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# Caffeine degradation using peroxydisulfate and peroxymonosulfate in the presence of $Mn_2O_3$ . Efficiency, reactive species formation and application in sewage treatment plant water

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1 **Caffeine degradation using peroxydisulfate and peroxymonosulfate in the**  
2 **presence of Mn<sub>2</sub>O<sub>3</sub>. Efficiency, reactive species formation and application in**  
3 **sewage treatment plant water**

4

5 Daqing Jia<sup>1</sup>, Olivier Monfort<sup>1,2</sup>, Khalil Hanna<sup>3,4</sup>, Gilles Mailhot<sup>1</sup>, Marcello Brigante<sup>1\*</sup>

6

7 <sup>1</sup> Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de Clermont-Ferrand,  
8 F-63000 Clermont–Ferrand, France.

9 <sup>2</sup> Comenius University in Bratislava, Faculty of Natural Sciences, Department of Inorganic Chemistry,  
10 Ilkovicova 6, Mlynska Dolina, 842 15 Bratislava, Slovakia.

11 <sup>3</sup> Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, UMR CNRS 6226, 11 Allée de  
12 Beaulieu, F-35708 Rennes Cedex 7, France.

13 <sup>4</sup> Institut Universitaire de France (IUF), MESRI, 1 rue Descartes, 75231 Paris, France.

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\* Corresponding author e-mail: marcello.brigante@uca.fr

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 ( $\text{Mn}_2\text{O}_3$ ) 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  $\text{Mn}_2\text{O}_3$ /PMS system. In  
28 comparison, a non-radical mechanism such as  $\text{Mn}_2\text{O}_3$  surface-activated PS promoted the  
29 removal of CAF in the system of  $\text{Mn}_2\text{O}_3$ /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  $\text{Mn}_2\text{O}_3$  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;  $\text{Mn}_2\text{O}_3$ ; 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 ( $\text{HO}^\bullet$ ) 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 ( $\text{MnO}_x$ ) are gaining stronger interests due to their versatile oxidation states (II, III, IV, and  
61 VII) (Zhong and Zhang, 2019).

62 Among the different  $\text{MnO}_x$ , manganese dioxide ( $\text{MnO}_2$ ) 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  $\alpha$ - and  $\delta$ - $\text{MnO}_2$  activated PMS through the generation of  $\text{SO}_4^{\bullet-}$  and  $\text{HO}^\bullet$  (Zhou  
66 et al., 2019). Zhu et al. demonstrated the rapid removal of bisphenol A (BPA) in the  $\beta$ -  
67  $\text{MnO}_2$ /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  $\text{MnO}_2$  were

69 investigated by Huang et al., and the results showed that the efficient oxidation of pollutants  
70 by  $\text{MnO}_2$  with or without oxidants was attributed to the occurrence of Mn(III) on the surface  
71 of  $\text{MnO}_2$  (Huang et al., 2019, p. 2, 2018). Therefore, it is believed that the presence of Mn(III)  
72 species in  $\text{MnO}_x$  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  $\gamma$ - $\text{MnOOH}$ /PS  
75 system through the formation of active intermediates between  $\gamma$ - $\text{MnOOH}$  and PS (Xu et al.,  
76 2021). Wang et al. indicated the good reactivity of octahedral  $\text{Mn}_3\text{O}_4$  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  $\text{Mn}_2\text{O}_3$  as the catalyst was also reported. For instance, Saputra et  
80 al. indicated that  $\text{Mn}_2\text{O}_3$  compared with  $\text{MnO}$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{MnO}_2$  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  $\text{Mn}_2\text{O}_3$  structures on PMS activation was also investigated  
83 by Saputra et al., and the results showed cubic- $\text{Mn}_2\text{O}_3$  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  $\text{Mn}_2\text{O}_3$  on PMS is not clear, and  
87 some important influence factors for the reactivity of  $\text{Mn}_2\text{O}_3$  such as solution pH were not  
88 investigated. Furthermore, Khan et al. investigated the activation of PS using synthesized  
89  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}_2$  for the degradation of phenol in solution (Khan et al., 2021). The results  
90 showed that phenol was efficiently removed in A- $\text{Mn}_2\text{O}_3$ /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- $\text{Mn}_2\text{O}_3$ /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  $\gamma$ -

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 Mn<sub>2</sub>O<sub>3</sub>/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 Mn<sub>2</sub>O<sub>3</sub> in the near-neutral solution and evaluate the suitability of the Mn<sub>2</sub>O<sub>3</sub> 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 Mn<sub>2</sub>O<sub>3</sub> to activate PS and PMS  
105 under different experimental conditions, i.e. pH, Mn<sub>2</sub>O<sub>3</sub> 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  $\text{Mn}_2\text{O}_3$  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 ( $298 \pm 2$  K) under stirring (700 rpm) to ensure  
130 homogeneity. 25  $\mu\text{M}$  of CAF was added to the 100 mL reaction solution containing a certain  
131 concentration of  $\text{Mn}_2\text{O}_3$ , then a predetermined amount of oxidants (*i.e.*  $\text{H}_2\text{O}_2$ , PS, PMS, and  
132  $\text{HSO}_3^-$ ) 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  $\mu\text{m}$  PTFE filter) to remove  $\text{Mn}_2\text{O}_3$  particles. The reaction was  
135 stopped by the addition of 100  $\mu\text{L}$  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 ( $\text{HO}^\bullet$ ) 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.  $\text{HO}^\bullet$ ,  
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  $\mu\text{m}$  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,  $250 \times 4.6$  mm, 5  $\mu\text{m}$  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  $\text{mL min}^{-1}$  and the detection wavelength of CAF was fixed at 272 nm. The pseudo-first-  
159 order rate constant of CAF ( $k'_{\text{CAF}}$ ) 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  $3\sigma$ , 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  $\mu\text{L}$  of PS or PMS sample was first transferred into 5 mL  
167 of the mixture of potassium iodide (KI, Sigma-Aldrich) and sodium bicarbonate ( $\text{NaHCO}_3$ ,  
168 Sigma-Aldrich) to generate iodine ( $\text{I}_2$ ). Then,  $\text{I}_2$  further reacted with iodide ( $\text{I}^-$ ) 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  $\mu$ L of sample  
177 was withdrawn and immediately mixed with 125  $\mu$ 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<sup>®</sup> 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  $\mu$ m  $\times$  100  $\text{\AA}$ ; 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<sup>-1</sup> and the  
191 injection volume of 10  $\mu$ L.

192

### 193 **3. Results and discussion**

### 194 3.1. Reactivity of Mn<sub>2</sub>O<sub>3</sub> with PS and PMS

195 The reactivity of Mn<sub>2</sub>O<sub>3</sub> with different radical precursors (i.e. H<sub>2</sub>O<sub>2</sub>, PS, PMS, and HSO<sub>3</sub><sup>-</sup>)  
196 was investigated. As shown in Fig. 1, the CAF degradation was observed only in the Mn<sub>2</sub>O<sub>3</sub>  
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 Mn<sub>2</sub>O<sub>3</sub> with PS and PMS was achieved (Table S3). Moreover, blank and adsorption tests  
201 showed that CAF removal by adsorption on Mn<sub>2</sub>O<sub>3</sub> 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 Mn<sub>2</sub>O<sub>3</sub>, the leaching of Mn<sup>2+</sup> in Mn<sub>2</sub>O<sub>3</sub> activated PS/PMS reactions and the homogeneous  
212 activation of PS/PMS by Mn<sup>2+</sup> were studied. As shown in Fig. S4. A negligible Mn<sup>2+</sup>  
213 concentration (~ 1 μM) was determined when 0.4 g L<sup>-1</sup> of Mn<sub>2</sub>O<sub>3</sub> was suspended in solution.  
214 Moreover, the degradation efficiency of CAF in the Mn<sup>2+</sup> activated PS/PMS system was far  
215 lower than Mn<sub>2</sub>O<sub>3</sub>, even the employed concentration of Mn<sup>2+</sup> was 10-1000 times higher than  
216 leached Mn<sup>2+</sup>. Thus, the removal of CAF was attributed to the activation of PS/PMS by  
217 Mn<sub>2</sub>O<sub>3</sub>.

218

### 219 3.1.1 Reactivity of Mn<sub>2</sub>O<sub>3</sub> with PS

220 In the system of Mn<sub>2</sub>O<sub>3</sub>/PS, only a negligible effect of TBA and 2-Pr was observed  
221 indicating that HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> 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 <sup>1</sup>O<sub>2</sub>. To identify whether <sup>1</sup>O<sub>2</sub> was generated in the Mn<sub>2</sub>O<sub>3</sub>/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 <sup>1</sup>O<sub>2</sub>. Other reasons  
229 can explain the inhibition of CAF by FFA, such as the scavenging of HO<sup>•</sup>, the increased PS  
230 consumption, and the occupied reactive sites on the Mn<sub>2</sub>O<sub>3</sub> surface (Appiani et al., 2017; Xu  
231 et al., 2021; Yang et al., 2018)). The scavenging of HO<sup>•</sup> 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 Mn<sub>2</sub>O<sub>3</sub> 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 <sup>1</sup>O<sub>2</sub> (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  $\text{Mn}_2\text{O}_3$  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  $\text{Mn}_2\text{O}_3$  in the absence of CAF. This result indicates that PS  
252 was absorbed on the active sites present on the surface of  $\text{Mn}_2\text{O}_3$ . 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.

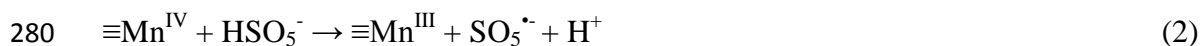
255 The non-radical mechanism of PS activation was further verified through the  
256 measurement of the Mn oxidation state in the  $\text{Mn}_2\text{O}_3/\text{PS}$  system. The average oxidation state  
257 (AOS) of samples was calculated from the binding energy difference ( $\Delta E$ ) of Mn 3s doublet  
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  $\text{Mn}_2\text{O}_3$  did not change after reaction with PS (AOS  $\sim 3.00$ ), indicating the  
260 activation of PS by  $\text{Mn}_2\text{O}_3$  was a non-radical catalytic process.

261

### 262 3.1.2 Reactivity of $\text{Mn}_2\text{O}_3$ with PMS

263 In the PMS-containing system, the presence of TBA and 2-Pr decreased the  $k'_{\text{CAF}}$  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  $\text{HO}^{\cdot}$ . 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  $\text{HO}^{\cdot}$  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  $\text{HO}^{\cdot}$  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.*  $\text{HO}^{\cdot}$  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 TEMP 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 TEMP signal was approximately equal to the TEMP signal 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 TEMP 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<sup>•</sup> might be responsible for the formation of <sup>•</sup>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<sub>2</sub>O<sub>3</sub>,  
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 Mn<sub>2</sub>O<sub>3</sub>/PMS system was measured, as shown in Fig. S9C.  
301 The AOS of Mn<sub>2</sub>O<sub>3</sub> 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 Mn<sub>2</sub>O<sub>3</sub>/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<sub>2</sub>O<sub>3</sub> were  
306 exhibited. In the Mn<sub>2</sub>O<sub>3</sub>/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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub>-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'<sub>CAF</sub> decreased from 4.7 × 10<sup>-3</sup> to 2.6 × 10<sup>-4</sup> min<sup>-1</sup> 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  $\sim 5.9$ ) 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  $\text{Mn}_2\text{O}_3$ , 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  $5 \text{ mM}$  PMS after  
348  $2 \text{ h}$ , while  $8 \text{ h}$  reaction time is required for the  $\text{Mn}_2\text{O}_3/\text{PS}$  system. The degradation of CAF  
349 ( $k'_{\text{CAF}}$ ) by  $\text{Mn}_2\text{O}_3$  ( $1.0 \text{ g L}^{-1}$ ) with PMS ( $5 \text{ mM}$ ) 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  $k'_{\text{CAF}}$  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  $10 \text{ mM}$ . The effects of PMS concentration on CAF degradation in the  
353 presence of  $\text{Mn}_2\text{O}_3$  ( $0.4 \text{ g L}^{-1}$ ) were similar, where an increase of  $k'_{\text{CAF}}$  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  $10 \text{ mM}$ . 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  $\text{Mn}_2\text{O}_3$ -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  $2 \text{ hours}$  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  $195.08 \text{ m/z}$ . 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  $202.15 \text{ m/z}$ ,  $[\text{M}+\text{H}-\text{H}_2\text{O}]^+ = 184.13 \text{ m/z}$ , 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-CH<sub>3</sub>-COOH) and formation of product P3 ( [M+H]<sup>+</sup> = 188.13 m/z,  
378 [M+H-H<sub>2</sub>O]<sup>+</sup> = 170.12 m/z and [M-H]<sup>-</sup> = 186.11 m/z) (Rosal et al., 2009). The intermediate  
379 P4 at [M+H]<sup>+</sup> = 174.11 m/z and [M-H]<sup>-</sup> = 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 Mn<sub>2</sub>O<sub>3</sub>/PMS system and this can be explained by  
382 the different types of active radicals generated in Mn<sub>2</sub>O<sub>3</sub> activated PS and PMS systems (see  
383 Table S5).

384 The mineralization efficiency of Mn<sub>2</sub>O<sub>3</sub> + 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 Mn<sub>2</sub>O<sub>3</sub>-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 Mn<sub>2</sub>O<sub>3</sub> + 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<sup>-1</sup>, Inorganic Carbon (IC) = 4.5 mg C L<sup>-1</sup>, pH = 8.1) and compared to milli-q water system  
395 using 0.4 and 1.0 g L<sup>-1</sup> of Mn<sub>2</sub>O<sub>3</sub> (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  $0.4 \text{ g L}^{-1}$  of  $Mn_2O_3$  was used, while only 20% of inhibition in  
411 STPW was determined in the presence of  $1.0 \text{ g L}^{-1}$ . 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<sup>•</sup> and  
423 SO<sub>4</sub><sup>•-</sup> 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 Mn<sub>2</sub>O<sub>3</sub>/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 Mn<sub>2</sub>O<sub>3</sub> 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 Mn<sub>2</sub>O<sub>3</sub> 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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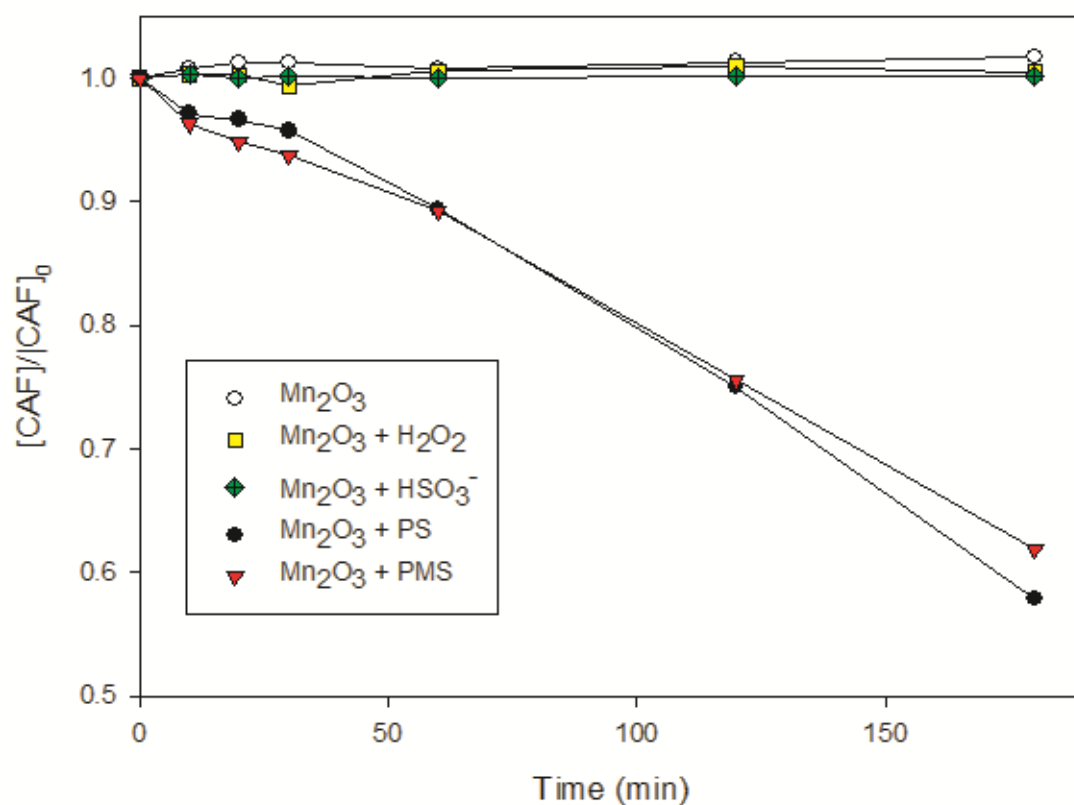
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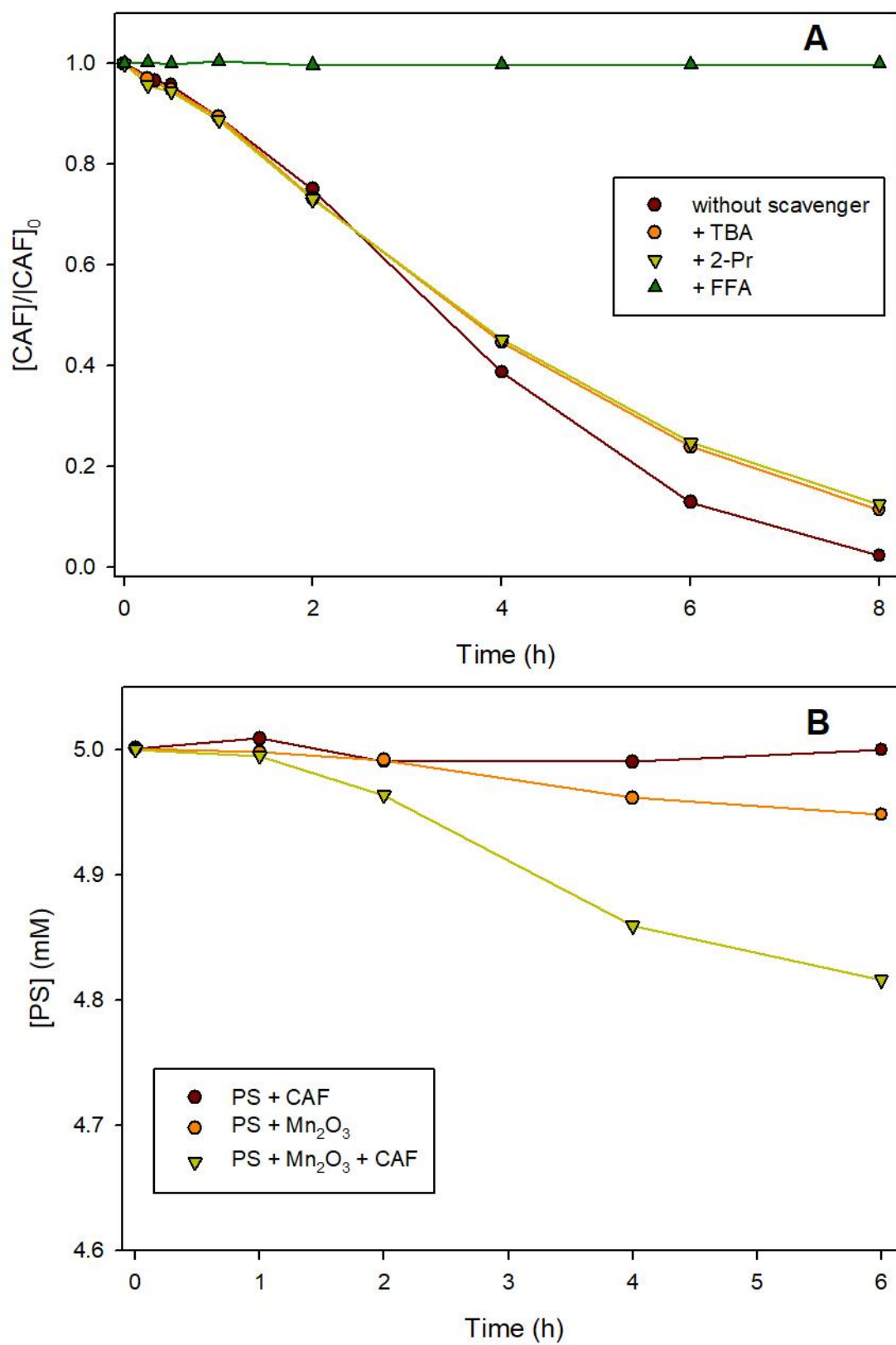
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610 **Fig. 1.** CAF (25  $\mu$ M) degradation in the presence of 0.4 g L<sup>-1</sup> of  $Mn_2O_3$  and different oxidants  
 611 at 5 mM, natural pH (see Table S2), and T = 298 K.

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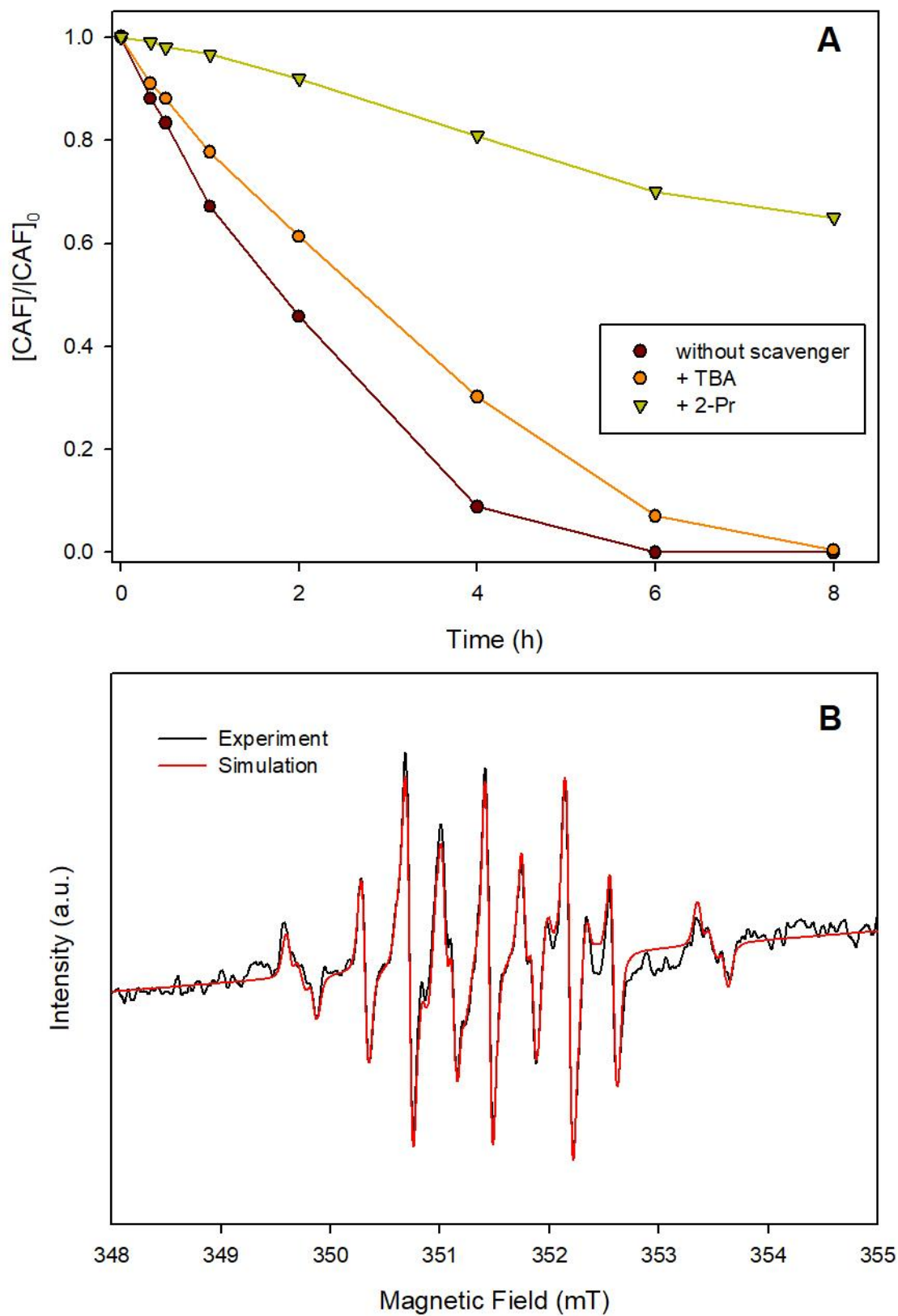


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615 **Fig. 2.** Determination of ROS species for CAF oxidation in Mn<sub>2</sub>O<sub>3</sub>/PS. **A:** CAF degradation

616 by Mn<sub>2</sub>O<sub>3</sub> with PS in the presence of different radical scavengers ([TBA]<sub>0</sub> = [2-Pr]<sub>0</sub> = 10 mM,

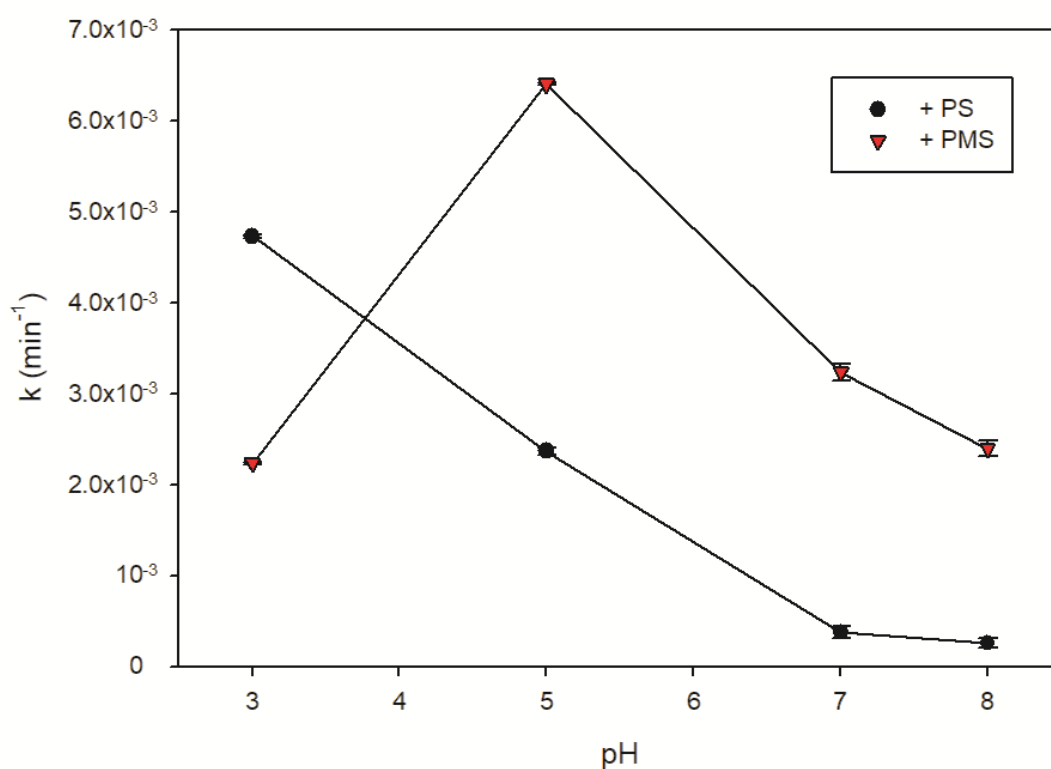
617 [FFA]<sub>0</sub> = 1 mM). **B**: PS decomposition in different processes. [Mn<sub>2</sub>O<sub>3</sub>]<sub>0</sub> = 0.4 g L<sup>-1</sup>, [CAF]<sub>0</sub> =  
618 25 μM, [PS]<sub>0</sub> = 5 mM, The pH of solution was 5.0 and T = 298 K.



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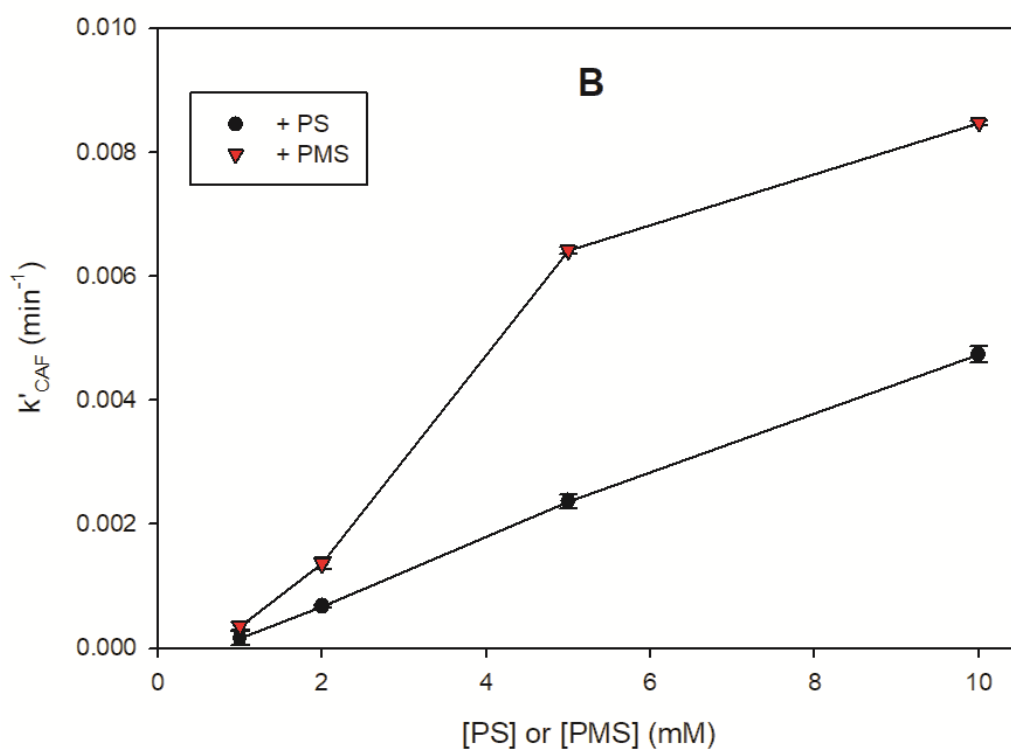
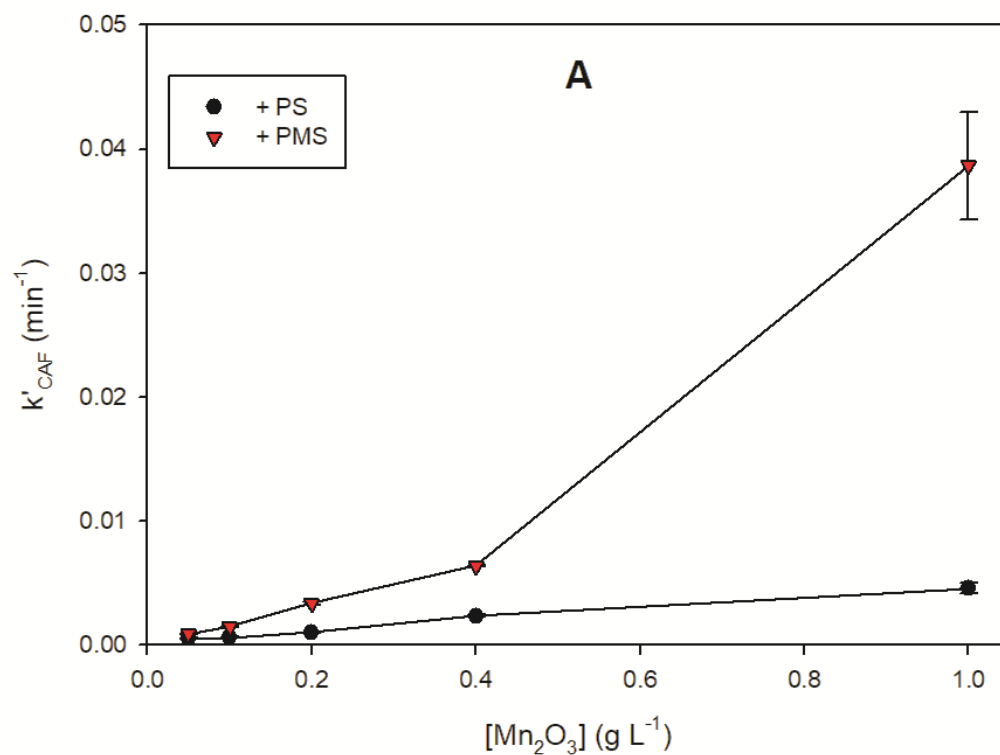
620 **Fig. 3.** Determination of reactive radical species for CAF degradation in  $\text{Mn}_2\text{O}_3/\text{PMS}$  system.  
 621 **A:** Quenching tests of CAF degradation in the process of  $\text{Mn}_2\text{O}_3 + \text{PMS}$  with various radical  
 622 scavengers ( $[\text{TBA}]_0 = [\text{2-Pr}]_0 = 10 \text{ mM}$ ,  $[\text{FFA}]_0 = 1 \text{ mM}$ ). **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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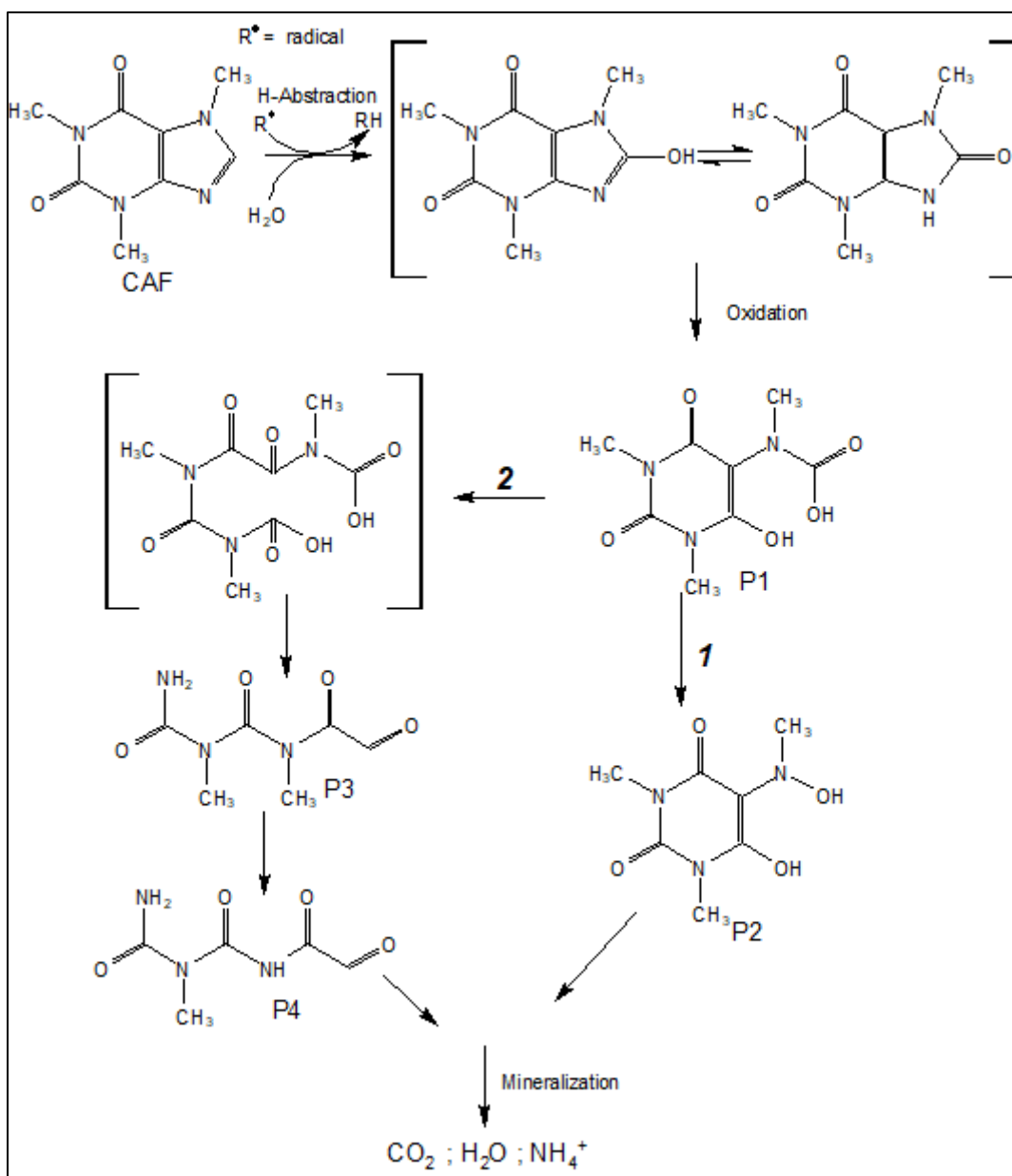


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628 **Fig. 4.** Degradation constant of CAF ( $k'_{\text{CAF}}$ ) in the systems  $\text{Mn}_2\text{O}_3 + \text{PS}$  and  $\text{Mn}_2\text{O}_3 + \text{PMS}$   
 629 under different pH values. Experimental conditions are  $[\text{Mn}_2\text{O}_3]_0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



631  
 632 **Fig. 5.** Degradation of CAF ( $k'_{\text{CAF}}$ ) in the system  $\text{Mn}_2\text{O}_3$  with PS and PMS. **A:** Effect of  
 633  $\text{Mn}_2\text{O}_3$  concentration in the presence of 5 mM PS and PMS. **B:** Effect of PS and PMS  
 634 concentrations using 0.4 g L<sup>-1</sup> of  $\text{Mn}_2\text{O}_3$ . Initial pH = 5.0, T = 298 K.



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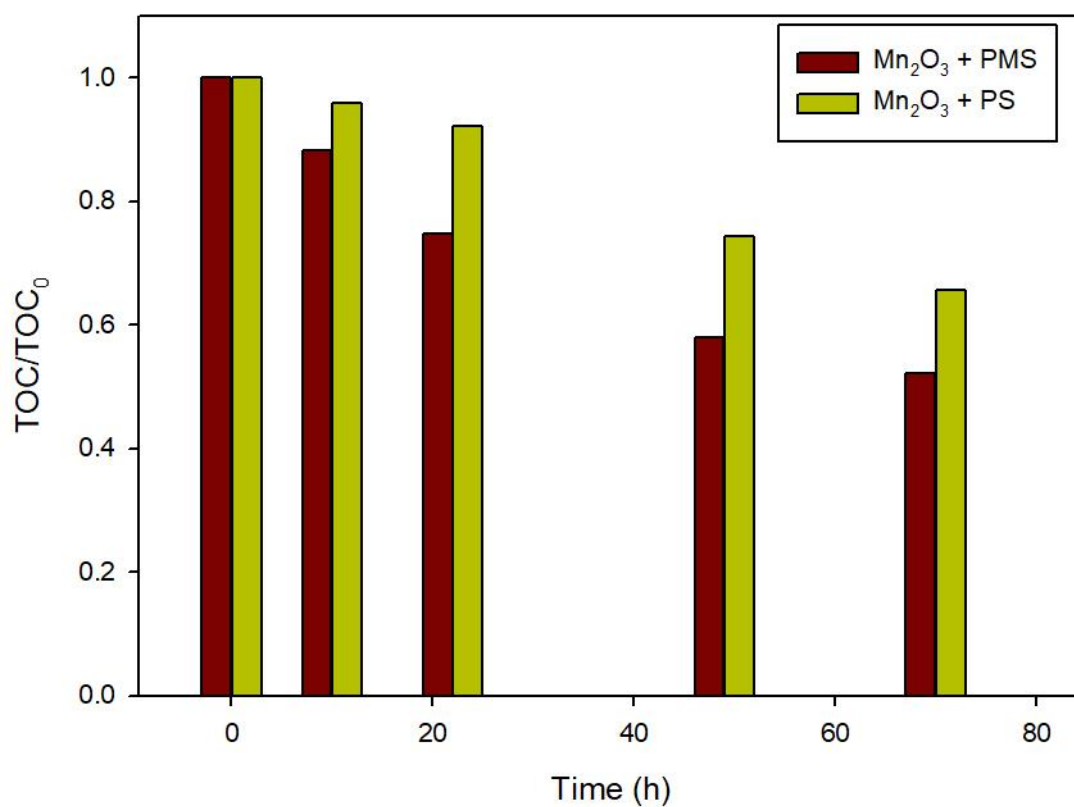
636 **Fig. 6.** Proposed degradation pathways of CAF in Mn<sub>2</sub>O<sub>3</sub>-activated PS and PMS systems. P2

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

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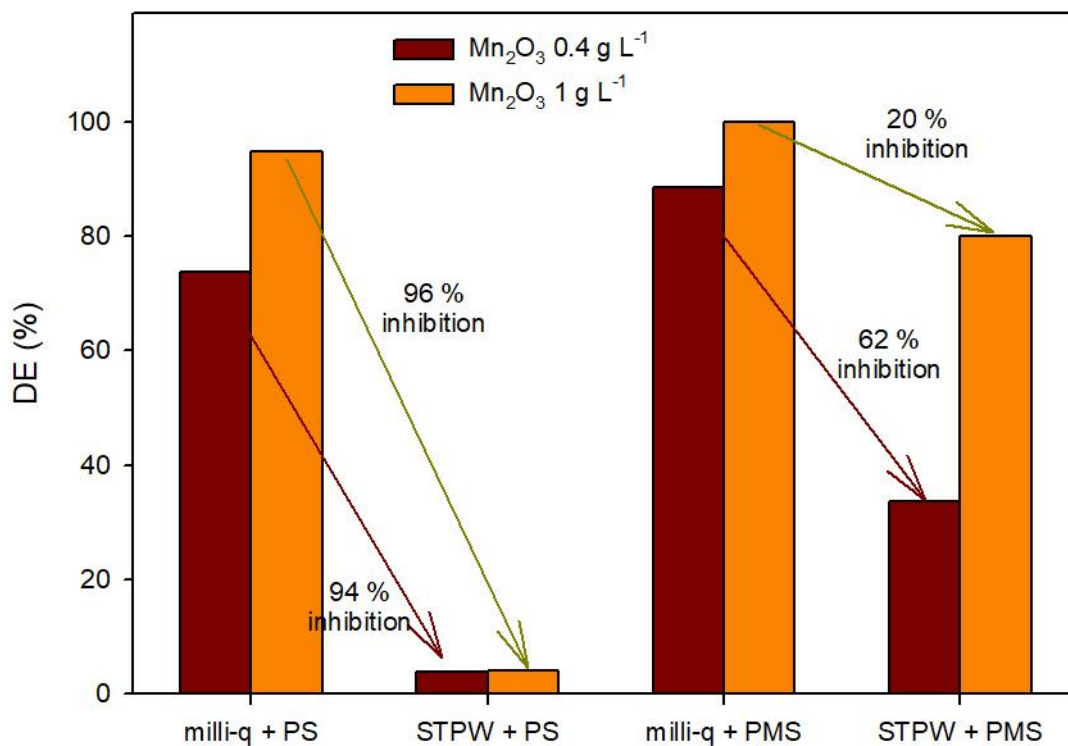
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641

642 **Fig. 7.** TOC decrease with time in Mn<sub>2</sub>O<sub>3</sub>-activated PS and PMS systems. Experimental  
 643 conditions: [Mn<sub>2</sub>O<sub>3</sub>]<sub>0</sub> = 0.4 g L<sup>-1</sup>, [CAF]<sub>0</sub> = 25 μM, [PS]<sub>0</sub> = [PMS]<sub>0</sub> = 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<sup>-1</sup> of Mn<sub>2</sub>O<sub>3</sub>. PS and PMS concentrations were 5 mM and

649 the pH of solutions was 8.0 ± 0.2.