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

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Supplementary Material

Text S1

Chemicals

Fe(III)-TAML was purchased from GreenOx Catalysts Inc. (Pittsburgh, PA, U.S.A.). Sodium phosphate, tribasic was obtained from Carlo Erba (Italy). All the other reagents, buffer solutions, and solvents were purchased from Sigma-Aldrich. Water was of Type I quality (TOC 2 ppb, resistivity $\geq 18.2 \text{ M}\Omega \text{ cm}$).

Preparation of the Fe-TAML stock solution

A stock solution of Fe-TAML was prepared by first dissolving 520 mg Fe-TAML in 200 mL of a sodium hydroxide solution (0.05 M). The supernatant of this solution was then used for further experiments. UV-Vis analysis was carried out, to determine the effective Fe-TAML concentration at pH 7, by measuring light absorbance at 360 nm. From the known Fe-TAML absorption coefficient at this wavelength ($6600 \text{ M}^{-1} \text{ cm}^{-1}$), a further stock solution with concentration of 3.1 mM was prepared. The stability of the catalyst in solution was spectrophotometrically checked every month. The stock solution was stored refrigerated (4 °C), under N₂ atmosphere.

Protocol of the oxidation experiments

The degradation experiments were carried out at room temperature, under continuous stirring, for a maximum of 30 min. Reactions were tested at different pH values (7 and 10), in 10 mL of phosphate buffer (total concentration 0.01 M). Under such conditions, the demetallation of Fe-TAML (decomplexation of the Fe-TAML complex, with likely formation of Fe(III) inorganic species) via the general acid mechanism can be considered negligible. As shown in previous literature reports, the demetallation kinetics of Fe-TAML increases as the pH decreases, or as the concentration of the buffering agents increases at constant pH (Polshin et al. 2008). For these reasons, and coherently with previous works, the phosphate buffer concentration used in this study was kept as low as possible.

Unless otherwise stated, the default initial concentrations in the experiments were as follows: 0.01 mM of Fe-TAML, 0.1 mM of phenol (PhOH), and 0.1 mM of reagent (H₂O₂ or MBS). During the tests, step-wise additions of reagent corresponding each to a 0.1 mM concentration in the reaction system were made every 10 min, for a total of three additions (40 μL of a concentrated 50 mM reagent solution was added each time, to limit dilution). In all of these latter cases, the overall molar ratios of Fe-TAML:contaminant:reagent were 1:10:30. The rationale for stepwise reagent addition is that too high concentration of H₂O₂ or MBS, at any given time in the system, would cause scavenging of the reactive species for degradation. Stepwise addition of the reagent provides the needed total amount, at the same time letting it to be degraded between successive addition steps, so that it never reaches too high concentration values, at which it would inhibit the reaction (Farinelli et al. 2019).

All the reactions were quenched by decreasing the pH, to a final value < 3 . Under acidic conditions, demetallation is promoted, and the catalytic reaction is stopped as a consequence (Ghosh et al. 2003).

Analytical methods

UV-Vis spectrophotometric measurements were performed using a Cary 100 Scan double-beam instrument (Varian). The concentrations of contaminants in solution were monitored by high-performance liquid chromatography, with diode array detection (HPLC-DAD). The used LaChrom Elite instrument (VWR-Hitachi) was equipped with a L-2200 Autosampler (injection volume 60 μL), a L-2130 quaternary pump for low-pressure gradients, a L-2300 column oven (set at 40 $^{\circ}\text{C}$), and a L-2455 DAD detector. The column was a RP-C18 LichroCART (VWR Int., length 125 mm, diameter 4 mm), packed with LiChrospher 100 RP-18 (5 μm diameter). Elution of phenol was carried out in isocratic mode, with a mixture of A = 5.7 mmol L^{-1} H_3PO_4 in water, and B = acetonitrile (A:B = 80:20), at a flow rate of 1 mL min^{-1} . The detection wavelength was 212 nm, and the retention time for phenol was 6.5 min. For nitrobenzene (NB), 4-nitrophenol (4NP), 3-nitrophenol (3NP), 2-nitrophenol (2NP), and aniline, the eluent was a mixture of A:B = 40:60, at flow rate 1.0 mL min^{-1} . The detection wavelength was 210 nm, and the retention times for NB, 2NP, 3NP, 4NP, and aniline were 6.8, 5.9, 3.5, 3.2, and 2.0 min, respectively.

EPR measurements

The presence of radical species was revealed by the spin-trap technique, using a X-band Bruker-EMX spectrometer, equipped with a cylindrical cavity operating at 100 kHz field modulation. Experimental parameters were as follows: microwave frequency 9.86 GHz; microwave power 5.4 mW; modulation amplitude 2 Gauss; conversion time 15.43 ms. Spin-traps, DMPO (5,5-dimethyl-1-pyrroline-N-oxide) or TEMP (2,2,6,6-tetramethylpiperidine), each 17 mM, were added (separately in different experiments) to the other reagents at $t = 0$ (García-Negueroles et al. 2019). Simulations of the EPR spectra were performed to compare the theoretical values associated with presence of sulfite radicals and the actual spectra detected experimentally.

Figure S1

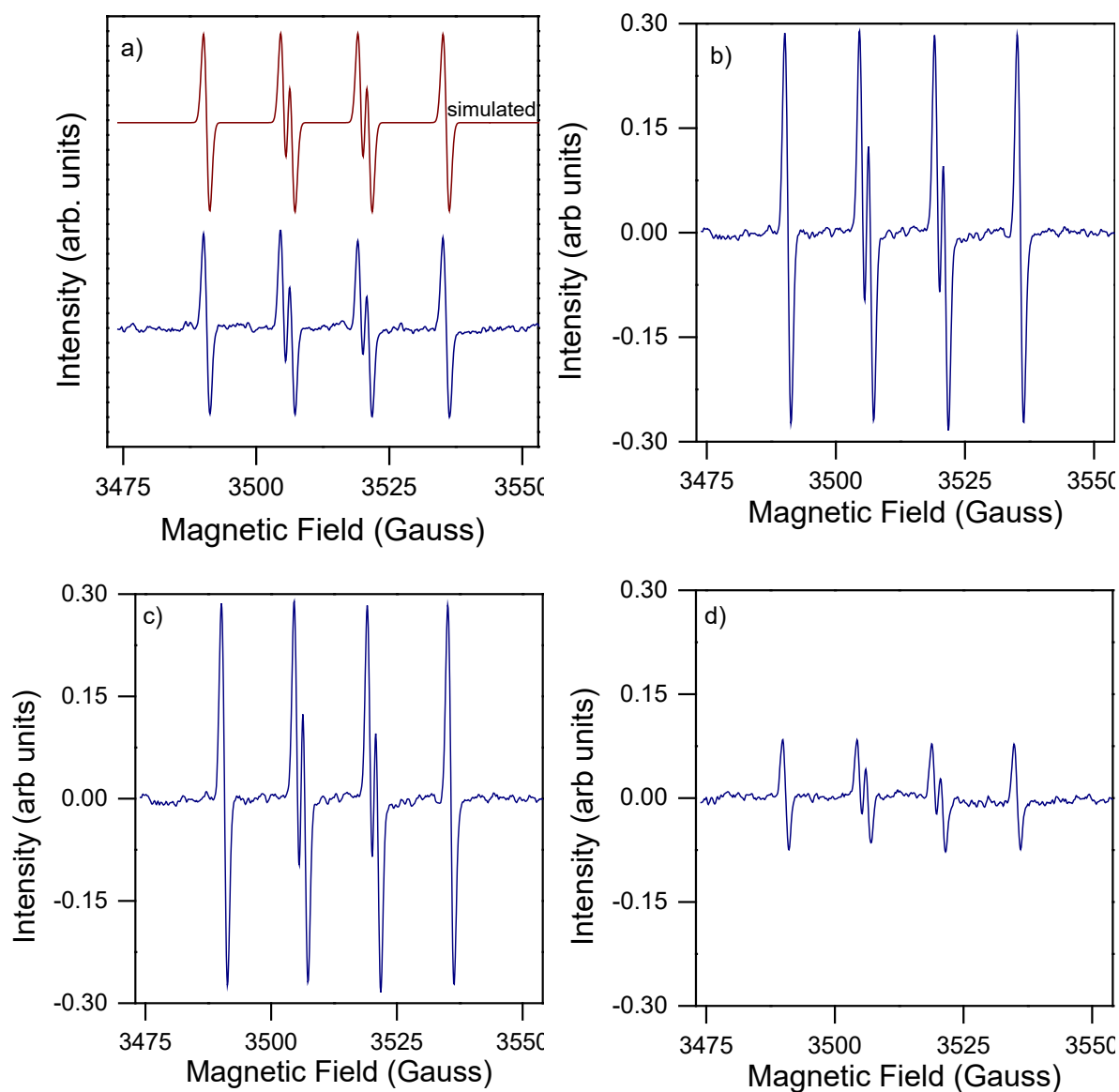


Figure S1. EPR spectra at 25 min reaction time of the systems: a) Fe-TAML 0.01 mM, PhOH 0.1 mM, MBS 0.3 mM; b) Fe-TAML 0.01 mM, PhOH 0.1 mM, MBS 0.3 mM, 2-PrOH 133 mM; c) Fe-TAML 0.01 mM, PhOH 0.1 mM, MBS 0.3 mM, t-BuOH 133 mM; d) Fe-TAML 0.01 mM, PhOH 0.1 mM, MBS 0.3 mM under nitrogen. DMPO 17 mM was used as spin-trap. The reactions occurred in the same conditions as those reported in Figure 1 of the main manuscript. Instrumental parameters are the same reported in the main manuscript (except the modulation amplitude: 1 Gauss).

Figure S2

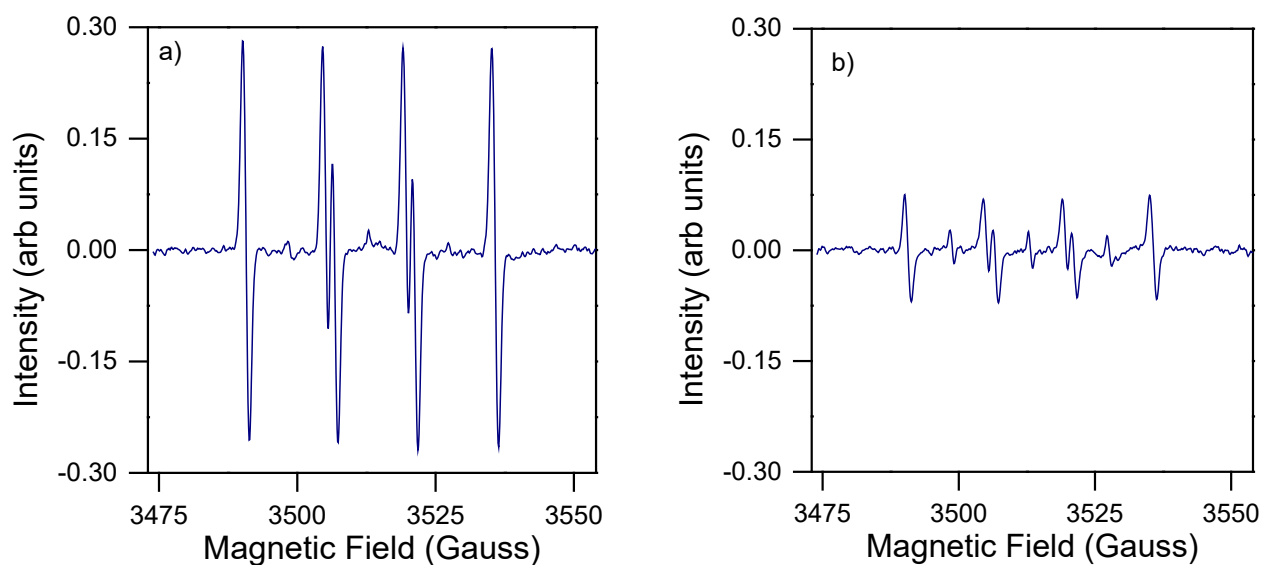


Figure S2. EPR spectra at 25 min of the systems: a) Fe-TAML 0.01 mM, PhOH 100 mM, MBS 0.3 mM; b) Fe-TAML 0.01 mM, MBS 0.3 mM, DMPO 17 mM used as radical trap. The reactions occurred in the same fashion as those reported in Figure 1 of the main manuscript. Instrumental parameters are the same reported in the main manuscript (except the modulation amplitude: 1 Gauss).

Figure S3

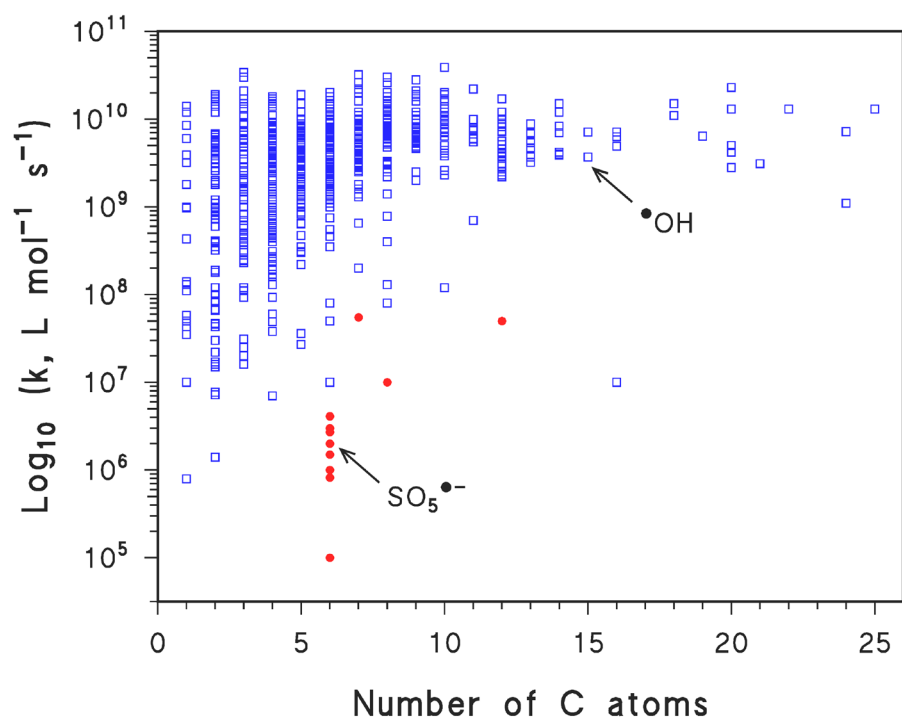


Figure S3. Second-order reaction rate constants of $\bullet\text{OH}$ and $\text{SO}_5^{\bullet-}$ with organic compounds, ordered according to the number of C atoms, from: Buxton et al. (1988), Neta et al. (1988).

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