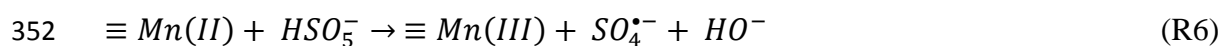
336

337 **Fig. 5.** Degradation of BPA, E2 and EE2 in the system γ -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 $[\text{BPA}] = [\text{E2}] = [\text{EE2}] = 5 \mu\text{M}$, $[\gamma$ -
 340 MnOOH] = 0.1 g L^{-1} and $[\text{PMS}] = 2 \text{ mM}$ at pH 6.5.

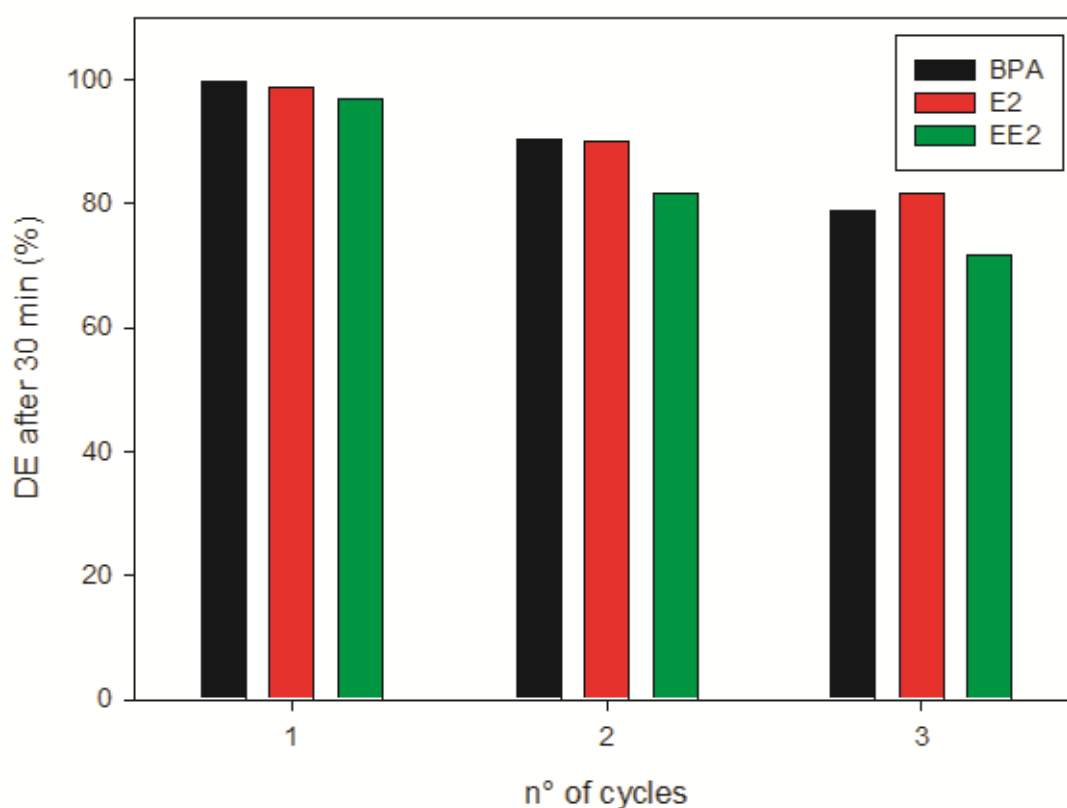
341

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

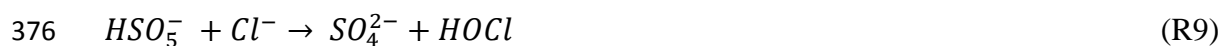
357

358 3.4. Effect of inorganic ions

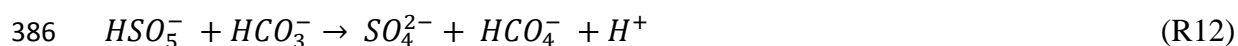
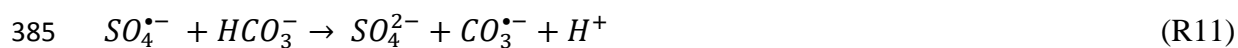
359 Inorganic anions are commonly detected in natural waters and they could affect the radical-
360 mediated degradation efficiency of organic pollutants. In the γ -MnOOH / PMS system, the
361 effect of chloride (Cl^-), bicarbonate (HCO_3^-), nitrite (NO_2^-) and nitrate (NO_3^-) anions was

362 investigated and BPA, E2, and EE2 degradations were followed using 0.1 g L⁻¹ of γ -MnOOH
363 and 2 mM of PMS.

364 As illustrated in Fig. 7A, increasing the concentration of Cl⁻ from 0 to 5 mM, the BPA, E2, and
365 EE2 degradation rates slightly increased indicating a positive effect of Cl⁻ 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⁻ was attributed to the generation
368 of reactive chlorine species such as Cl[•] and HOCl (R7 to R9) (Wang and Wang, 2021). In fact,
369 despite a different reactivity constant between Cl[•] and Cl₂^{•-} 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⁻ concentration in absence of γ -MnOOH (R9) (Fig. S6)
373 (Lente et al., 2009).



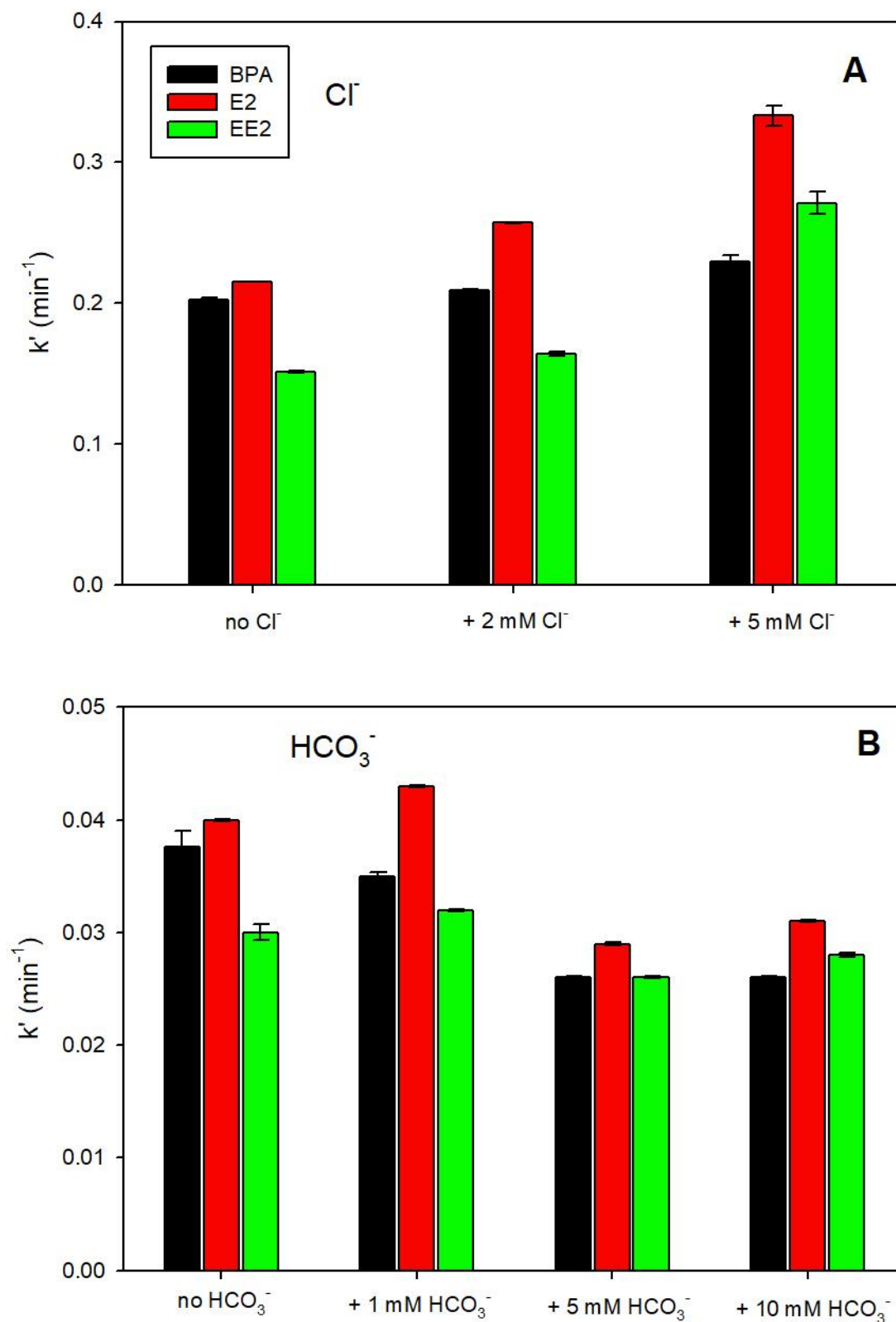
377 Bicarbonate ions (HCO₃⁻) are generally considered as interfering species during oxidative
378 processes based on radical species generation due to their reactivity with radicals and
379 generation of less oxidative species such as CO₃^{•-} (Buxton et al., 1988; Clifton and Huie, 1989).
380 However, a negligible impact on the EDCs degradation was observed with the addition of
381 HCO₃⁻ (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 HCO₃⁻ by
383 PMS leading to the formation of HCO₄⁻ as reported in Fig. S7 (R12) (Wang and Wang, 2021).



387 The effect of nitrogen anions (NO_2^- and NO_3^-) on BPA, E2 and EE2 degradation were
388 investigated, individually. As shown in Fig. S8, no effect of both NO_2^- and NO_3^- on the
389 degradation of the three EDCs was observed.

390

391



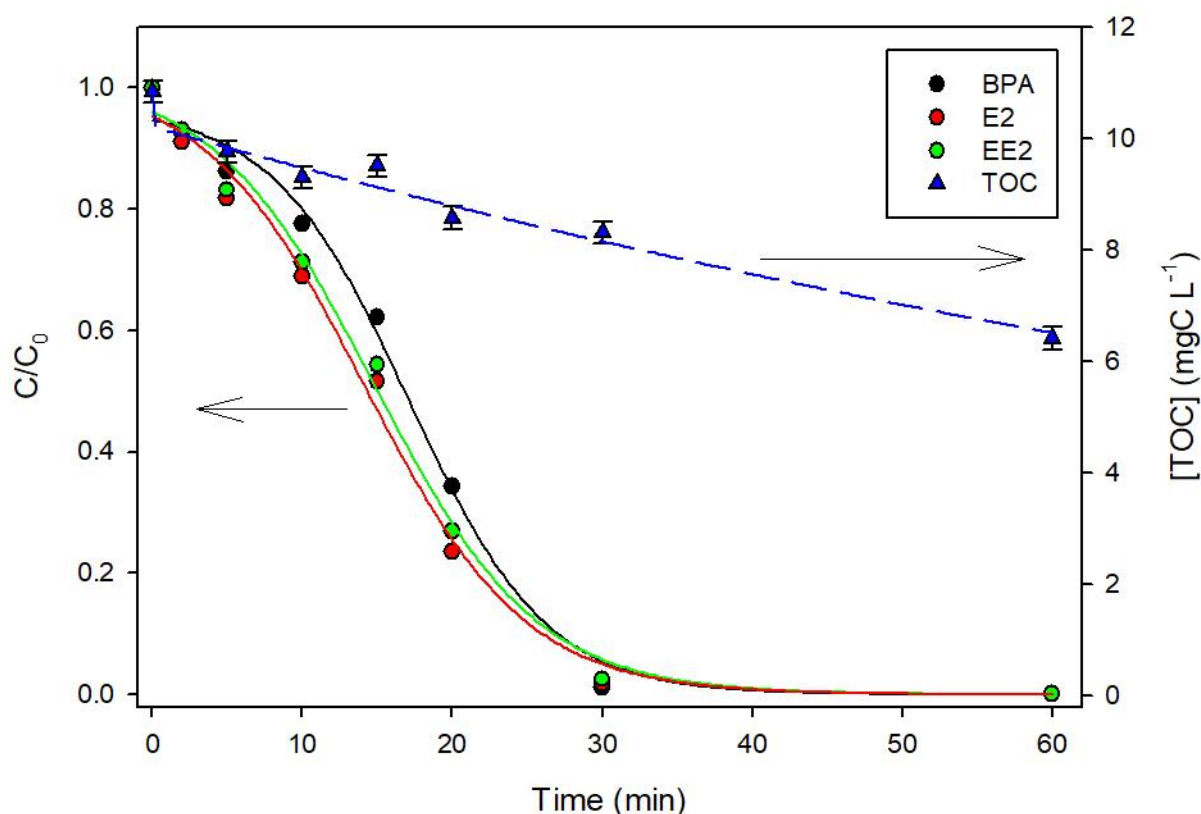
392
 393 **Fig. 7.** Effect of chloride ions (Cl⁻) (A) and bicarbonate ions (HCO₃⁻) (B) on the degradation of
 394 BPA, E2, and EE2 using γ -MnOOH/PMS system. Experimental conditions are: [γ -MnOOH] =
 395 0.1 g L⁻¹, [PMS] = 2 mM, [BPA] = [E2] = [EE2] = 5 μ M, pH = 6.5 (for Cl⁻) and pH = 8.0 (for

396 HCO_3^-). Error bars are determined from the σ -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 γ -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 mgC L^{-1} (in which 2.8 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 γ -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 γ -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 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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