

The dominant role of the peroxymonosulfate radical for removing contaminants in a Fenton process with metabisulfite

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1 **First evidence of a key role of the peroxymonosulfate radical (SO<sub>5</sub><sup>•-</sup>) in a**  
2 **Fenton-like process based on metabisulfite**

3  
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14  
15 **Abstract**

16 The complex of iron and tetra-amido macrocyclic ligand (Fe-TAML), or Collin's reagent, is a  
17 promising catalyst to carry out Fenton-like degradation of contaminants. Previously, the  
18 ability of Fe-TAML to activate sulfite and metabisulfite (S<sub>2</sub>O<sub>5</sub><sup>2-</sup>, MBS) other than hydrogen  
19 peroxide, was reported, which could lead to cheaper, safer, and almost equally efficient  
20 oxidation of contaminants. However, the actual species involved in the Fe-TAML/MBS is not  
21 yet clear. Experiments reported here included a combination of tests involving the presence  
22 of various scavengers, modified atmospheres (air vs. N<sub>2</sub>), as well as measurements with  
23 electron paramagnetic resonance. Specifically, the tests were designed to positively exclude  
24 the presence of various active species and identify the most likely one. Thus, we theorize the  
25 involvement of the peroxymonosulfate radical (SO<sub>5</sub><sup>•-</sup>) in the presence of the Collin's reagent  
26 and metabisulfite and provide indirect evidence of the activity of this species. Specifically,  
27 we demonstrated that this system triggers a Fenton-like process, able to induce the  
28 degradation of phenol. The exploitation of such a reactive species may be favourable, as it  
29 may selectively induce the degradation of target contaminants in the presence of excess  
30 interfering agents, starting from the cheap, safe, and easily handled metabisulfite, which is an  
31 interesting substitute for hydrogen peroxide.

32  
33 **Keywords:** metabisulfite; peroxymonosulfate radical; Fenton; advanced oxidation.

## 35        **1. Introduction**

36 Fe-TAML (TAML = tetra-amido macrocyclic ligand), or Collin's reagent, is a promising  
37 catalyst to carry out Fenton-like degradation of contaminants. Its main advantages over the  
38 traditional Fenton reaction are as follows: (i) it can work in a wide pH range (7-11) (Collins  
39 2002, Chahbane et al. 2007, Beach et al. 2009), hence it may not require pH adjustment; (ii) it  
40 shows its highest efficiency at pH 10-11, allowing for co-precipitation of inorganic cations  
41 (e.g., toxic metals, cations), potentially present in the effluent, and for contaminant  
42 degradation in the same step, thereby avoiding *ad hoc* choice of pH conditions for  
43 degradation; (iii) the Fe-TAML complex avoids precipitation of iron as hydroxide, which  
44 would otherwise produce sludge, or add to sludge formed by precipitation of hydroxides of  
45 other metals and, finally, (iv) Fe-TAML is a catalyst with high turn-over number, which  
46 ensures high process efficiency.

47 In our previous work (Farinelli et al. 2019), the ability of Fe-TAML to activate sulfite and  
48 metabisulfite (MBS) other than hydrogen peroxide was reported. The use of MBS in place of  
49 hydrogen peroxide in advanced oxidation processes (AOPs) is favourable, since MBS is  
50 much cheaper, safer, and almost equally efficient toward contaminant degradation compared  
51 to hydrogen peroxide (Farinelli et al. 2021). The ability of Fe-TAML/MBS to degrade toxic  
52 emerging contaminants in water was observed, in a comparable way as the Fe-TAML/H<sub>2</sub>O<sub>2</sub>  
53 system, with a marked preference of both reagents for electron-rich aromatic compounds  
54 (e.g., phenols). Previous literature conclusively proved that Fe-TAML/H<sub>2</sub>O<sub>2</sub> generates ferryl  
55 as active species (Chahbane et al. 2007, Ghosh et al. 2008), which is more selective (i.e., able  
56 to discriminate among different contaminants) if compared with the hydroxyl radical that is  
57 the main reactive species in Fenton reaction at acidic pH (Miklos et al. 2018, Wang et al.  
58 2019, Coha et al. 2021). By use of •OH and SO<sub>4</sub><sup>•-</sup> radical quenchers, such as 2-propanol (2-  
59 PrOH) and t-butanol (t-BuOH) (Buxton et al. 1988, Neta et al. 1988), we were able to show  
60 that these radicals are not involved in degradation processes triggered by Fe-TAML/MBS.  
61 Still, it is not yet clear whether the actual species involved in the Fe-TAML/MBS process is  
62 ferryl, as in the case of Fe-TAML/H<sub>2</sub>O<sub>2</sub>. Therefore, this work aims at understanding the  
63 details of the reaction pathways triggered by Fe-TAML/MBS, and at proving which reactive  
64 species is/are involved. Such understanding would support the safe and effective employment  
65 of an organometallic catalyst able to activate non-conventional radical species, thus opening  
66 the route to a more sustainable catalytic process.

## 67        **2. Experimental**

68 Degradation experiments were carried out at room temperature, under continuous stirring, for  
69 a maximum of 30 min, at pH 7 and 10, in 10 mL of 0.01 M phosphate buffer. Substrates to be  
70 degraded (phenol, nitrobenzene, spin traps) were reacted with Fe-TAML and: (i) MBS, (ii)  
71 H<sub>2</sub>O<sub>2</sub>, or (iii) sulfite, where addition of the latter reagents was carried out in multiple steps, to  
72 avoid them to reach excessively high concentration values at a single time point, hence  
73 prevent quenching of the reactive species. The time trend of phenol and nitrobenzene was  
74 monitored by liquid chromatography (HPLC-DAD), while the spin traps DMPO (5,5-

75 dimethyl-1-pyrroline-N-oxide) or TEMP (2,2,6,6-tetramethylpiperidine) were used to detect  
76 radical species by EPR (electron paramagnetic resonance). Further details are provided in  
77 Text S1 of the Supporting Material (hereinafter, SM).

### 78 3. Results and Discussion

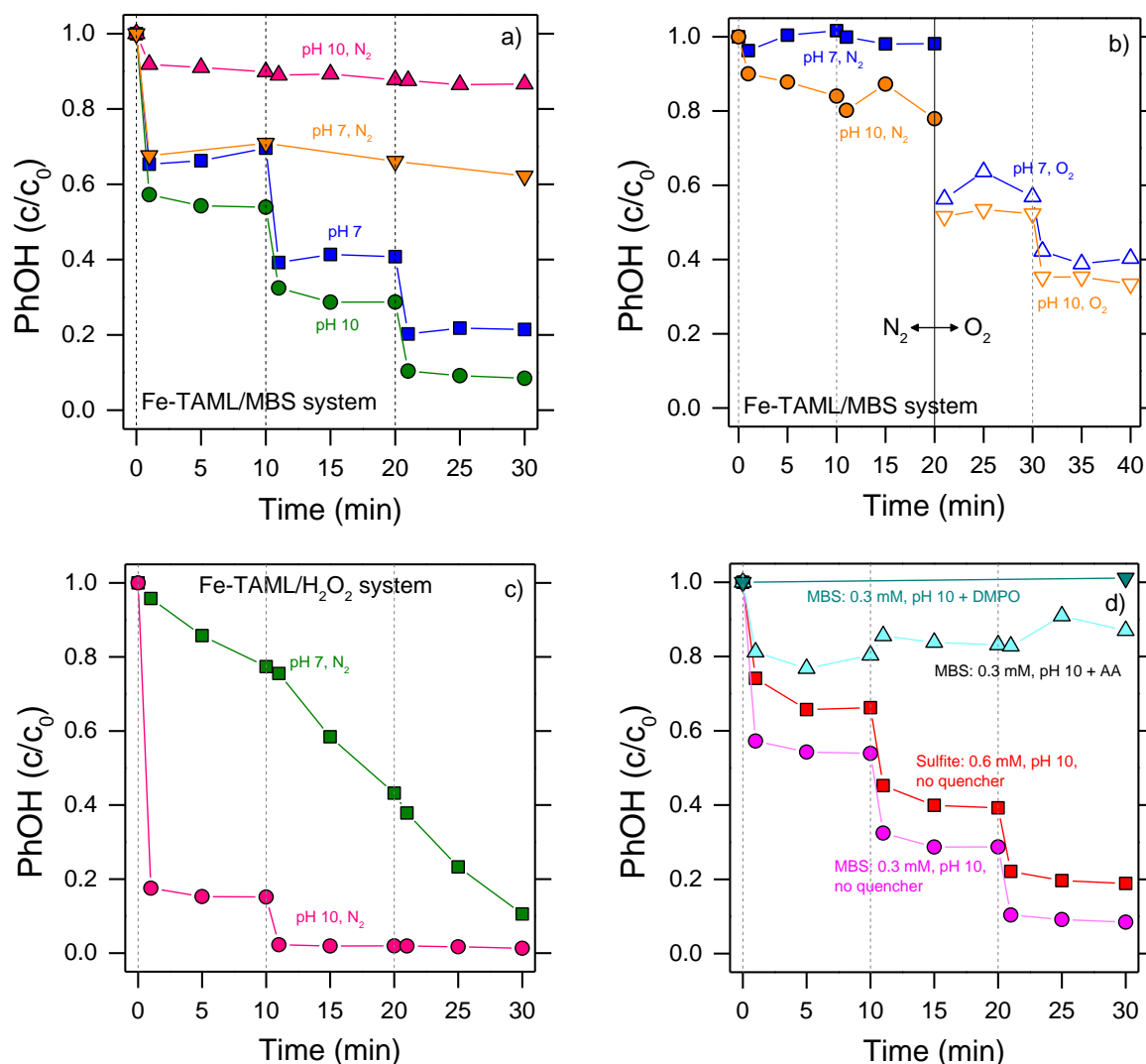
#### 79 3.1 Evidence suggests involvement of oxygen and of a radical active species

80 **Fig. 1** shows the activity of the Fe-TAML/MBS (or H<sub>2</sub>O<sub>2</sub>, or sulfite) system toward phenol  
81 (PhOH), in different conditions. **Fig. 1a, b** shows that an inert (N<sub>2</sub>) atmosphere can inhibit the  
82 degradation of PhOH, in the case of Fe-TAML/MBS. In contrast, the reaction activated by  
83 Fe-TAML/H<sub>2</sub>O<sub>2</sub> occurs efficiently under nitrogen as well (**Fig. 1c**). These results may  
84 suggest that different reactive species may be involved in the two systems. Furthermore,  
85 although PhOH degradation by Fe-TAML/MBS is not active under nitrogen, it resumes as  
86 soon as oxygen is added to the reaction environment (**Fig. 1b**). Moreover, one does not need  
87 to further add MBS to start degradation, as residual MBS previously added into the reaction  
88 system may be sufficient. Some MBS decomposition under N<sub>2</sub> cannot be ruled out, which  
89 would explain the lower efficiency of the reactions in **Fig. 1b** compared to those presented in  
90 **Fig. 1a**. This experiment strongly supports the key involvement of oxygen in PhOH  
91 degradation with Fe-TAML/MBS.

92 Considering that MBS is a reductant, which has often been used as •OH scavenger to quench  
93 the traditional Fenton process (Bektaşoğlu et al. 2006), it is not possible to exclude that Fe-  
94 TAML/MBS may trigger a reductive pathway. To test this hypothesis, PhOH was replaced  
95 with nitrobenzene as substrate, to check for transformation intermediates. Indeed,  
96 nitrobenzene is well known to undergo reduction to aniline (Daems et al. 2018), while it is  
97 oxidized to nitrophenols in the presence of oxidizing species, such as •OH (Vione et al.  
98 2016). Interestingly, nitrobenzene was not degraded at all by Fe-TAML/MBS, and no  
99 intermediates (either aniline or nitrophenols) were detected as a consequence. On the one  
100 side, this finding excludes that effective reducing agents may be produced by Fe-  
101 TAML/MBS. On the other hand, it provides evidence against •OH as reactive species, while  
102 Fe-TAML/MBS is likely to involve a mildly oxidising agent, which degrades electron-rich  
103 PhOH, but it is ineffective towards electron-poor nitrobenzene.

104 As neither 2-PrOH nor t-BuOH are reported to behave as effective quenchers for degradation  
105 by Fe-TAML/MBS (Farinelli et al. 2019), we searched for alternative reaction quenchers.  
106 Ascorbic acid (AA) is a strong anti-oxidant and radical scavenger (Niki 1991) (although its  
107 possible ability to scavenge non-radical oxidants cannot be ruled out), and we verified its  
108 effectiveness in the present context (see **Fig. 1d**). Moreover, further evidence for the possible  
109 involvement of a radical species in the process was sought by using DMPO to trap radicals  
110 and allow for their characterization. **Fig. 1d** shows that DMPO is very efficient as reaction  
111 quencher, thereby suggesting that an active radical species could be involved. Below, we  
112 provide additional results to identify such radical.

113

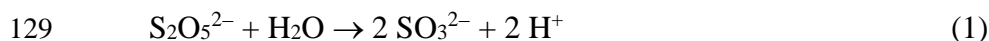


114 **Fig. 1.** Phenol (PhOH) degradation by Fe-TAML. Reagents were: a), b) MBS; c)  $\text{H}_2\text{O}_2$ ; d) MBS or  
 115 sulfite. “ $\text{N}_2$ ” means that the reaction occurred under nitrogen. The reactions occurred in phosphate  
 116 buffer (10 mM), by adding 0.1 mM of reagent (MBS,  $\text{H}_2\text{O}_2$ ) or 0.2 mM (sulfite) every 10 minutes (the  
 117 vertical dashed lines in all the graphs indicate the times when an aliquot of reagent was added). Initial  
 118 conditions were  $[\text{Fe-TAML}] = 0.01 \text{ mM}$  and  $[\text{PhOH}] = 0.1 \text{ mM}$ . The solid line in graph b) indicates  
 119 the step where oxygen at 500 mBar was added to the reaction environment. In d), AA = ascorbic acid;  
 120 DMPO = 5,5-dimethyl-1-pyrroline N-oxide (radical trap). Lines connecting the data points are only  
 121 intended as guides for the eye. The results suggest the involvement of oxygen and of an active radical  
 122 species in PhOH degradation with Fe-TAML/MBS.

123

124 **3.2 Evidence suggests that the active species is an S-based radical, with the exclusion of**  
125 **SO<sub>4</sub><sup>•-</sup>**

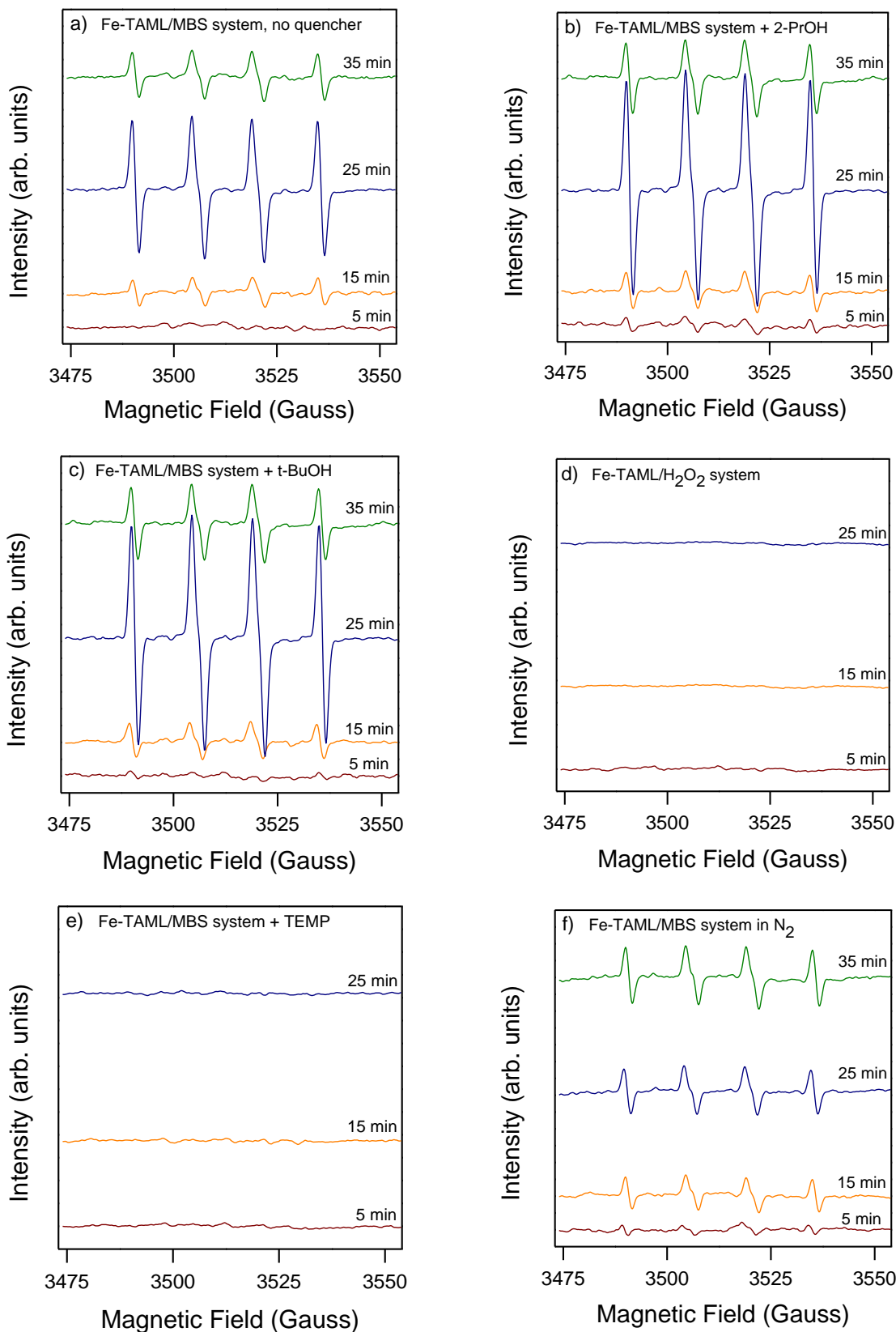
126 A potentially important issue is that MBS (S<sub>2</sub>O<sub>5</sub><sup>2-</sup>) gives sulfite (SO<sub>3</sub><sup>2-</sup>) in aqueous solution  
127 (Maylor et al. 1971). Therefore, the Fenton reactivity of MBS could well be accounted for by  
128 SO<sub>3</sub><sup>2-</sup>.



130 To check for this issue, we carried out the degradation of PhOH + Fe-TAML, by replacing  
131 0.3 mM MBS with a double concentration (0.6 mM) of sulfite, in agreement with the  
132 stoichiometry of reaction (1). SO<sub>3</sub><sup>2-</sup> is indeed Fenton-active, although to a slightly lesser  
133 extent than MBS (**Fig. 1d**). MBS may react as SO<sub>3</sub><sup>2-</sup> under Fenton conditions (the Fenton-  
134 like reactivity of sulfite is shown in several studies) (Jia et al. 2019), but MBS is a more  
135 effective way to add sulfite to the system. Sulfite is actually unstable in aqueous solution in  
136 the presence of oxygen; therefore, the presence of high concentrations of SO<sub>3</sub><sup>2-</sup> from the very  
137 start could trigger degradation/auto-oxidation reactions. In contrast, MBS would yield sulfite  
138 more gradually, minimizing any self-degradation process involving sulfite.

139 Experiments were carried out by using the EPR technique, to get insight into the possible  
140 radical species which occur(s) in the Fe-TAML/MBS system. We separately used two spin  
141 traps, namely, DMPO that reacts with a plethora of different radicals, and TEMP, which is  
142 specific for singlet oxygen. The DMPO data are shown in **Fig. 2a-d**. First of all, EPR  
143 measurements allowed for the detection of a radical species that formed gradually in the  
144 system, reaching a maximum around 25 min after the start of the reaction, and declining  
145 afterwards (**Fig. 2a**). Interestingly, the detected radical was not quenched by **either** 2-PrOH **or**  
146 t-BuOH (**Fig. 2b/c**). This finding is consistent with our previous results (Farinelli et al. 2019),  
147 that neither 2-PrOH nor t-BuOH are able to inhibit the degradation of PhOH under  
148 comparable conditions.

149 Additional experiments showed that the same radical(s) detected with Fe-TAML/MBS were  
150 not formed in Fe-TAML/H<sub>2</sub>O<sub>2</sub> (**Fig. 2d**), thereby suggesting that the reactive species could be  
151 different in Fe-TAML/MBS, compared to Fe-TAML/H<sub>2</sub>O<sub>2</sub> (in the latter case, ferryl is well  
152 known to play a role) (Ghosh et al. 2008). Moreover, significant occurrence of singlet oxygen  
153 in Fe-TAML/MBS could be excluded by TEMP addition (**Fig. 2e**).



154 **Fig. 2.** EPR spectra at different reaction times: a) Fe-TAML 0.01 mM, PhOH 0.1 mM, MBS 0.3 mM; b) Fe-  
 155 TAML 0.01 mM, PhOH 0.1 mM, MBS 0.3 mM, 2-PrOH 133 mM; c) Fe-TAML 0.01 mM, PhOH 0.1 mM,  
 156 MBS 0.3 mM, t-BuOH 133 mM; d) Fe-TAML 0.01 mM, PhOH 0.1 mM, H<sub>2</sub>O<sub>2</sub> 0.3 mM; e) Fe-TAML 0.01 mM,  
 157 PhOH 0.1 mM, MBS 0.3 mM; f) Fe-TAML 0.01 mM, PhOH 0.1 mM, MBS 0.3 mM under nitrogen. DMPO 17

158 mM was used as spin trap in a), b), c), d) and f), while in e) TEMP 17 mM was used as spin trap. The reactions  
159 occurred in the same conditions as those reported in Fig. 1, but all at pH 10, i.e., the best pH value observed for  
160 PhOH degradation. The results suggest that the active species is an S-based radical, with the exclusion of  $\text{SO}_4^{\bullet-}$ ,  
161 and that the pathway likely involves the sulfite radical ( $\text{SO}_3^{\bullet-}$ ).

162

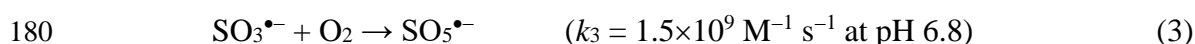
163 An initial examination of the EPR spectrum, obtained from DMPO/PhOH/Fe-TAML/MBS  
164 (**Fig. 2a**), suggested that the detected species would be an S-based radical, with the exclusion  
165 of  $\text{SO}_4^{\bullet-}$  for the reasons explained above (inability of either 2-PrOH or t-BuOH to inhibit  
166 phenol degradation; Farinelli et al., 2019). Although different radicals could in principle  
167 account for EPR observations, simulations of the EPR spectra (see SM, **Fig. S1**) suggest that  
168 the sulfite radical ( $\text{SO}_3^{\bullet-}$ ) is a peculiarly good match. The parameters of the simulation were  
169 as follows:  $a_N = 14.5$  Gauss;  $a_H = 16.027$  Gauss;  $g = 2.0055$  (correlation coefficient =  
170 0.9995), in agreement with literature data for the DMPO- $\text{SO}_3^{\bullet-}$  adduct (Covello and  
171 Thompson 1985).

### 172 **3.3 Main thesis: peroxymonosulfate radical ( $\text{SO}_5^{\bullet-}$ ) is the active species, with sulfite** 173 **radical ( $\text{SO}_3^{\bullet-}$ ) acting as a precursor in the presence of oxygen**

174 The formation of  $\text{SO}_3^{\bullet-}$  in the studied system can be easily explained:



176 The radical  $\text{SO}_3^{\bullet-}$  is not highly reactive with organic compounds (Neta et al. 1988), but we  
177 speculate that it is not the real reactive species, but rather its precursor. Indeed, Neta *et al.*  
178 reported that  $\text{SO}_3^{\bullet-}$  is able to react with oxygen in solution, to generate a more powerful  
179 oxidant species, the peroxymonosulfate radical ( $\text{SO}_5^{\bullet-}$ ), according to fast reaction (3):



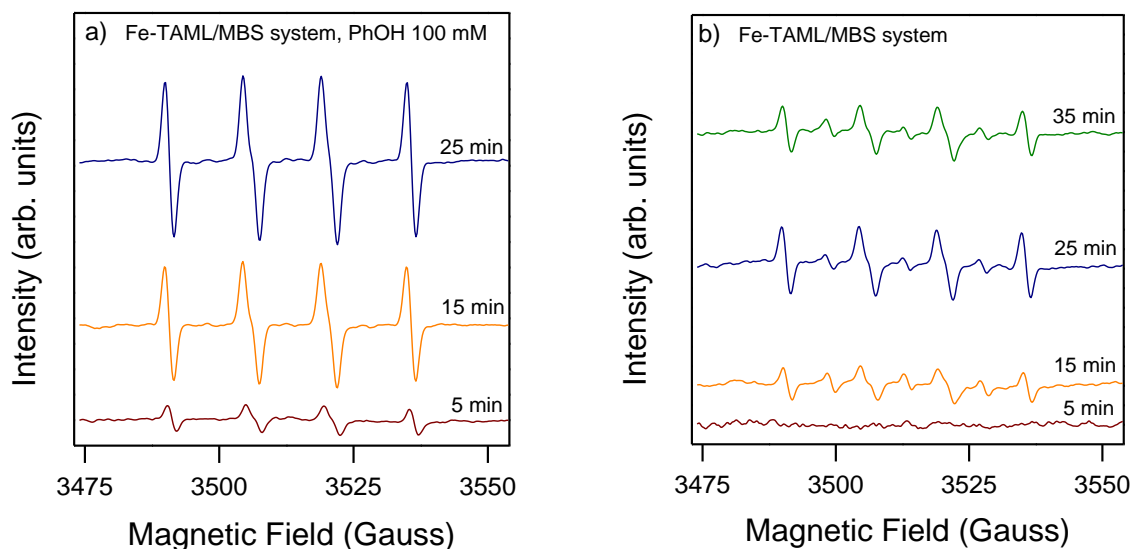
181 Interestingly, the radical  $\text{SO}_5^{\bullet-}$  shows a certain reactivity toward organic compounds ( $k \sim$   
182  $10^6 \div 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ), and is most reactive at basic pH (10-11) (Neta et al. 1988). This is exactly  
183 the pH range where Fe-TAML/MBS shows the highest degradation potential (see our  
184 previous work, and **Fig. 1a**), although it should be considered that also Fe-TAML/ $\text{H}_2\text{O}_2$   
185 reacts best under basic conditions. Another interesting issue is that  $\text{SO}_5^{\bullet-}$  reacts fast with AA  
186 ( $k \sim 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) (Neta et al. 1988), in keeping with the observed behaviour of AA as  
187 effective reaction quencher (see **Fig. 1d**).

188 Moreover, it is known that neither  $\text{SO}_3^{\bullet-}$  nor  $\text{SO}_5^{\bullet-}$  are reactive towards t-BuOH and 2-PrOH  
189 (Neta and Huie 1985, Neta et al. 1988). In our case, the inability of either alcohol to scavenge  
190  $\text{SO}_3^{\bullet-}$  would explain why this radical was still detected by EPR, upon addition of either t-  
191 BuOH or 2-PrOH (see **Fig. 2b,c**). Furthermore, inability to scavenge **either**  $\text{SO}_3^{\bullet-}$  **or**  $\text{SO}_5^{\bullet-}$   
192 would explain why the two alcohols were not able to inhibit PhOH degradation by Fe-  
193 TAML/MBS (see our previous work, Farinelli et al. 2019).

194 It is known that the  $\text{SO}_5^{\bullet-}$  radicals will go through self-combination to yield  $\text{SO}_4^{\bullet-}$  radicals  
195 and  $\text{O}_2$  (Das 2001). If the degradation of phenol involved  $\text{SO}_4^{\bullet-}$ , the reaction should be  
196 quenched in the presence of 2-PrOH or t-BuOH. However, quenching of phenol degradation  
197 by either alcohol was not observed. Because the couple 2-PrOH/t-BuOH is able to efficiently  
198 scavenge both  $\bullet\text{OH}$  and  $\text{SO}_4^{\bullet-}$ , it is possible to exclude these two radicals as potential reactive  
199 species that degrade phenol. What likely happens here is that reaction between phenol and  
200  $\text{SO}_5^{\bullet-}$  prevents self-combination of  $\text{SO}_5^{\bullet-}$  radicals to give  $\text{SO}_4^{\bullet-}$ .

201 Our working hypothesis is that: (i) the Fe-TAML/MBS system first yields  $\text{SO}_3^{\bullet-}$  in reaction  
202 (2), and  $\text{SO}_3^{\bullet-}$  is then transformed into  $\text{SO}_5^{\bullet-}$  in the presence of oxygen (reaction 3), from  
203 which one derives that (ii)  $\text{SO}_5^{\bullet-}$  is the actual reactive species involved in degradation  
204 processes. The formation of  $\text{SO}_3^{\bullet-}$  should not require oxygen and, coherently,  $\text{SO}_3^{\bullet-}$  was also  
205 detected by EPR under  $\text{N}_2$  atmosphere (**Fig. 2f**). However, PhOH degradation by Fe-  
206 TAML/MBS was not operational under  $\text{N}_2$  (**Fig. 1**), which further supports our hypothesis  
207 that  $\text{SO}_5^{\bullet-}$  was involved in PhOH degradation rather than  $\text{SO}_3^{\bullet-}$  (indeed,  $\text{SO}_5^{\bullet-}$  cannot be  
208 formed without  $\text{O}_2$ ). The reason why  $\text{SO}_5^{\bullet-}$  was not detected by EPR, even in the presence of  
209 air, can be found in the kinetic competition for  $\text{SO}_3^{\bullet-}$  between the spin trap DMPO (17 mM)  
210 and  $\text{O}_2$  (0.3 mM in air-equilibrated solutions). DMPO usually reacts at diffusion control with  
211 radicals ( $k \sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ), while the reaction (3) between  $\text{SO}_3^{\bullet-}$  and  $\text{O}_2$  has  $k_3 = 1.5 \times 10^9 \text{ M}^{-1}$   
212  $\text{ s}^{-1}$  (Neta et al. 1988). As a consequence,  $\text{SO}_3^{\bullet-}$  would react with 17 mM DMPO almost  $10^3$   
213 times faster than with 0.3 mM  $\text{O}_2$ . This means that DMPO would scavenge  $\text{SO}_3^{\bullet-}$  almost  
214 entirely and prevent the subsequent formation of  $\text{SO}_5^{\bullet-}$  at significant concentrations. This  
215 observation also explains why DMPO was so effective at inhibiting PhOH degradation by Fe-  
216 TAML/MBS (**Fig. 1d**).

217 Additional evidence against  $\text{SO}_3^{\bullet-}$  as the reactive species for PhOH degradation came from  
218 PhOH scavenging experiments, followed by EPR detection. The rationale here is that since  
219 PhOH is degraded by Fe-TAML/MBS, it has to react with the relevant reactive species.  
220 Therefore, it should be possible for PhOH to inhibit the formation of the adduct between  
221 DMPO and the reactive species, and to thus decrease the EPR signal, provided that PhOH  
222 concentration was high enough, and that the reactive species was actually responsible for the  
223 EPR signal. To enable proper scavenging, the concentration of PhOH was increased by 1000  
224 times, compared to previous experiments (i.e., 100 mM vs. 0.1 mM). The results (**Fig. 3a**)  
225 suggest that  $\text{SO}_3^{\bullet-}$  was also detected, which makes evidence against significant reaction  
226 between phenol and  $\text{SO}_3^{\bullet-}$ , and rules out  $\text{SO}_3^{\bullet-}$  as the ultimate reactive species for phenol  
227 degradation. Finally, further experiment showed that PhOH is not needed for radical  
228 formation (**Fig. 3b**), which is an expected finding if the detected radical is  $\text{SO}_3^{\bullet-}$ , formed in  
229 reaction (2).



230 **Fig. 3.** EPR spectra at different reaction times of the systems: a) Fe-TAML 0.01 mM, PhOH 100 mM, MBS 0.3  
 231 mM; b) Fe-TAML 0.01 mM, MBS 0.3 mM. DMPO 17 mM was used as spin trap in a) and b). The reactions  
 232 occurred in the same conditions as those reported in **Fig. 1, 2**. The results suggest that  $\text{SO}_5^{\bullet-}$  is the ultimate  
 233 active species, formed from sulfite in the presence of dissolved oxygen.

234

235 Based on the whole data set, we can conclude that the Fe-TAML/MBS system initially yields  
 236  $\text{SO}_3^{\bullet-}$  that, in the presence of dissolved oxygen, gives the more powerful oxidant  $\text{SO}_5^{\bullet-}$ . The  
 237 latter can be involved in the degradation of electron-rich organic compounds, such as PhOH  
 238 (but not nitrobenzene, for instance). To successfully quench PhOH degradation, a compound  
 239 should either react directly with  $\text{SO}_5^{\bullet-}$  (AA), or scavenge  $\text{SO}_3^{\bullet-}$  (DMPO), thereby preventing  
 240  $\text{SO}_5^{\bullet-}$  formation. It should be noted that direct evidence of  $\text{SO}_5^{\bullet-}$  formation was deduced by  
 241 eliminating other possible reactions. Indeed, the observations of this led the authors to  
 242 propose the initial formation of  $\text{SO}_5^{\bullet-}$ , but we cannot exclude the presence of radicals formed  
 243 upon transformation of the substrate; in any case,  $\text{SO}_5^{\bullet-}$  should be initially formed to trigger  
 244 such reactions.

#### 245 4. Conclusion

246 In this study, we propose  $\text{SO}_5^{\bullet-}$  as the primary reactive species involved in the system Fe-  
 247 TAML/MBS, even if  $\text{SO}_3^{\bullet-}$  is the species detected by EPR.  $\text{SO}_5^{\bullet-}$  would be extremely  
 248 promising, since it shows comparable reactivity and selectivity of a metal-based active  
 249 species, such as ferryl, but is generated by employing cheaper and safer reagent (MBS instead  
 250 of  $\text{H}_2\text{O}_2$ ). Moreover,  $\text{SO}_5^{\bullet-}$  is significantly less reactive but more selective than  $\bullet\text{OH}$  (see **Fig.**  
 251 **S3**, SM), thus it could induce degradation of some contaminants even in the presence of an  
 252 excess of interfering species.

253 Despite the generation of  $\text{SO}_3^{\bullet-}$  or other sulfate radicals by nanoparticles or transition metals  
 254 is well studied in the literature (Ranguelova et al. 2012, Wu et al. 2018, Li et al. 2020, Wu et  
 255 al. 2021, Wu et al. 2022), the generation of sulfate radical active species through a

256 biodegradable organometallic catalyst has not been investigated. This pathway of active  
257 species formation can open new routes in the design of more sustainable and highly effective  
258 catalytic processes. The employment of an organometallic catalyst potentially allows for an  
259 easier optimization of the process by modifying the chemical structure of the catalyst, while  
260 the same flexibility is not possible in the case of transition metals or nanoparticles.  
261 Furthermore, the latter species are not biodegradable or easy to remove, hence may be  
262 considered less sustainable options compared to organometals. Another interesting aspect is  
263 that, although  $\text{SO}_5^{\bullet-}$  is a highly oxidative radical, it has been observed and here theorized of  
264 being generated in systems containing reductive reagents (Jiang et al. 2015), e.g., MBS.

265

## 266 **Acknowledgments**

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282 data curation, writing – original draft, visualization; Angela Garcia Gil: investigation, data  
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