

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

Original

The dominant role of the peroxymonosulfate radical for removing contaminants in a Fenton process with metabisulfite / Farinelli, G.; Gil, A. G.; Marugan, J.; Minella, M.; Fabbri, D.; Laurenti, E.; Tiraferri, A.; Vione, D.. - In: ENVIRONMENTAL CHEMISTRY LETTERS. - ISSN 1610-3661. - (2024). [10.1007/s10311-023-01645-8]

Availability:

This version is available at: 11583/2982026 since: 2023-09-12T07:11:26Z

Publisher:

Springer

Published

DOI:10.1007/s10311-023-01645-8

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

Springer postprint/Author's Accepted Manuscript

This version of the article has been accepted for publication, after peer review (when applicable) and is subject to Springer Nature's AM terms of use, but is not the Version of Record and does not reflect post-acceptance improvements, or any corrections. The Version of Record is available online at: <http://dx.doi.org/10.1007/s10311-023-01645-8>

(Article begins on next page)

1 **First evidence of a key role of the peroxymonosulfate radical (SO₅^{•-}) in a**
2 **Fenton-like process based on metabisulfite**

3
4 **Giulio Farinelli,^{a*} Angela Garcia Gil,^b Javier Marugan,^b Marco Minella,^c Debora**
5 **Fabbri,^c Enzo Laurenti,^c Alberto Tiraferri,^a Davide Vione^{c*}**

6
7 * Giulio Farinelli, giulio.farinelli@umontpellier.fr

8 * Davide Vione, davide.vione@unito.it

9 ^a *Department of Environment, Land and Infrastructure Engineering, Politecnico di Torino, Corso*
10 *Duca degli Abruzzi, 24, Torino 10129, Italy*

11 ^b *Department of Chemical and Environmental Technology, ESCET, Universidad Rey Juan Carlos, C/*
12 *Tulipán s/n, Móstoles, Madrid 28933, Spain*

13 ^c *Dipartimento di Chimica, Università di Torino, Via Pietro Giuria 5, Torino 10125, Italy*

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 (S₂O₅²⁻, 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. N₂), 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 (SO₅^{•-}) 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/H₂O₂
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/H₂O₂ 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 SO₄^{•-} 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/H₂O₂. 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 H₂O₂, 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

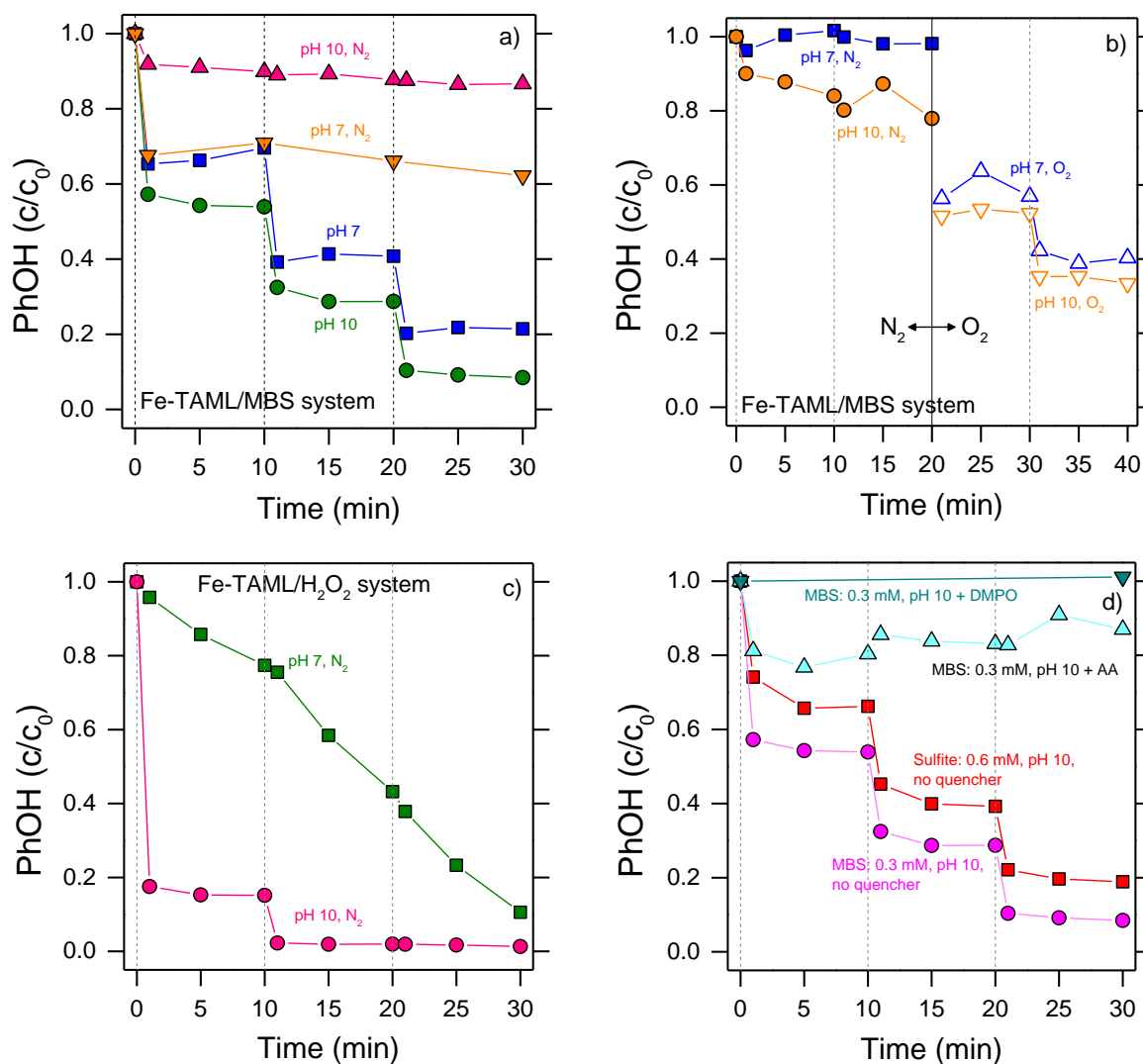
79 3.1 Evidence suggests involvement of oxygen and of a radical active species

80 **Fig. 1** shows the activity of the Fe-TAML/MBS (or H₂O₂, or sulfite) system toward phenol
81 (PhOH), in different conditions. **Fig. 1a, b** shows that an inert (N₂) atmosphere can inhibit the
82 degradation of PhOH, in the case of Fe-TAML/MBS. In contrast, the reaction activated by
83 Fe-TAML/H₂O₂ 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 N₂ 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

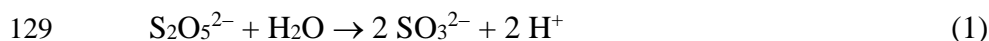


114 **Fig. 1.** Phenol (PhOH) degradation by Fe-TAML. Reagents were: a), b) MBS; c) H₂O₂; d) MBS or
 115 sulfite. “N₂” means that the reaction occurred under nitrogen. The reactions occurred in phosphate
 116 buffer (10 mM), by adding 0.1 mM of reagent (MBS, H₂O₂) or 0.2 mM (sulfite) every 10 minutes (the
 117 vertical dashed lines in all the graphs indicate the times when an aliquot of reagent was added). Initial
 118 conditions were [Fe-TAML] = 0.01 mM and [PhOH] = 0.1 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 **SO₄^{•-}**

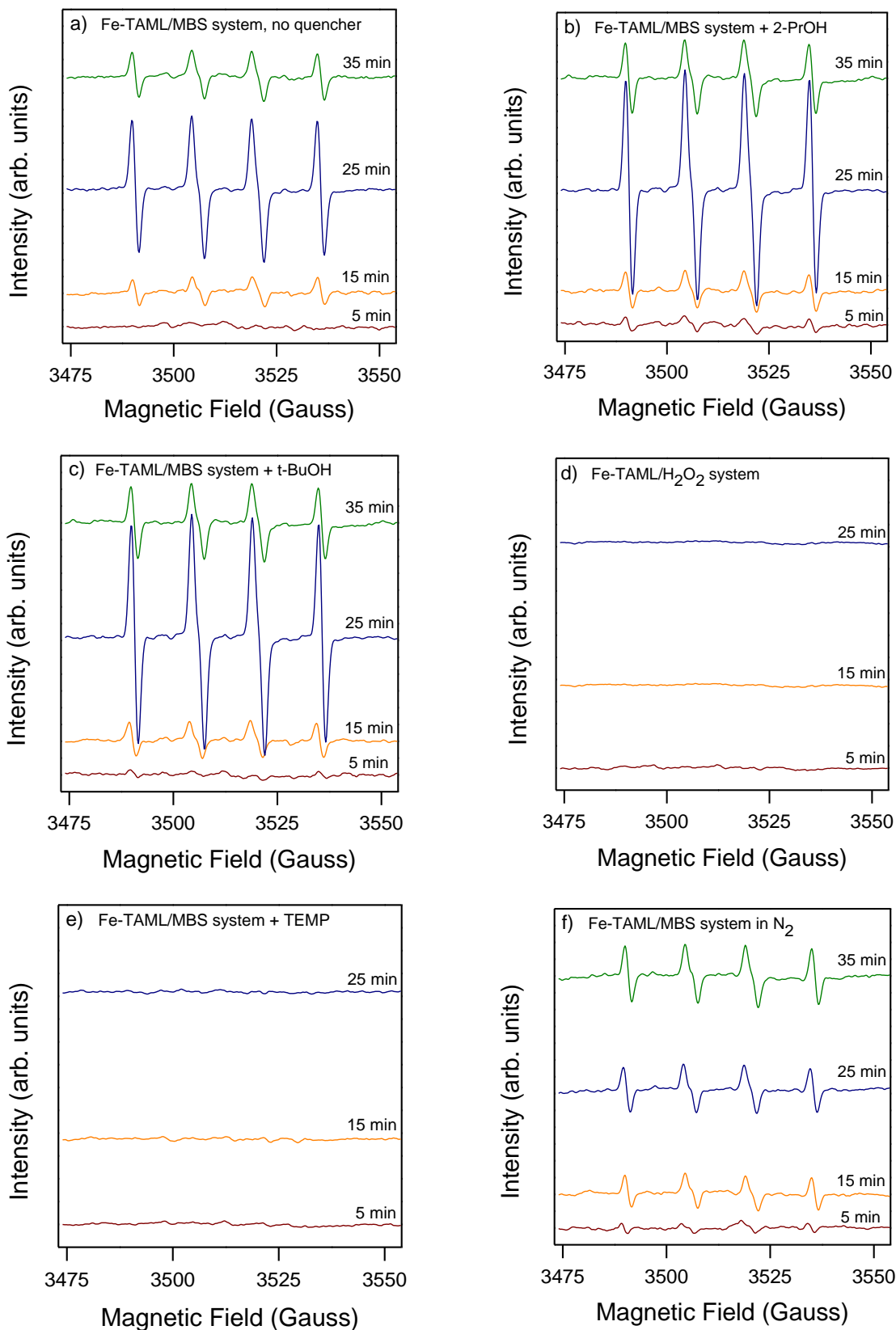
126 A potentially important issue is that MBS (S₂O₅²⁻) gives sulfite (SO₃²⁻) in aqueous solution
127 (Maylor et al. 1971). Therefore, the Fenton reactivity of MBS could well be accounted for by
128 SO₃²⁻.



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). SO₃²⁻ is indeed Fenton-active, although to a slightly lesser
133 extent than MBS (**Fig. 1d**). MBS may react as SO₃²⁻ 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 SO₃²⁻ 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/H₂O₂ (**Fig. 2d**), thereby suggesting that the reactive species could be
151 different in Fe-TAML/MBS, compared to Fe-TAML/H₂O₂ (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, H₂O₂ 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

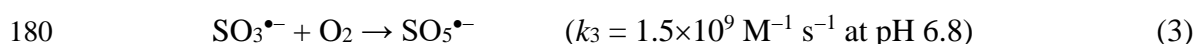
163 An initial examination of the EPR spectrum, obtained from DMPO/PhOH/Fe-TAML/MBS
164 (**Fig. 2a**), suggested that the detected species would be an S-based radical, with the exclusion
165 of $\text{SO}_4^{\bullet-}$ for the reasons explained above (inability of either 2-PrOH or t-BuOH to inhibit
166 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):



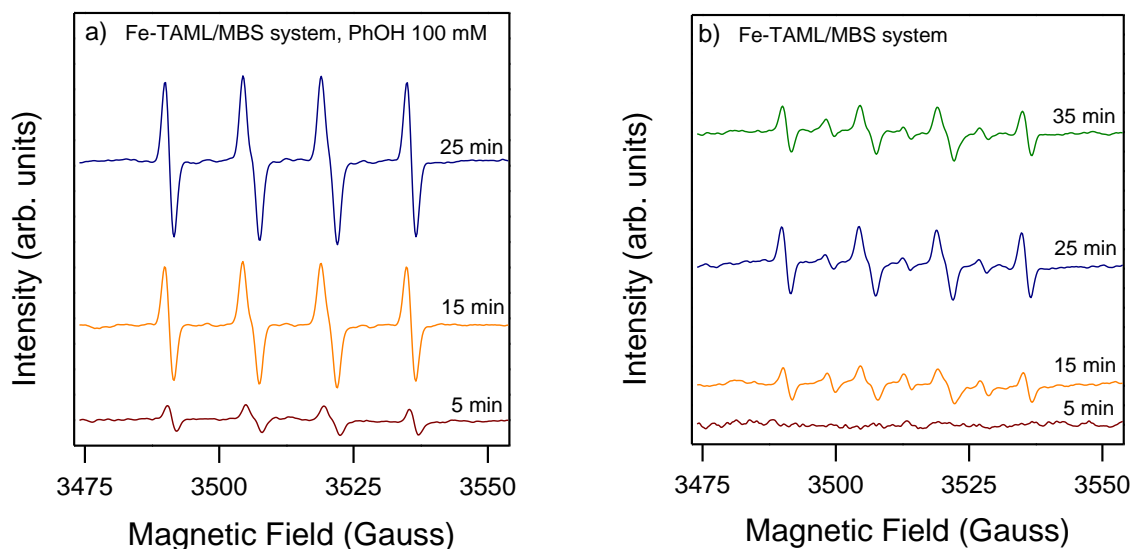
181 Interestingly, the radical $\text{SO}_5^{\bullet-}$ shows a certain reactivity toward organic compounds ($k \sim$
182 $10^6 \div 10^8 \text{ M}^{-1} \text{ s}^{-1}$), and is most reactive at basic pH (10-11) (Neta et al. 1988). This is exactly
183 the pH range where Fe-TAML/MBS shows the highest degradation potential (see our
184 previous work, and **Fig. 1a**), although it should be considered that also Fe-TAML/ H_2O_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 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 N_2 atmosphere (**Fig. 2f**). However, PhOH degradation by Fe-
206 TAML/MBS was not operational under 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 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 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 O_2 has $k_3 = 1.5 \times 10^9 \text{ M}^{-1}$
212 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 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 H_2O_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**

267 We thank the support of Politecnico di Torino and Università degli Studi di Torino. MM and
268 DV **acknowledge** support from the Project CH4.0 under the MIUR program "Dipartimenti di
269 Eccellenza 2023-2027" (CUP: D13C2200352001).

270

271 **Declarations**

272 **Funding:** Politecnico di Torino, Università degli Studi di Torino, Italian Ministry of
273 University

274 **Conflicts of interest/Competing interests:** There are not conflict of interests/competing
275 interests to declare.

276 **Ethics approval:** Not applicable.

277 **Consent to participate:** Not applicable.

278 **Consent for publication:** All authors agree on the publication.

279 **Availability of data and material:** The data will be made available upon request.

280 **Code availability:** Not applicable.

281 **Authors' contributions:** Giulio Farinelli: conceptualization, methodology, investigation,
282 data curation, writing – original draft, visualization; Angela Garcia Gil: investigation, data
283 curation, validation; Javier Marugan: supervision, writing – review & editing; Marco
284 Minella: conceptualization, visualization, supervision, writing – original draft, resources;
285 Debora Fabbri: methodology, validation, writing – review & editing; Enzo Laurenti:
286 validation, writing – review & editing; Alberto Tiraferri: supervision, project administration,
287 funding acquisition, writing – review & editing; Davide Vione: conceptualization, formal
288 analysis, resources, writing – review & editing, supervision, project administration, funding
289 acquisition.

290

291 **References**

- 292 Beach ES, Duran JL, Horwitz CP et al (2009) Activation of Hydrogen Peroxide by an Fe-TAML
293 Complex in Strongly Alkaline Aqueous Solution: Homogeneous Oxidation Catalysis with
294 Industrial Significance. *Industrial & Engineering Chemistry Research* 48(15):7072-7076.
295 <https://doi.org/10.1021/ie9005723>
- 296 Bektaşoğlu B, Esin Çelik S, Özyürek M et al (2006) Novel hydroxyl radical scavenging antioxidant
297 activity assay for water-soluble antioxidants using a modified CUPRAC method. *Biochemical
298 and Biophysical Research Communications* 345(3):1194-1200.
299 <https://doi.org/10.1016/j.bbrc.2006.05.038>
- 300 Buxton GV, Greenstock CL, Helman WP et al (1988) Critical Review of rate constants for reactions
301 of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot\text{OH}/\cdot\text{O}^-$) in Aqueous Solution.
302 *Journal of Physical and Chemical Reference Data* 17(513) <https://doi.org/10.1063/1.555805>
- 303 Chahbane N, Popescu D-L, Mitchell DA et al (2007) FeIII–TAML-catalyzed green oxidative
304 degradation of the azo dye Orange II by H₂O₂ and organic peroxides: products, toxicity,
305 kinetics, and mechanisms. *Green Chemistry* 9(1):49-57. <https://doi.org/10.1039/B604990G>
- 306 Coha M, Farinelli G, Tiraferri A et al (2021) Advanced oxidation processes in the removal of organic
307 substances from produced water: Potential, configurations, and research needs. *Chemical
308 Engineering Journal* 414:128668. <https://doi.org/10.1016/j.cej.2021.128668>
- 309 Collins TJ (2002) TAML Oxidant Activators: A New Approach to the Activation of Hydrogen
310 Peroxide for Environmentally Significant Problems. *Accounts of Chemical Research*
311 35(9):782-790. <https://doi.org/10.1021/ar010079s>
- 312 Covello PS, Thompson JE (1985) Spin trapping evidence for formation of the sulfite radical anion
313 during chloroplast-mediated oxidation of bisulfite ion. *Biochimica et Biophysica Acta (BBA)*
314 - General Subjects 843(1):150-154. [https://doi.org/10.1016/0304-4165\(85\)90062-5](https://doi.org/10.1016/0304-4165(85)90062-5)
- 315 Daems N, Wouters J, Van Goethem C et al (2018) Selective reduction of nitrobenzene to aniline over
316 electrocatalysts based on nitrogen-doped carbons containing non-noble metals. *Applied
317 Catalysis B: Environmental* 226:509-522. <https://doi.org/10.1016/j.apcatb.2017.12.079>
- 318 Das TN (2001) Reactivity and Role of SO₅^{•-} Radical in Aqueous Medium Chain Oxidation of Sulfite
319 to Sulfate and Atmospheric Sulfuric Acid Generation. *The Journal of Physical Chemistry A*
320 105(40):9142-9155. <https://doi.org/10.1021/jp011255h>
- 321 Farinelli G, Giagnorio M, Ricceri F et al (2021) Evaluation of the effectiveness, safety, and feasibility
322 of 9 potential biocides to disinfect acidic landfill leachate from algae and bacteria. *Water
323 Research* 191:116801. <https://doi.org/10.1016/j.watres.2020.116801>
- 324 Farinelli G, Minella M, Sordello F et al (2019) Metabisulfite as an Unconventional Reagent for Green
325 Oxidation of Emerging Contaminants Using an Iron-Based Catalyst. *ACS Omega*
326 4(24):20732-20741. <https://doi.org/10.1021/acsomega.9b03088>
- 327 Ghosh A, Mitchell DA, Chanda A et al (2008) Catalase–Peroxidase Activity of Iron(III)–TAML
328 Activators of Hydrogen Peroxide. *Journal of the American Chemical Society* 130(45):15116-
329 15126. <https://doi.org/10.1021/ja8043689>
- 330 Jia L, Pei X, Yang F, 2019. Electrolysis-Assisted Mn(II)/Sulfite Process for Organic Contaminant
331 Degradation at Near-Neutral pH. *Water*.

- 332 Jiang B, Liu Y, Zheng J et al (2015) Synergetic Transformations of Multiple Pollutants Driven by
333 Cr(VI)–Sulfite Reactions. *Environmental Science & Technology* 49(20):12363-12371.
334 <https://doi.org/10.1021/acs.est.5b03275>
- 335 Li R, Dong H, Tian R et al (2020) Activation of sulfite by different Fe0-based nanomaterials for
336 oxidative removal of sulfamethazine in aqueous solution. *Separation and Purification*
337 *Technology* 250:117230. <https://doi.org/10.1016/j.seppur.2020.117230>
- 338 Maylor R, Gill JB, Goodall DC (1971) Some studies on anhydrous cobalt sulphite. *Journal of*
339 *Inorganic and Nuclear Chemistry* 33(7):1975-1979. [https://doi.org/10.1016/0022-](https://doi.org/10.1016/0022-1902(71)80558-4)
340 [1902\(71\)80558-4](https://doi.org/10.1016/0022-1902(71)80558-4)
- 341 Miklos DB, Remy C, Jekel M et al (2018) Evaluation of advanced oxidation processes for water and
342 wastewater treatment – A critical review. *Water Research* 139:118-131.
343 <https://doi.org/10.1016/j.watres.2018.03.042>
- 344 Neta P, Huie RE (1985) Free-radical chemistry of sulfite. *Environmental Health Perspectives* 64:209-
345 217. <https://doi.org/10.1289/ehp.8564209>
- 346 Neta P, Huie RE, Ross AB (1988) Rate Constants for Reactions of Inorganic Radicals in Aqueous
347 Solution. *Journal of Physical and Chemical Reference Data* 17(1027)
348 <https://doi.org/10.1063/1.555808>
- 349 Niki E (1991) Action of ascorbic acid as a scavenger of active and stable oxygen radicals. *The*
350 *American Journal of Clinical Nutrition* 54(6):S1119-S1124.
351 <https://doi.org/10.1093/ajcn/54.6.1119s>
- 352 Rangelova K, Rice AB, Khajo A et al (2012) Formation of reactive sulfite-derived free radicals by
353 the activation of human neutrophils: An ESR study. *Free Radical Biology and Medicine*
354 52(8):1264-1271. <https://doi.org/10.1016/j.freeradbiomed.2012.01.016>
- 355 Vione D, De Laurentiis E, Berto S et al (2016) Modeling the photochemical transformation of
356 nitrobenzene under conditions relevant to sunlit surface waters: Reaction pathways and
357 formation of intermediates. *Chemosphere* 145:277-283.
358 <https://doi.org/10.1016/j.chemosphere.2015.11.039>
- 359 Wang W, Wang H, Li G et al (2019) Catalyst-free activation of persulfate by visible light for water
360 disinfection: Efficiency and mechanisms. *Water Research* 157:106-118.
361 <https://doi.org/10.1016/j.watres.2019.03.071>
- 362 Wu D, Ye P, Wang M et al (2018) Cobalt nanoparticles encapsulated in nitrogen-rich carbon
363 nanotubes as efficient catalysts for organic pollutants degradation via sulfite activation.
364 *Journal of Hazardous Materials* 352:148-156. <https://doi.org/10.1016/j.jhazmat.2018.03.040>
- 365 Wu S, Shen L, Lin Y et al (2021) Sulfite-based advanced oxidation and reduction processes for water
366 treatment. *Chemical Engineering Journal* 414:128872.
367 <https://doi.org/10.1016/j.cej.2021.128872>
- 368 Wu Y, Xing D, Zhang L et al (2022) Application of a novel heterogeneous sulfite activation with
369 copper(i) sulfide (Cu₂S) for efficient iohexol abatement. *RSC Advances* 12(13):8009-8018.
370 <https://doi.org/10.1039/D2RA00773H>
- 371