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1 **Caffeine degradation using peroxydisulfate and peroxymonosulfate in the**
2 **presence of Mn₂O₃. Efficiency, reactive species formation and application in**
3 **sewage treatment plant water**

4
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18 **Abstract**

19 The crucial role of manganese(III) species in the oxidative and catalytic reactivity of
20 manganese oxides have been widely reported. However, the direct activation of radical
21 precursors by Mn(III) oxides is still a matter of discussion. In this work, the ability of
22 Mn(III)-bearing oxide (Mn_2O_3) for activation of peroxydisulfate (PS) and peroxymonosulfate
23 (PMS) was evaluated and compared using caffeine (CAF) as a model pollutant. Complete
24 CAF removal was achieved with 5 mM of PS or PMS after 8 h of reaction time, whereas 48%
25 of mineralization was obtained after 70 h of reaction when PMS was used as oxidant. Electron
26 paramagnetic resonance spin trapping (EPR) and radical scavenging experiments showed that
27 the sulfate radical ($\text{SO}_4^{\cdot-}$) was the dominant radical in the Mn_2O_3 /PMS system. In
28 comparison, a non-radical mechanism such as Mn_2O_3 surface-activated PS promoted the
29 removal of CAF in the system of Mn_2O_3 /PS. Liquid chromatography coupled to mass
30 spectrometry analyses enabled the detection of main degradation products and the proposition
31 of the CAF degradation pathways. Investigations in the real sewage treatment plant water
32 showed that the decrease of CAF removal observed in wastewater as compared to pure water
33 can be alleviated by increasing the Mn_2O_3 dosage. These findings highlight the great ability of
34 Mn-species in PS or PMS activation in different water matrices, which have important
35 implications for the development of novel wastewater treatment technologies.

36

37 **Keywords:** AOPs; Caffeine; Mn_2O_3 ; Peroxymonosulfate; Peroxydisulfate; Wastewater

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44 **1. Introduction**

45 Advanced oxidation processes (AOPs) constitute a promising technology for the
46 remediation of environmental compartments (Miklos et al., 2018). AOPs are efficient in the
47 removal of harmful and persistent organic pollutants in water due to the generation of strongly
48 reactive species (Deng and Zhao, 2015). Hydroxyl radical (HO^\bullet) belongs to the reactive
49 oxygen species (ROS) and has a high oxidation potential ($E^0 = 2.73 \text{ V vs NHE}$ (Normal
50 Hydrogen Electrode)) (W. Dong et al., 2019). Similarly, the reactive sulfur species (RSS)
51 such as sulfate radical ($\text{SO}_4^{\bullet-}$) ($E^0 = 2.6 \text{ V vs NHE}$) have also caught the attention of the
52 scientific community due to their efficient oxidation abilities (Sbardella et al., 2020).
53 Generation of ROS and RSS is usually performed through the activation of radical precursors
54 by the catalytic processes, such as direct photolysis (Gabet et al., 2021), homogeneous metal
55 ions activation (Jin et al., 2019), and heterogeneous metal oxides catalysis (Yin et al., 2018).
56 The metal oxides-based heterogeneous AOPs represent one of the most investigated strategies
57 for organic pollutants removal in the laboratory and pilot scales (Jia et al., 2018). Among
58 various metal oxides, iron oxides are by far the most studied metal oxides for reactive radicals
59 generation in water (Pi et al., 2019). However, other metal oxides such as manganese oxides
60 (MnO_x) are gaining stronger interests due to their versatile oxidation states (II, III, IV, and
61 VII) (Zhong and Zhang, 2019).

62 Among the different MnO_x , manganese dioxide (MnO_2) has attracted increasing attention
63 due to its good oxidative and catalytic performance for the elimination of pollutants
64 (Kamagate et al., 2020). For instance, Zhou et al. indicated the efficient degradation of 4-
65 nitrophenol by α - and δ - MnO_2 activated PMS through the generation of $\text{SO}_4^{\bullet-}$ and HO^\bullet (Zhou
66 et al., 2019). Zhu et al. demonstrated the rapid removal of bisphenol A (BPA) in the β -
67 MnO_2 /PS system due to the formation of singlet oxygen ($^1\text{O}_2$) (Zhu et al., 2019). Moreover,
68 the influence factors for the good catalytic and oxidative performance of various MnO_2 were

69 investigated by Huang et al., and the results showed that the efficient oxidation of pollutants
70 by MnO_2 with or without oxidants was attributed to the occurrence of Mn(III) on the surface
71 of MnO_2 (Huang et al., 2019, p. 2, 2018). Therefore, it is believed that the presence of Mn(III)
72 species in MnO_x can improve the activation efficiency of PS/PMS. Given the above, the
73 direct activation of PS/PMS by Mn(III) oxides was investigated by previous studies. For
74 example, Xu et al. reported the efficient elimination of p-chloroaniline in the γ - MnOOH /PS
75 system through the formation of active intermediates between γ - MnOOH and PS (Xu et al.,
76 2021). Wang et al. indicated the good reactivity of octahedral Mn_3O_4 on PMS activation for
77 ciprofloxacin degradation due to the presence of high contents of Mn(III), Mn(IV) and
78 hydroxyl groups (-OH) (Wang et al., 2021). Moreover, the degradation of organic pollutants
79 by PMS using synthesized Mn_2O_3 as the catalyst was also reported. For instance, Saputra et
80 al. indicated that Mn_2O_3 compared with MnO , Mn_3O_4 , MnO_2 showed the highest reactivity in
81 PMS activation for phenol degradation due to the formation of both $\text{SO}_4^{\bullet-}$ and $\text{SO}_5^{\bullet-}$ radicals
82 (Saputra et al., 2013). The effect of Mn_2O_3 structures on PMS activation was also investigated
83 by Saputra et al., and the results showed cubic- Mn_2O_3 has higher PMS catalysis efficiency
84 due to its high surface area and surface atoms arrangement (Saputra et al., 2014). These
85 experiments demonstrated well the effect of Mn oxidation states and catalyst structures on the
86 activation of PMS. However, the catalytic mechanism of Mn_2O_3 on PMS is not clear, and
87 some important influence factors for the reactivity of Mn_2O_3 such as solution pH were not
88 investigated. Furthermore, Khan et al. investigated the activation of PS using synthesized
89 Mn_2O_3 and MnO_2 for the degradation of phenol in solution (Khan et al., 2021). The results
90 showed that phenol was efficiently removed in A- Mn_2O_3 /PS system due to the generation of
91 singlet oxygen ($^1\text{O}_2$). Although the authors adopted different experimental methods to identify
92 the generated reactive species and investigated various influence parameters for the reactivity
93 of A- Mn_2O_3 /PS system, it should be noted that the experiments were conducted in the acidic
94 environment (pH~3.2). Moreover, since different reactive species were generated in γ -

95 MnOOH/PS system under different solution pH (Li et al., 2016), thus it is reasonable to
96 deduce that the type of generated reactive species in the Mn₂O₃/PS system can be influenced
97 by solution pH. However, the authors only studied the generated reactive species in the acidic
98 solution. Therefore, it is meaningful to investigate the mechanism of PS/PMS activation by
99 Mn₂O₃ in the near-neutral solution and evaluate the suitability of the Mn₂O₃ activated
100 PS/PMS system in real polluted waters. Caffeine (CAF) was used as a model of organic
101 contaminants since its adverse effects on aquatic organisms and human beings (Buerge et al.,
102 2003). Moreover, CAF as the emerging contaminant has been widely detected in different
103 water matrices at concentrations ranging from ng/L to µg/L (Li et al., 2020).

104 In this work, we investigated and compared the ability of Mn₂O₃ to activate PS and PMS
105 under different experimental conditions, i.e. pH, Mn₂O₃ dosage, and radical precursor
106 concentrations. Reactive radical species and non-radical pathways were identified and their
107 contribution to the pollutant removal was quantified using chemical scavenging experiments,
108 electron paramagnetic resonance spectroscopy (EPR) and X-ray photoelectron spectroscopy
109 (XPS). Moreover, the CAF degradation pathway, main degradation products and
110 mineralization efficiency were reported. Finally, the ability of both systems was compared in
111 real sewage treatment plant water, where 80 % of CAF degradation was obtained by the
112 proposed method after 20 hours.

113

114

115 **2. Materials and Methods**

116 **2.1. Chemicals**

117 All chemicals were reagent-grade (see Text S1 in Supplementary Materials) and used as
118 received. Ultrapure water (Millipore, resistivity 18.2 MΩ cm) was used in the preparation of
119 all solutions.

120

121 **2.2. Catalyst characterization**

122 The purity of the used Mn_2O_3 sample (Sigma-Aldrich) was confirmed by powder X-ray
123 diffraction (XRD) (Fig. S1). The average oxidation state (AOS) of Mn after reaction was
124 obtained using X-ray photoelectron spectroscopy (XPS). The analysis conditions of XRD and
125 XPS were presented in Text S2.

126

127 **2.3. Experimental procedures**

128 The chemical reactions were performed in a borosilicate brown bottle in which 100 mL of
129 solution was kept at room temperature (298 ± 2 K) under stirring (700 rpm) to ensure
130 homogeneity. 25 μM of CAF was added to the 100 mL reaction solution containing a certain
131 concentration of Mn_2O_3 , then a predetermined amount of oxidants (*i.e.* H_2O_2 , PS, PMS, and
132 HSO_3^-) was added to start the reaction. The solution pH was fixed by adding 0.1 M sodium
133 hydroxide and perchloric acid. 2 mL of samples were withdrawn at the predetermined interval
134 times and were filtered (0.20 μm PTFE filter) to remove Mn_2O_3 particles. The reaction was
135 stopped by the addition of 100 μL of methanol (HPLC grade, Sigma-Aldrich) and then the
136 samples were analyzed by HPLC.

137 To determine the involvement of reactive radical species leading to the degradation of
138 CAF, a kinetic competition study was performed using different radical scavengers such as
139 *tert*-butanol (TBA) and 2-Propanol (2-Pr) to quench hydroxyl radical (HO^\bullet) and sulfate
140 radical ($\text{SO}_4^{\bullet-}$) (Buxton et al., 1988; Clifton and Huie, 1989). Furfuryl alcohol (FFA) was used
141 to trap singlet oxygen ($^1\text{O}_2$) (Appiani et al., 2017). The contribution of main radical species to
142 the degradation of CAF was estimated considering the second-order rate constants between
143 the selected radicals and quenchers or CAF (see Table S1). The quenching efficiency was
144 determined as $C_1 \times k_1 / (C_1 \times k_1 + C_2 \times k_2)$. Where C_1 was the initial concentration of organic

145 scavengers and k_1 was the second-order rate constant with selected oxidant species (i.e. HO^\bullet ,
146 $\text{SO}_4^{\bullet-}$, or $^1\text{O}_2$), C_2 and k_2 were the concentration of CAF and reactivity constant with the
147 oxidant species.

148 Sewage treatment plant water (STPW) was collected in December 2019 from the urban
149 treatment plant named “3 rivières” in Clermont-Ferrand and used after 0.45 μm filtration
150 using PTFE filter. The main physicochemical characteristics are reported in Table S2.

151

152 **2.4. Chemical analysis and kinetics**

153 CAF concentration was determined by a high-performance liquid chromatography system
154 (HPLC, Alliance 2695 Waters) equipped with a photodiode array detector (DAD) and C18
155 column (Agilent Eclipse XDB, 250×4.6 mm, 5 μm of particle size). The mobile phase was a
156 mixture of acetonitrile (ACN) and milli-q water acidified with 0.1 % phosphoric acid in
157 gradient eluent mode ($V_{\text{ACN}} / V_{\text{water}}$ from 20/80 to 70/30 in 6 min). The flow rate was set at
158 0.8 mL min^{-1} and the detection wavelength of CAF was fixed at 272 nm. The pseudo-first-
159 order rate constant of CAF (k'_{CAF}) was determined from the slope of $\ln(C/C_0)$ vs time plot,
160 where C_0 and C are the concentration of CAF at time 0 and t respectively. The error bars
161 associated to the degradation constant data represent 3σ , derived from the scattering of the
162 experimental data around the fit curves (intra-series variability).

163 To investigate the mineralization of CAF, total organic carbon (TOC) analysis (TOC-L
164 CPH CN200, SHIMADZU) was performed.

165 PS and PMS concentrations were measured using a modified spectrophotometric method
166 (Wacławek et al., 2015). Briefly, 100 μL of PS or PMS sample was first transferred into 5 mL
167 of the mixture of potassium iodide (KI, Sigma-Aldrich) and sodium bicarbonate (NaHCO_3 ,
168 Sigma-Aldrich) to generate iodine (I_2). Then, I_2 further reacted with iodide (I^-) leading to the

169 formation of complex (I_3^-). Finally, I_3^- was detected using a Varian Cary 3 UV-visible
170 spectrophotometer (Abs at 351 nm) and quantified using a calibration curve.

171 The identification of radicals was performed by electron paramagnetic resonance
172 spectroscopy (EPR). The X-band cw-EPR spectra (modulation frequency of 100 kHz) were
173 monitored at 293 K with the *EMXplus* spectrometer (Bruker) equipped with the High
174 Sensitivity Probe-head (Bruker) in the small quartz flat cell (Wilmad-LabGlass, WG 808-Q)
175 using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO, Sigma-Aldrich) and 2,2,6,6-tetramethyl-4-
176 piperidinol (TEMP, Sigma-Aldrich) as the spin trapping agents. Typically, 375 μ L of sample
177 was withdrawn and immediately mixed with 125 μ L of DMPO (100 mM) or TEMP (100
178 mM), then the mixture was transferred into an EPR quartz capillary tube (0.5 mm, 100 mm)
179 for measurement. The EPR spectrometer settings were as follows: microwave frequency, ~
180 9.87 GHz; microwave power, ~6.87 mW; center field, ~352.7 mT; sweep width, 20 mT;
181 sweep time, 30 s; sample *g*-factors, 2.0; modulation amplitude, 1.0 G. The experimental EPR
182 spectra were analyzed by the WinEPR software (Bruker) and the calculations of spin-
183 Hamiltonian parameters and relative concentrations of individual DMPO-adducts were
184 performed with the EasySpin toolbox working on MatLab[®] platform (Stoll and Schweiger,
185 2006).

186 The identification of CAF transformation intermediates was obtained by an LC-MS
187 system coupled with an ESI ion source (MSD VL). The column was a Phenomenex Kinetex
188 C18 column (2.6 μ m \times 100 \AA ; 100 \times 2.1 mm) using an initial gradient of 5% ACN and 95%
189 water acidified with 1% formic acid (Sigma-Aldrich), followed by a linear gradient to 95%
190 ACN within 15 min and kept constant during 10 min. The flow rate was 0.2 mL min⁻¹ and the
191 injection volume of 10 μ L.

192

193 **3. Results and discussion**

194 3.1. Reactivity of Mn₂O₃ with PS and PMS

195 The reactivity of Mn₂O₃ with different radical precursors (i.e. H₂O₂, PS, PMS, and HSO₃⁻)
196 was investigated. As shown in Fig. 1, the CAF degradation was observed only in the Mn₂O₃
197 activated PS and PMS (5 mM) systems. Up to 40% of removal extent was observed after 3 h
198 of reaction time in the unbuffered solutions. Although the solution pH dropped to 5.5 ± 0.2
199 and 2.7 ± 0.2 with the addition of PS and PMS, the purpose of checking the reactivity of
200 Mn₂O₃ with PS and PMS was achieved (Table S3). Moreover, blank and adsorption tests
201 showed that CAF removal by adsorption on Mn₂O₃ or direct oxidation by radical precursors
202 was negligible whatever the investigated pH (Fig. S2 and S3). The formation of radical
203 species and their relative contribution to the CAF degradation were determined by chemical
204 scavenging and EPR experiments. Before starting the scavenging tests, suitable
205 concentrations of scavengers were determined through the calculation of scavenging
206 efficiency with reactive oxygen species (ROS). As shown in Table S4, in the presence of 10
207 mM of TBA, 10 mM of 2-Pr and 1 mM of FFA, a scavenging efficiency of 97.4, 93.2 and
208 99.4 % of the corresponding ROS was achieved. Thus, the proposed scavenger concentration
209 was enough to inhibit almost the whole radical reactions. In addition, to verify if the
210 degradation of CAF was originated from the heterogeneous reaction between PS/PMS and
211 Mn₂O₃, the leaching of Mn²⁺ in Mn₂O₃ activated PS/PMS reactions and the homogeneous
212 activation of PS/PMS by Mn²⁺ were studied. As shown in Fig. S4. A negligible Mn²⁺
213 concentration (~ 1 μM) was determined when 0.4 g L⁻¹ of Mn₂O₃ was suspended in solution.
214 Moreover, the degradation efficiency of CAF in the Mn²⁺ activated PS/PMS system was far
215 lower than Mn₂O₃, even the employed concentration of Mn²⁺ was 10-1000 times higher than
216 leached Mn²⁺. Thus, the removal of CAF was attributed to the activation of PS/PMS by
217 Mn₂O₃.

218

219 3.1.1 Reactivity of Mn₂O₃ with PS

220 In the system of Mn₂O₃/PS, only a negligible effect of TBA and 2-Pr was observed
221 indicating that HO[•] and SO₄^{•-} were not the main radical species involving in the CAF
222 degradation (Fig. 2A). However, in the presence of 1 mM of FFA, the CAF degradation
223 constant (k'_{CAF}) dropped from $2.4 \times 10^{-3} \text{ min}^{-1}$ to $2.6 \times 10^{-5} \text{ min}^{-1}$, corresponding to 99% of
224 inhibition after 8 h (Fig. S5). The inhibition of CAF degradation in the presence of FFA can
225 be due to the quenching of ¹O₂. To identify whether ¹O₂ was generated in the Mn₂O₃/PS
226 system, the EPR experiments were conducted using TEMP as the spin trapping agent and no
227 signal corresponding to the formation of TEMPO was observed (Fig. S6), thus indicating the
228 inhibition of CAF degradation by FFA was not related to the scavenging of ¹O₂. Other reasons
229 can explain the inhibition of CAF by FFA, such as the scavenging of HO[•], the increased PS
230 consumption, and the occupied reactive sites on the Mn₂O₃ surface (Appiani et al., 2017; Xu
231 et al., 2021; Yang et al., 2018)). The scavenging of HO[•] was excluded since CAF degradation
232 was not inhibited in the presence of TBA (Fig. 2A) while CAF removal was completely
233 suppressed after the simultaneous addition of 2-Pr and FFA (Fig. S7). Moreover, the PS
234 decomposition due to the reactivity with FFA was negligible (Fig. S8) compared to the
235 reactivity in the presence of PMS (Yang et al., 2018). Therefore, the inhibition of CAF
236 degradation in presence of FFA was attributed to the adsorption of FFA on the surface of
237 Mn₂O₃ and competing with PS ions for the active sites. The results are in agreement with
238 previous studies which reported FFA can affect the surface properties of catalysts (Guan et
239 al., 2017; Xu et al., 2021).

240 Therefore, a non-radical mechanism of PS activation is proposed and it generally
241 includes the generation of ¹O₂ (as mentioned just above, this hypothesis is excluded), the
242 surface-activated PS species, or the electron transfer process (Ding et al., 2020). It is worth
243 noting that the electron transfer mechanism in PS activation usually happens when carbon-
244 based materials were used as catalysts (Lee et al., 2015). Therefore, the removal of CAF in

245 the $\text{Mn}_2\text{O}_3/\text{PS}$ system was attributed to the formation of Mn_2O_3 surface-activated PS. The
246 result is in agreement with previous studies which indicated $^1\text{O}_2$ was not generated but the
247 active intermediates formed between PS and catalyst were responsible for the degradation of
248 pollutants (Li et al., 2016; Xu et al., 2021).

249 To better understand the role of PS, the concentration of PS in different systems was
250 monitored (Fig. 2B). The depletion of PS by CAF alone was negligible, whereas a small
251 amount of PS was consumed by Mn_2O_3 in the absence of CAF. This result indicates that PS
252 was absorbed on the active sites present on the surface of Mn_2O_3 . CAF as an electron donor
253 leads to the increased consumption of activated PS since in the $\text{Mn}_2\text{O}_3/\text{PS}$ system the
254 depletion of PS was enhanced. Moreover, the decrease trend of PS was close to that of CAF.

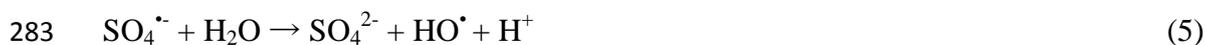
255 The non-radical mechanism of PS activation was further verified through the
256 measurement of the Mn oxidation state in the $\text{Mn}_2\text{O}_3/\text{PS}$ system. The average oxidation state
257 (AOS) of samples was calculated from the binding energy difference (ΔE) of Mn 3s doublet
258 splitting as following: $\text{AOS} = 8.956 - 1.126 \times \Delta E$ (W. Yang et al., 2020). Fig. S9 shows that
259 the AOS of Mn_2O_3 did not change after reaction with PS (AOS ~ 3.00), indicating the
260 activation of PS by Mn_2O_3 was a non-radical catalytic process.

261

262 3.1.2 Reactivity of Mn_2O_3 with PMS

263 In the PMS-containing system, the presence of TBA and 2-Pr decreased the k'_{CAF} from
264 $6.5 \times 10^{-3} \text{ min}^{-1}$ to $4.0 \times 10^{-3} \text{ min}^{-1}$ and $7.0 \times 10^{-4} \text{ min}^{-1}$, respectively (Fig. 3A and Fig. S10)
265 indicating the predominant role of $\text{SO}_4^{\cdot-}$ compared to HO^{\cdot} . PMS can react with both $\equiv\text{Mn}^{\text{III}}$
266 (Eq. 1) and $\equiv\text{Mn}^{\text{IV}}$ (Eq. 2) leading to the formation of $\text{SO}_4^{\cdot-}$ and $\text{SO}_5^{\cdot-}$ (He et al., 2020).
267 Moreover, $\text{SO}_5^{\cdot-}$ self-reaction in water can lead to the formation of $\text{SO}_4^{\cdot-}$ (Eq. 3) (Yermakov et
268 al., 1993). Formation of HO^{\cdot} occurs through $\text{SO}_4^{\cdot-}$ reaction with water and hydroxide,
269 although the latter reaction is only relevant in alkaline solution (Eqs. 4 and 5) (Hayon et al.,

1972). The generation of $\text{SO}_4^{\cdot-}$ and HO^{\cdot} was further identified by EPR experiments. As shown in Fig. 3B, the EPR spectrum represents a superposition of two individual signals (according to the results of the best simulation fit), including the nine-line signal of 5,5-dimethyl-2-oxo-pyrroline-1-oxyl ($\cdot\text{DMPO-X}$) with the characteristic spin-Hamiltonian parameters ($a_N = 0.732$ mT, $a_H^\gamma(2H) = 0.406$ mT; $g = 2.0070 \pm 0.0001$), which is often produced by over-oxidation of DMPO in the presence of reactive oxygen species (*e.g.* HO^{\cdot} or $^1\text{O}_2$) (Fontmorin et al., 2016). The second signal is characterized by the hyperfine coupling constants ($a_N = 1.373$ mT, $a_H^\beta = 1.019$ mT, $a_H^\gamma = 0.135$ mT, $a_H^\delta = 0.073$ mT), which correlate well with $\cdot\text{DMPO-SO}_4^-$ spin-adduct with limited stability in aqueous media (Buettner, 1987).



Since the addition of FFA exhibited a strong inhibition effect ($\sim 85\%$) on CAF degradation (Fig. S11A), thus, to verify whether the generated $\cdot\text{DMPO-X}$ was derived from the reaction with $^1\text{O}_2$, the EPR experiment was further performed. As shown in Fig. S11B, in the presence of 25 mM of TEMP, a typical TEMPO signal (three-line signal with 1:1:1 intensity ratio) was observed in the presence of PMS alone which can be attributed to the self-decomposition of PMS (X. Yang et al., 2020). In $\text{Mn}_2\text{O}_3/\text{PMS}$ system, the TEMPO signal was approximately equal to the TEMPO intensity from PMS alone, indicating that no further $^1\text{O}_2$ was generated in the $\text{Mn}_2\text{O}_3/\text{PMS}$ system. Moreover, the addition of FFA in the $\text{Mn}_2\text{O}_3/\text{PMS}$ system also showed a negligible effect on the intensity of the TEMPO signal. Thus, the formation of $\cdot\text{DMPO-X}$ in the system of $\text{Mn}_2\text{O}_3/\text{PMS}$ cannot be contributed to $^1\text{O}_2$. On the

294 other side, the generated HO^\bullet might be responsible for the formation of $^\bullet\text{DMPO-X}$, consistent
295 with the observations of Yang et al. (X. Yang et al., 2020).

296 The decomposition of PMS was further investigated. Fig. S11C shows that PMS can be
297 decomposed by FFA alone, and the depletion efficiency of PMS is higher than Mn_2O_3 ,
298 suggesting the inhibition of CAF degradation in presence of FFA might be also attributed to
299 the increased consumption of PMS.

300 Besides, the AOS of Mn in the $\text{Mn}_2\text{O}_3/\text{PMS}$ system was measured, as shown in Fig. S9C.
301 The AOS of Mn_2O_3 was increased to 3.10 after reacting with PMS, suggesting the generation
302 of Mn (IV). It is known that Mn (IV) can oxidize organic pollutants compounds through a
303 heterogeneous electron transfer process (Huang et al., 2019), thus the non-radical degradation
304 of CAF in the $\text{Mn}_2\text{O}_3/\text{PMS}$ system might be related to the formation of Mn (IV).

305 In summary, different activation mechanisms of PS and PMS by the same Mn_2O_3 were
306 exhibited. In the $\text{Mn}_2\text{O}_3/\text{PS}$ system, the catalyst surface-activated PS molecules were the
307 primary reactive species that are responsible for the degradation of pollutants. This can be
308 attributed to the symmetric structure of PS which facilitates the contained O-O bonds binding
309 to Mn_2O_3 surface through the substitution with surface hydroxyl groups (-OH) (Z. Dong et al.,
310 2019; Xu et al., 2021; Zhu et al., 2019). In comparison, the activation of PMS by Mn_2O_3 was
311 mainly processed with the generation of radicals. It can be explained by the fact that the
312 unsymmetric structure of PMS can be easier activated by catalysts, the causes are in
313 agreement with the results of previous research (Anipsitakis and Dionysiou, 2004; Lin et al.,
314 2019, 2014).

315

316 **3.2. Effect of pH**

317 The CAF removal by Mn_2O_3 -mediated activation of PS or PMS was also investigated over
318 a wide range of initial pH (3-8) and degradation pseudo-first order rates were plotted versus
319 pH (Fig. 4). In the presence of PS, k'_{CAF} decreased from 4.7×10^{-3} to $2.6 \times 10^{-4} \text{ min}^{-1}$ from pH

320 3 to 8. It should be noted that the neutral form of CAF predominates over the investigated pH
321 range ($pK_a = 10.4$). The greater efficiency observed at low pH might result from the favorable
322 electrostatic interactions between positively charged Mn_2O_3 (PZC ~ 5.9) and PS (Salla et al.,
323 2020). The system Mn_2O_3 /PMS exhibited an improved k'_{CAF} with increasing the solution pH
324 from $2.2 \times 10^{-3} \text{ min}^{-1}$ to $6.4 \times 10^{-3} \text{ min}^{-1}$, followed by a decrease to $2.4 \times 10^{-3} \text{ min}^{-1}$ (Fig. 4).
325 The low efficiency at low pH may come from the impact of H^+ concentration on the reactivity
326 of $SO_4^{\cdot-}$, resulting in the low CAF degradation (Huang et al., 2009). Since the oxidation
327 potential of HO^{\cdot} is lower than $SO_4^{\cdot-}$ under alkaline environments, the transformation from
328 $SO_4^{\cdot-}$ to HO^{\cdot} may explain the low efficiency at high pH values. To further explore this
329 transformation process, the scavenging tests with the addition of TBA and 2-Pr were
330 conducted under various initial solution pH (Fig. S12). The contribution of HO^{\cdot} and $SO_4^{\cdot-}$ in
331 the degradation of CAF was also assessed using Eq. S1 (Text S3). As shown in Fig. S12D, the
332 radical involvement percentage (RI) of HO^{\cdot} after 6 h of CAF degradation first decreased from
333 10% to 7% and then increased to 34% as the initial solution pH increased from 3 to 8. In the
334 meanwhile, the RI percentage of $SO_4^{\cdot-}$ first increased from 55% to 63% and then decreased to
335 50%. The results fully and directly demonstrated the transformation between HO^{\cdot} and $SO_4^{\cdot-}$
336 with the change of solution pH. In summary, neutral or basic conditions are suitable for the
337 activation of PMS by Mn_2O_3 , while PS activation by Mn_2O_3 was enhanced in acidic
338 conditions only.

339

340 **3.3. Effects of Mn_2O_3 and oxidant dosages**

341 The effect of Mn_2O_3 concentration on CAF degradation in presence of PS under initial
342 solution pH 5 was then investigated (Fig. 5A and Fig. S13A). An increase of Mn_2O_3 dosage
343 from 0.05 to 1.0 $g L^{-1}$ led to an increase of k'_{CAF} from $5.4 \times 10^{-4} \text{ min}^{-1}$ to $4.6 \times 10^{-3} \text{ min}^{-1}$.
344 Similarly, the removal of CAF by Mn_2O_3 activated PMS was increased with the increase in
345 Mn_2O_3 concentration (Fig. S13B). This effect can be attributed to the increase of the active

346 surface area of Mn_2O_3 , leading to more active sites for radical precursor activation. It is worth
347 noting that complete removal of CAF was obtained for $1.0 \text{ g L}^{-1} \text{ Mn}_2\text{O}_3$ and 5 mM PMS after
348 2 h , while 8 h reaction time is required for the $\text{Mn}_2\text{O}_3/\text{PS}$ system. The degradation of CAF
349 (k'_{CAF}) by Mn_2O_3 (1.0 g L^{-1}) with PMS (5 mM) was $3.9 \times 10^{-2} \text{ min}^{-1}$, which results in an 8-
350 fold increase compared to that in $\text{Mn}_2\text{O}_3/\text{PS}$ system ($4.6 \times 10^{-3} \text{ min}^{-1}$). Fig. 5B shows the
351 increase of the k'_{CAF} from $1.6 \times 10^{-4} \text{ min}^{-1}$ to $4.7 \times 10^{-3} \text{ min}^{-1}$ with the increase of PS
352 concentration from 1 to 10 mM . The effects of PMS concentration on CAF degradation in the
353 presence of Mn_2O_3 (0.4 g L^{-1}) were similar, where an increase of k'_{CAF} from $3.5 \times 10^{-4} \text{ min}^{-1}$
354 to $8.5 \times 10^{-3} \text{ min}^{-1}$ with increasing PMS concentration from 1 to 10 mM . These enhanced
355 degradations with the increase of radical precursor concentrations ($\leq 10 \text{ mM}$) can be
356 attributed to the promotion of the number of reactive radicals as discussed in *section 3.1*.

357

358 **3.4. CAF degradation pathway and mineralization**

359 The main transformation intermediates of CAF in Mn_2O_3 -activated PS and PMS systems
360 were identified by LC-MS analysis. The experimental conditions were: $[\text{Mn}_2\text{O}_3]_0 = 0.4 \text{ g L}^{-1}$,
361 $[\text{CAF}] = 25 \text{ }\mu\text{M}$ and $[\text{PS}] = [\text{PMS}]_0 = 5 \text{ mM}$, initial solution $\text{pH} = 5.0$ and analysis was
362 performed after 2 hours of reaction. The molecular formulas, structures, retention time, and
363 positive/negative molecular ions (m/z) of intermediates are summarized in Table S5, and the
364 possible degradation pathways of CAF are shown in Fig. 6. CAF was identified at $[\text{M}+\text{H}]^+ =$
365 195.08 m/z . The first transformation step was the hydrogen abstraction (C8 position) and then
366 water molecule addition generating an intermediate with a keto-enol equilibrium. Further
367 oxidation steps lead to the formation of product P1 at $[\text{M}-\text{H}]^- = 228.19 \text{ m/z}$. Similar
368 transformation processes in CAF oxidation were reported in the previous study (Lin and
369 Chen, 2016; Qi et al., 2013). Subsequently (pathway 1), the intermediate P2 ($[\text{M}+\text{H}]^+ =$
370 202.15 m/z , $[\text{M}+\text{H}-\text{H}_2\text{O}]^+ = 184.13 \text{ m/z}$, and $[\text{M}-\text{H}]^- = 200.13 \text{ m/z}$) generated from the

371 decarboxylation of P1 through the attack of radicals and followed by the addition of hydroxyl
372 group was identified.

373 In pathway 2, the C=C bond of product P1 was attacked by radical species, opening the six-
374 member ring and leading to the formation of two carbonyl groups (-C=O) on the carbon
375 bonding with nitrogen (Rosal et al., 2009; Wang et al., 2017). Then the newly formed
376 carbonyl groups might be further attacked by radicals and the C-N broke leading to the loss of
377 nitrogen derivative (-N-CH₃-COOH) and formation of product P3 ([M+H]⁺ = 188.13 m/z,
378 [M+H-H₂O]⁺ = 170.12 m/z and [M-H]⁻ = 186.11 m/z) (Rosal et al., 2009). The intermediate
379 P4 at [M+H]⁺ = 174.11 m/z and [M-H]⁻ = 172.09 m/z were further identified, which was
380 originated from P3 through the demethylation process. It is worth noting that not all the
381 intermediates (P1-P4) were observed in the Mn₂O₃/PMS system and this can be explained by
382 the different types of active radicals generated in Mn₂O₃ activated PS and PMS systems (see
383 Table S5).

384 The mineralization efficiency of Mn₂O₃ + PS and PMS systems was monitored by
385 measuring TOC over reaction time. As shown in Fig. 7, 34% and 48% of TOC degradation
386 were reached in Mn₂O₃-activated PS and PMS system in 70 h, while complete removal of
387 CAF was achieved before 8 h of reaction time (Fig. S14). However, the oxidation process
388 remains active for a long time, over 70 h, suggesting the long-term efficiency of the
389 investigated process.

390

391 **3.5. Degradation efficiency in sewage treatment plant waters (STPW)**

392 To assess the performance and ability of Mn₂O₃ + PS and PMS to degrade CAF in the real
393 water body, the degradation was evaluated in STPW (Total Organic Carbon (TOC) = 39.7 mg
394 C L⁻¹, Inorganic Carbon (IC) = 4.5 mg C L⁻¹, pH = 8.1) and compared to milli-q water system
395 using 0.4 and 1.0 g L⁻¹ of Mn₂O₃ (Fig. S15). The degradation efficiency of CAF (DE) was
396 determined from the percentage of CAF degraded after 20 hours of reaction and inhibition in

397 STPW was observed in all experiments (Fig. 8). Generally, this effect can be attributed to the
398 radical scavenging ability of natural organic matter and inorganic carbon (i.e. hydrogen
399 carbonate ions) of STPW that are recognized to be the main inhibitors of radicals in AOPs
400 (Huang et al., 2018). However, in Mn_2O_3/PS system, the main reactive species are the Mn_2O_3
401 surface-activated PS. The inhibition of CAF degradation in STPW was mainly attributed to
402 the increased ionic strength (Zhang et al., 2014).

403 The inhibition effect (IE) of STPW was determined as $IE = \left(1 - \frac{DE_{STPW}}{DE_{milli-q}}\right) \times$
404 100, in which DE_{STPW} and $DE_{milli-q}$ were the CAF degradation efficiencies in STPW and
405 milli-q water after 20 hours. It is interesting to note that, in the presence of PS, about 95 % of
406 inhibition was reported using two different Mn_2O_3 concentrations. The results verified again
407 the non-radical mechanism in the Mn_2O_3/PS system and the formation of Mn_2O_3 surface-
408 activated PS. However, a decrease of inhibition effect with the increase of Mn_2O_3
409 concentration was observed using PMS. The CAF degradation efficiency drops from 88.6 to
410 33.6 % (IE of 62%) when 0.4 g L^{-1} of Mn_2O_3 was used, while only 20% of inhibition in
411 STPW was determined in the presence of 1.0 g L^{-1} . Increasing in the production of reactive
412 species is expected when a higher amount of solid (higher exposed surface area) is used. This
413 finding highlights the crucial role of Mn in promoting oxidation reactions and suggests that
414 manganese-mediated advanced oxidation processes (Mn-AOPs) could be a promising process
415 for wastewater treatment.

416

417 4. Conclusion

418 Mn_2O_3 exhibited higher activation capability for PS and PMS compared with H_2O_2 and
419 HSO_3^- . CAF degradation in the Mn_2O_3 -activated PS and PMS was highly influenced by the
420 initial solution pH. PS was efficiently activated by Mn_2O_3 under acidic pH, while under

421 neutral or alkaline conditions, environmentally relevant pH values, higher degradation was
422 observed using PMS. Chemical quenching and EPR experiments demonstrated that HO[•] and
423 SO₄^{•-} were the main radicals generated in the system with PMS. In addition, a non-radical
424 mechanism could contribute to the degradation of CAF in the Mn₂O₃/PS system. The
425 degradation efficiency was tested in real STPW and, despite the inhibition of CAF
426 degradation was observed due to the water constituents (mainly inorganic and organic
427 carbon), the central role of Mn₂O₃ activation for highly reactive species formation was
428 demonstrated in particular when PMS was used (about 80 % of CAF degradation was
429 obtained in STPW after 20 hours). Comparison of obtained results in pure and real STPW
430 indicates that a lower inhibition effect (20 %) was obtained using PMS compared to the PS
431 system. Given the ability of Mn₂O₃ to activate PS and PMS, the manganese-based oxidation
432 processes (Mn-AOPs) reactions can be considered as a promising treatment technology for
433 the removal of organic pollutants in water.

434

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445

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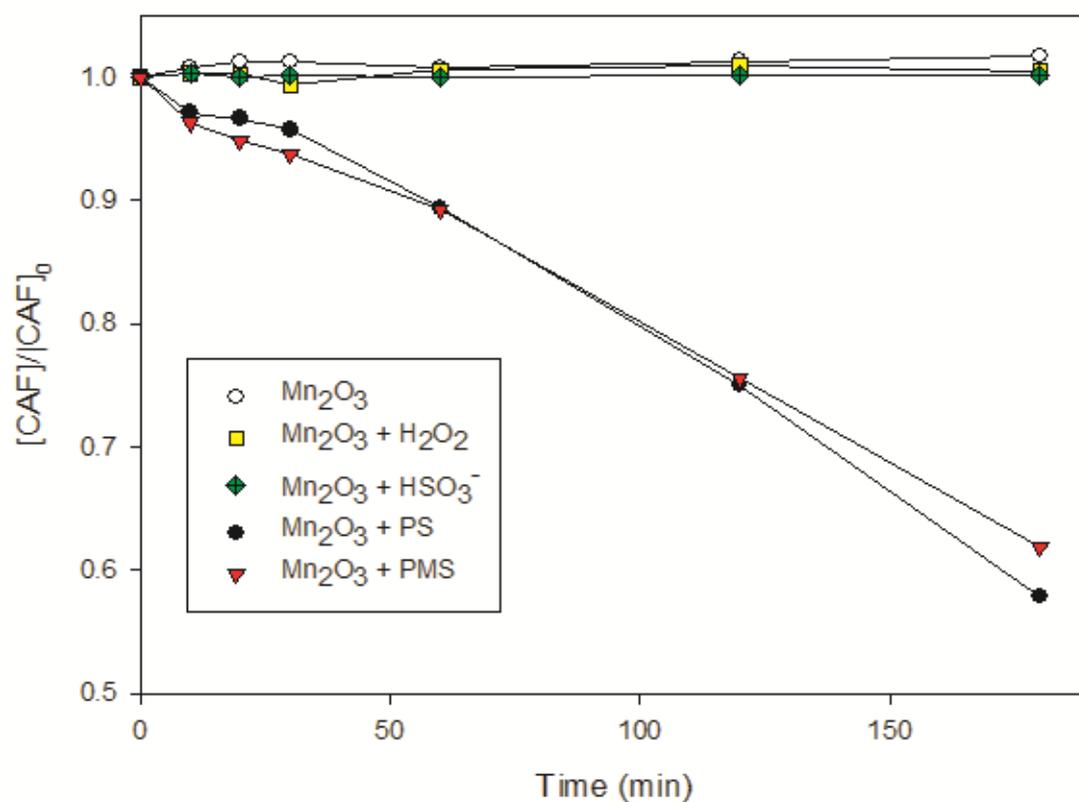
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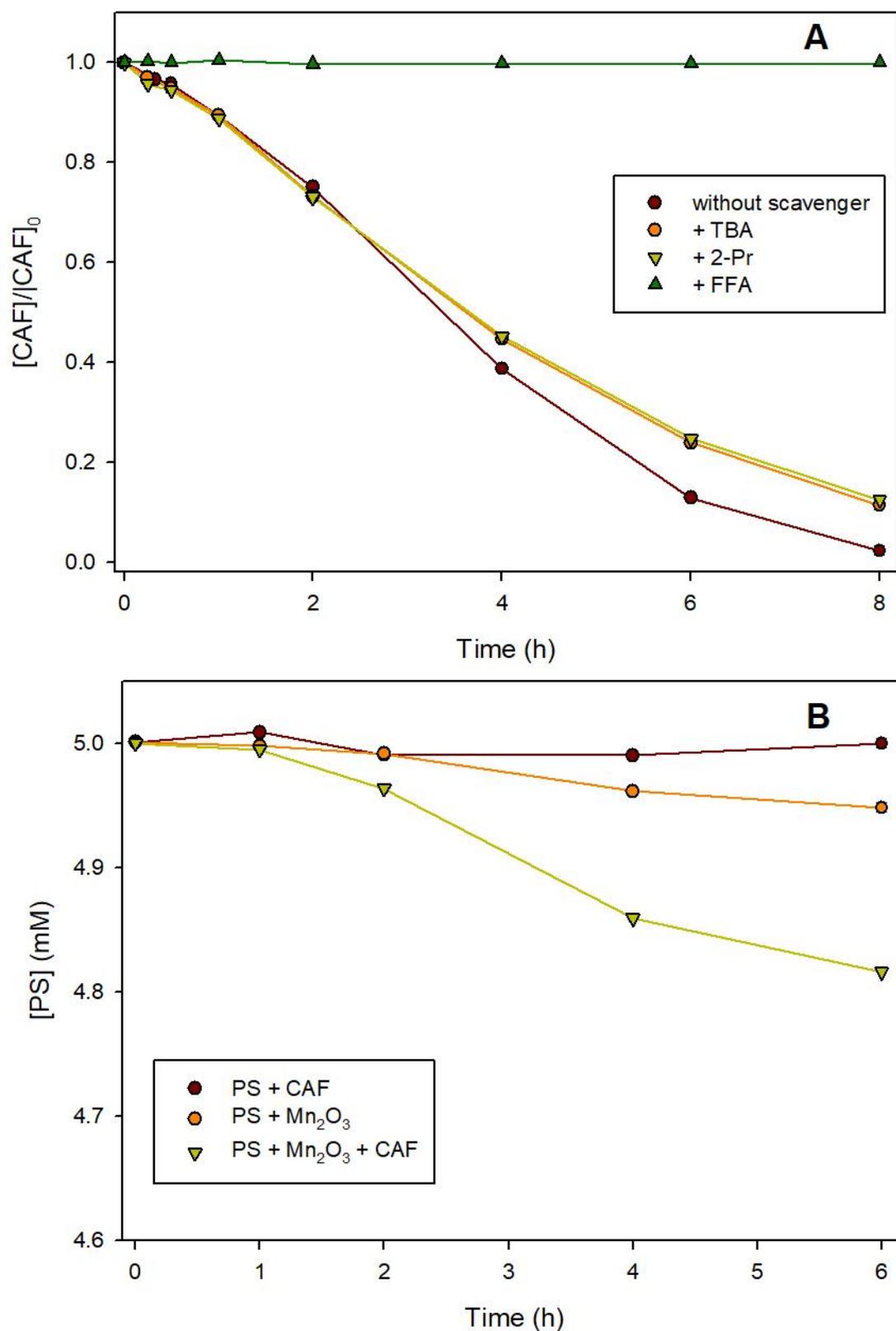
609

610 **Fig. 1.** CAF (25 μ M) degradation in the presence of 0.4 g L⁻¹ of Mn_2O_3 and different oxidants

611 at 5 mM, natural pH (see Table S2), and T = 298 K.

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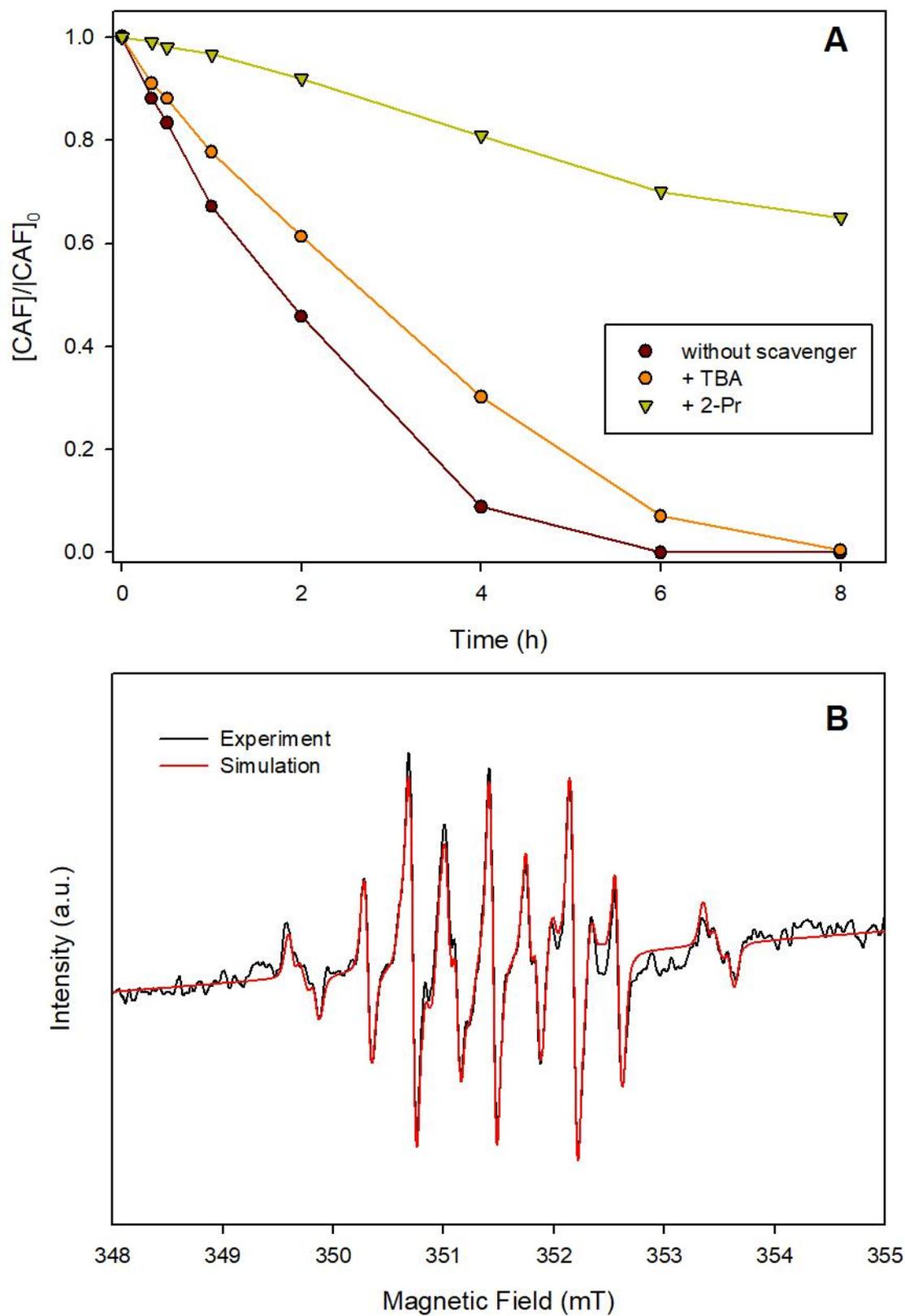


614

615 **Fig. 2.** Determination of ROS species for CAF oxidation in Mn₂O₃/PS. **A:** CAF degradation

616 by Mn₂O₃ with PS in the presence of different radical scavengers ([TBA]₀ = [2-Pr]₀ = 10 mM,

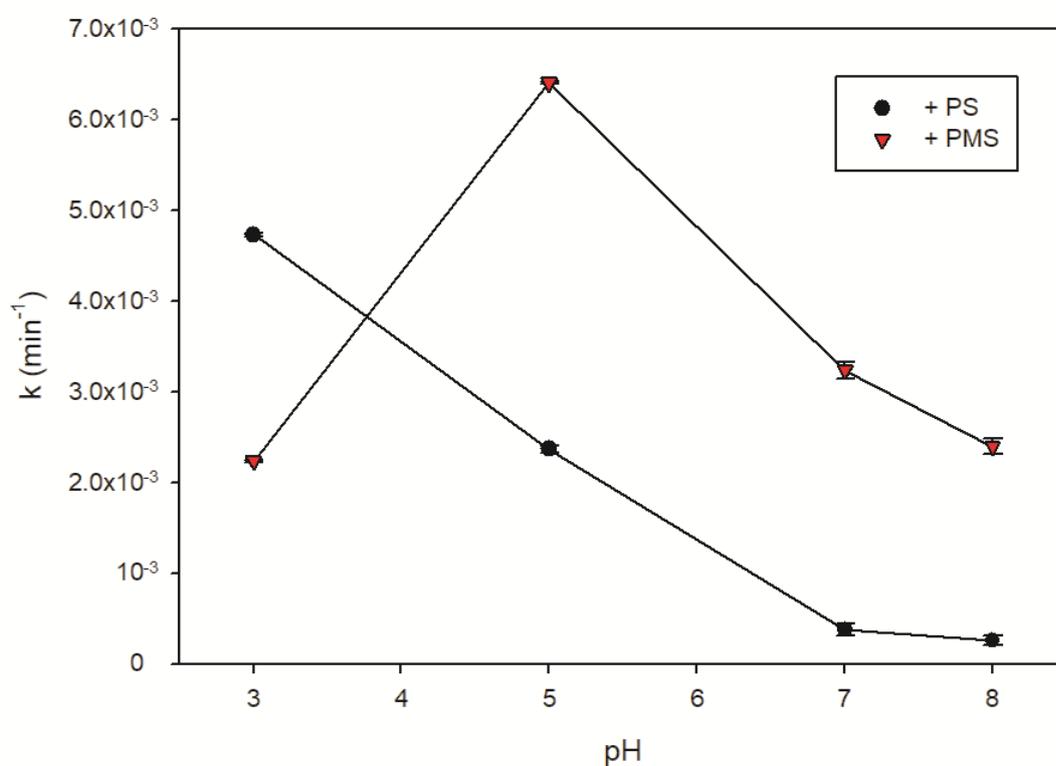
617 [FFA]₀ = 1 mM). **B**: PS decomposition in different processes. [Mn₂O₃]₀ = 0.4 g L⁻¹, [CAF]₀ =
618 25 μM, [PS]₀ = 5 mM, The pH of solution was 5.0 and T = 298 K.



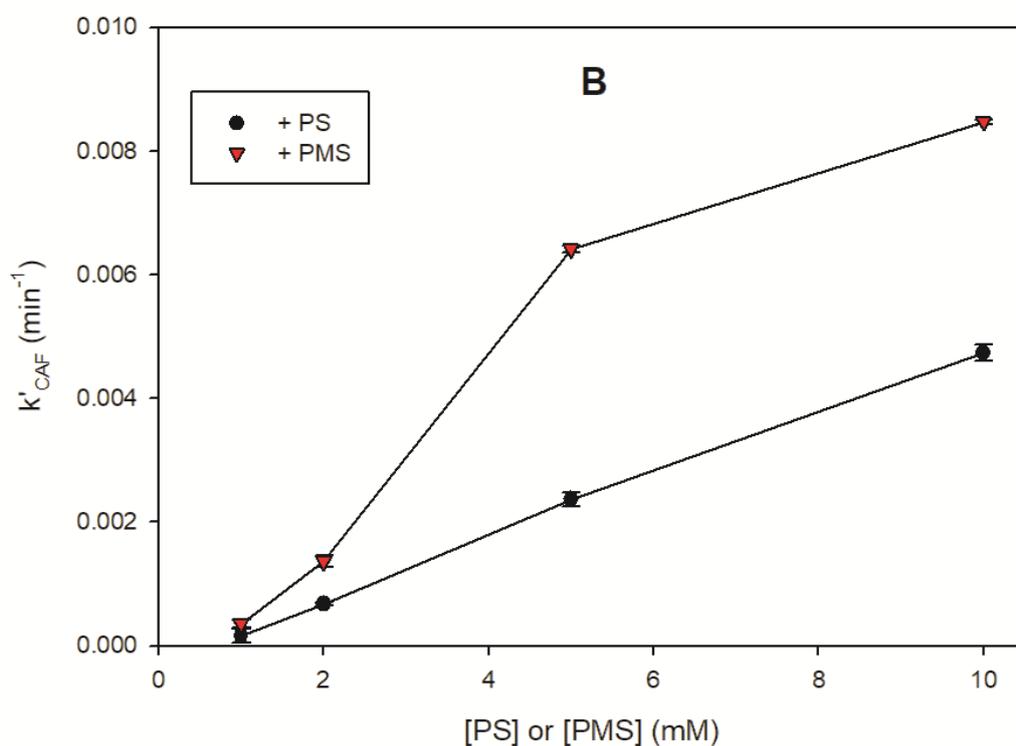
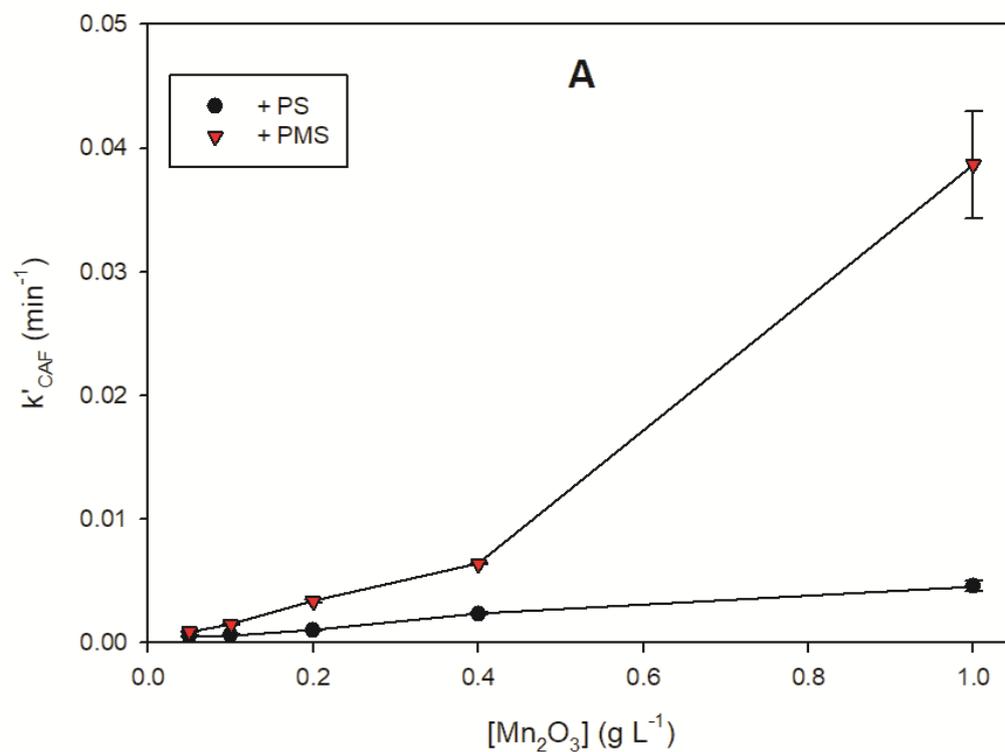
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620 **Fig. 3.** Determination of reactive radical species for CAF degradation in $\text{Mn}_2\text{O}_3/\text{PMS}$ system.
621 **A:** Quenching tests of CAF degradation in the process of $\text{Mn}_2\text{O}_3 + \text{PMS}$ with various radical
622 scavengers ($[\text{TBA}]_0 = [\text{2-Pr}]_0 = 10 \text{ mM}$, $[\text{FFA}]_0 = 1 \text{ mM}$). **B:** The normalized experimental
623 (black line) and simulated (red line) EPR spectra measured in the suspension of
624 $\text{PMS}/\text{Mn}_2\text{O}_3/\text{DMPO}/\text{water}$ ($[\text{DMPO}]_0 = 25 \text{ mM}$). $[\text{Mn}_2\text{O}_3]_0 = 0.4 \text{ g L}^{-1}$, $[\text{CAF}]_0 = 25 \text{ }\mu\text{M}$,
625 $[\text{PMS}]_0 = 5 \text{ mM}$, The pH of solution was 5.0 and $T = 298 \text{ K}$.

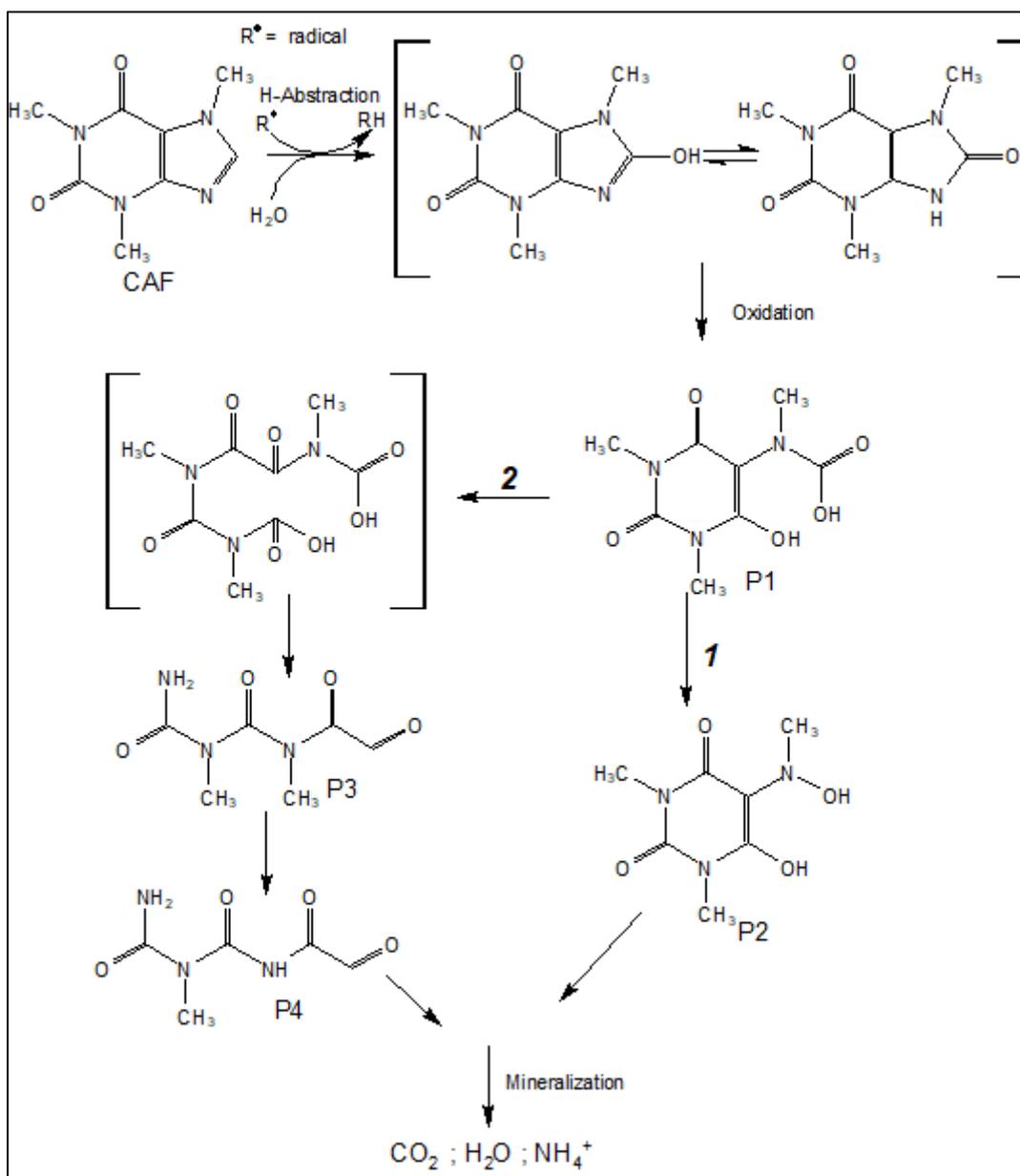
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627
628 **Fig. 4.** Degradation constant of CAF (k'_{CAF}) in the systems $\text{Mn}_2\text{O}_3 + \text{PS}$ and $\text{Mn}_2\text{O}_3 + \text{PMS}$
629 under different pH values. Experimental conditions are $[\text{Mn}_2\text{O}_3]_0 = 0.4 \text{ g L}^{-1}$, $[\text{CAF}]_0 = 25$
630 μM , $[\text{PS}]_0 = [\text{PMS}]_0 = 5 \text{ mM}$, $T = 298 \text{ K}$.



631
 632 **Fig. 5.** Degradation of CAF (k'_{CAF}) in the system Mn_2O_3 with PS and PMS. **A:** Effect of
 633 Mn_2O_3 concentration in the presence of 5 mM PS and PMS. **B:** Effect of PS and PMS
 634 concentrations using 0.4 g L⁻¹ of Mn_2O_3 . Initial pH = 5.0, T = 298 K.



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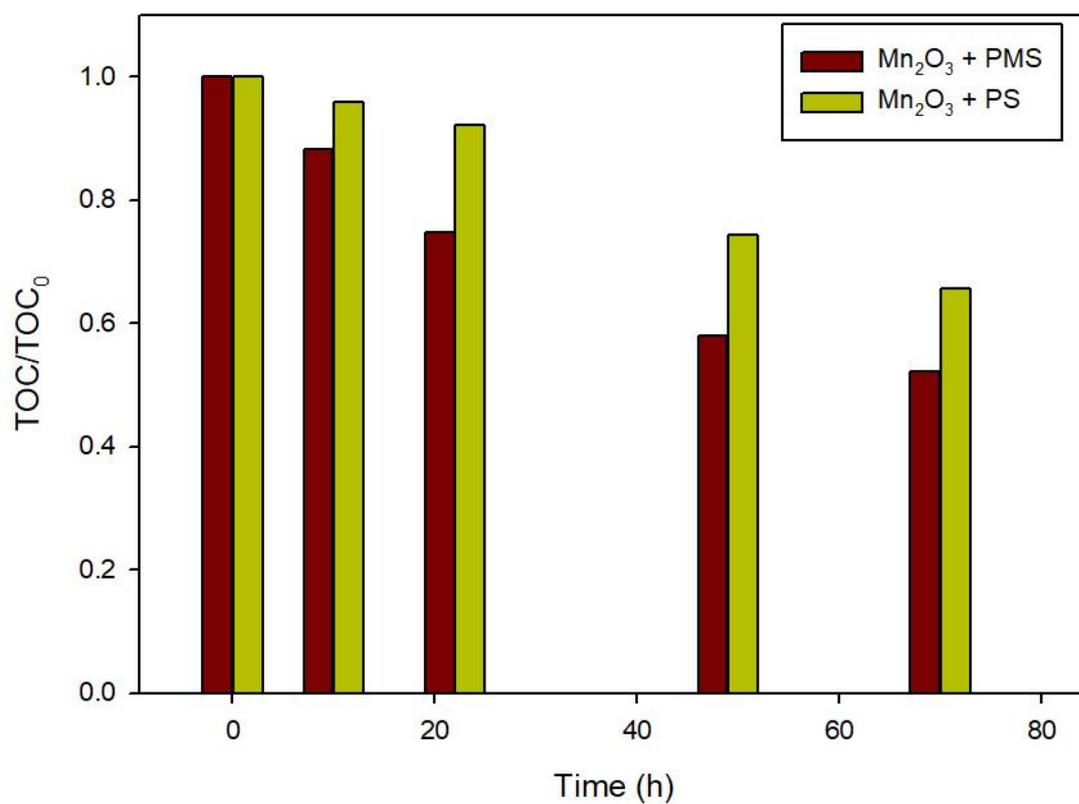
636 **Fig. 6.** Proposed degradation pathways of CAF in Mn_2O_3 -activated PS and PMS systems. P2

637 and P4 were identified only in the presence of PS (see table S5).

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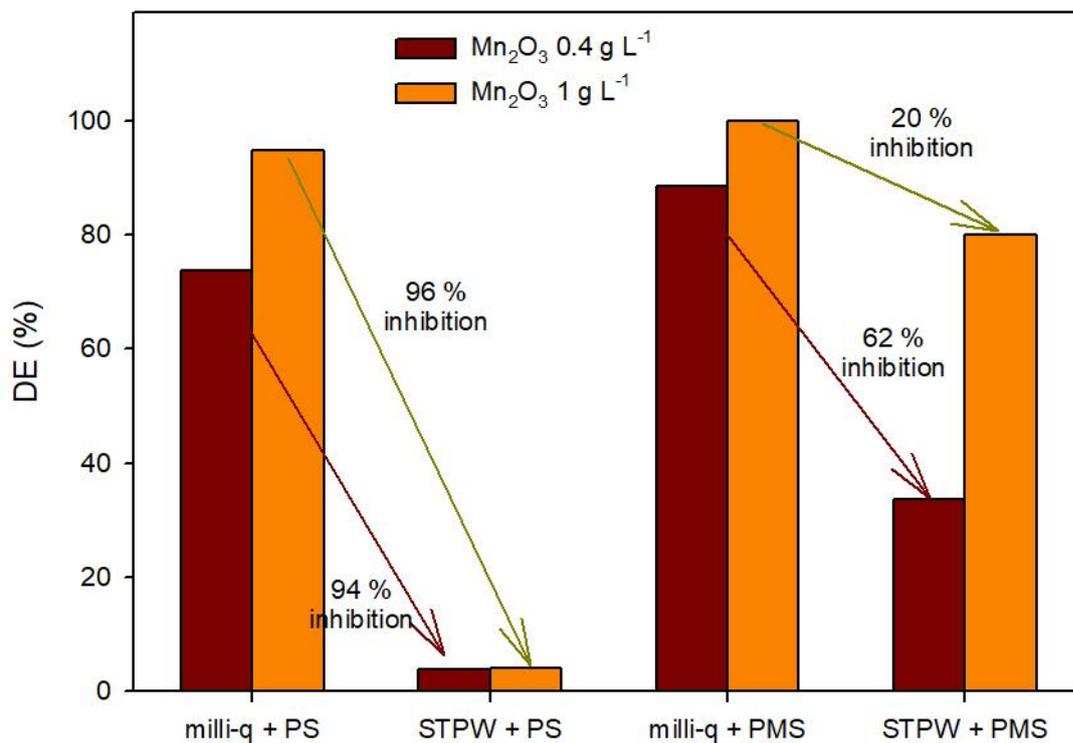
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641

642 **Fig. 7.** TOC decrease with time in Mn₂O₃-activated PS and PMS systems. Experimental
 643 conditions: [Mn₂O₃]₀ = 0.4 g L⁻¹, [CAF]₀ = 25 μM, [PS]₀ = [PMS]₀ = 5 mM, initial solution
 644 pH = 5.0, T = 25 ± 2 °C.

645



646

647 **Fig. 8.** The degradation efficiency of CAF after 20 hours of reaction in milli-q and STP

648 waters (STPW) using 0.4 and 1.0 g L⁻¹ of Mn₂O₃. PS and PMS concentrations were 5 mM and

649 the pH of solutions was 8.0 ± 0.2.