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29 November 2024

SUPPLEMENTARY MATERIAL

Natural Iron Ligands Promote a Metal-Based Oxidation Mechanism for the Fenton Reaction in Water Environments

Giulio Farinelli,[†] Marco Minella,[‡] Marco Pazzi,[‡] Stefanos Giannakis,[§] Cesar Pulgarin,[‖] Davide Vione,*,[‡] Alberto Tiraferri*,[†]

[†]Department of Environment, Land and Infrastructure Engineering (DIATI), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Turin, Italy

[‡]Department of Chemistry, University of Turin, Via Pietro Giuria 7, 10125 Turin, Italy

[§]Universidad Politécnica de Madrid, E.T.S. Ingenieros de Caminos, Canales y Puertos, Departamento de Ingeniería Civil: Hidráulica, Energía y Medio Ambiente, Unidad docente Ingeniería Sanitaria, c/ Profesor Aranguren, s/n, ES-28040 Madrid, España

[‖]SB, ISIC, Group of Advanced Oxidation Processes, Ecole Polytechnique Fédérale de Lausanne (EPFL), Station 6, 1015 Lausanne, Switzerland

Corresponding Authors
Email: alberto.tiraferri@polito.it; davide.vione@unito.it
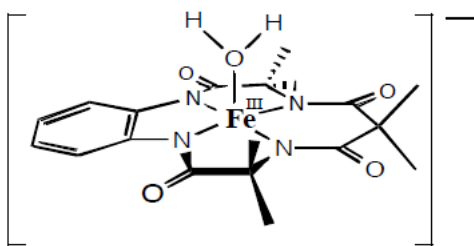
Figure S1. Fe-TAML molecular structure

Table S1. Oxidation of cyclohexane at different pH values with citric acid as iron ligand

pH	A (M)	K (M)	A/K
3	2.77×10^{-9}	2.75×10^{-10}	10.07
5	3.94×10^{-9}	5.37×10^{-10}	7.35
6	3.24×10^{-9}	3.82×10^{-10}	8.48
7	5.31×10^{-9}	6.16×10^{-10}	8.62

Reactants: cyclohexane (0.1 mM), hydrogen peroxide (0.001 mM), iron(II) (0.1 µM).

Table S2. Oxidation of cyclohexane at different pH values with malic acid as iron ligand

pH	A (M)	K (M)	A/K
3	1.82×10^{-9}	1.02×10^{-10}	17.79
5	1.65×10^{-9}	1.14×10^{-10}	14.48
6	4.56×10^{-9}	2.89×10^{-10}	15.81
7	3.47×10^{-9}	2.26×10^{-10}	15.38

Reactants: cyclohexane (0.1 mM), hydrogen peroxide (0.001 mM), iron(II) (0.1 µM).

Table S3. Oxidation of cyclohexane at different pH values with quinic acid as iron ligand

| pH	A (M)	K (M)	A/K
3	5.54×10^{-9}	1.97×10^{-10}	28.14
5	5.90×10^{-9}	1.88×10^{-10}	31.29
6	5.02×10^{-9}	2.17×10^{-10}	23.15
7	2.90×10^{-9}	1.05×10^{-10}	27.70

Reactants: cyclohexane (0.1 mM), hydrogen peroxide (0.001 mM), iron(II) (0.1 µM).

Degradation experiments were carried out in magnetically stirred beakers (the total volume of the aqueous phase was 50 mL). The reaction mixture contained phenol, Fe^{2+} (as $FeSO_4$) or FeIII-TAML, H_2O_2, a reagent for pH adjustment ($HClO_4$ for pH 3, NaOH for pH 10) and, where relevant, t-butanol (TBA). At scheduled time intervals, a measured 2 mL sample aliquot was withdrawn from the reaction mixture and diluted 1:1 with the same volume of methanol to stop the Fenton reaction. Phenol was quantified by high performance liquid chromatography (HPLC), using a VWR-Hitachi Elite LaChrom instrument equipped with L2455 diode array detector (DAD), L2130 quaternary pump module, L2300 column oven (set at 40 °C), L2200 autosampler (sample injection volume 60 µL), Duratec vacuum degasser and reverse-phase column Merck LiChroCART, packed with LiChrospher 100 RP18 (125 mm × 4 mm × 5 µm). The chromatographic elution conditions were A:B = 70:30, where A is an aqueous solution of H_3PO_4 (pH 2.8) and B is methanol, at 1.0 mL/min flow rate. These conditions gave a column dead time of 1.2 min and a phenol retention time of 5.2 min. The detection wavelength was 210 nm.

Considering that the Fenton reaction can produce both $^\bullet$OH and ferryl (FeIV) species, and because TBA is a selective $^\bullet$OH scavenger, the goal of this series of experiments was to get insight into the relative roles of $^\bullet$OH vs. ferryl in the Fenton degradation of phenol. The experimental results are reported in Figure S2 for Fe^{2+} + H_2O_2 at pH 3 (S2a) and Fe-TAML + H_2O_2 at pH 10 (S2b). In the latter case, it is interesting to observe that TBA had practically no effect on phenol degradation, which is consistent with the almost exclusive involvement of ferryl in the process. The opposite result was obtained with Fe^{2+} + H_2O_2 at pH 3, where the large inhibition effect carried out by TBA suggests that $^\bullet$OH plays a key role in the traditional Fenton process. Therefore, one can conclude that $^\bullet$OH is largely involved in phenol degradation by Fe^{2+} + H_2O_2 at pH 3, while ferryl operates in the presence of Fe-TAML + H_2O_2 at pH 10.
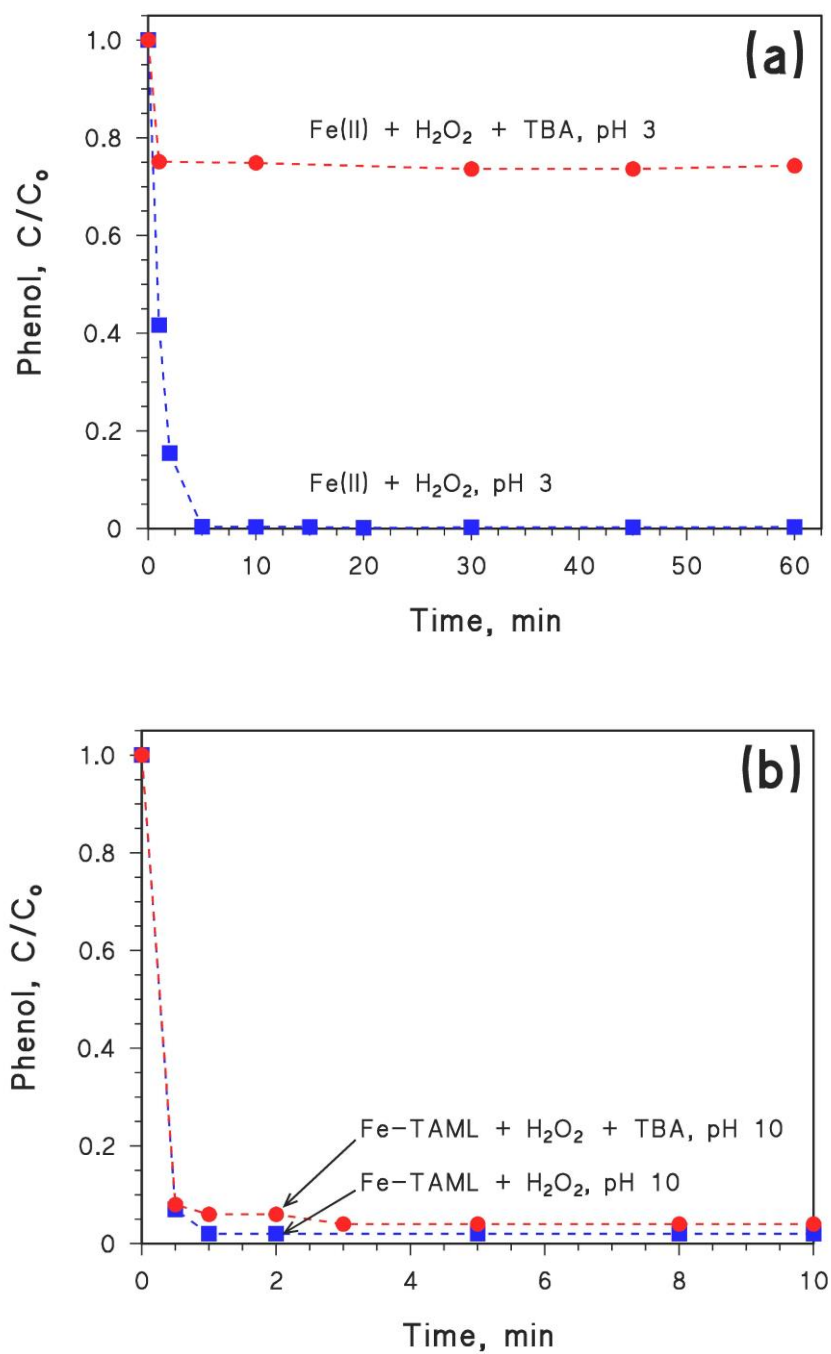
Figure S2. (a) Time trends of 0.1 mM phenol in the presence of 0.1 mM Fe^{2+} and 1 mM H_2O_2, at pH 3 by $HClO_4$, with and without 4 mM TBA. (b) Time trends of 0.1 mM phenol in the presence of 0.01 mM Fe-TAML and 0.1 mM H_2O_2, at pH 10 by NaOH, with and without 4 mM TBA.
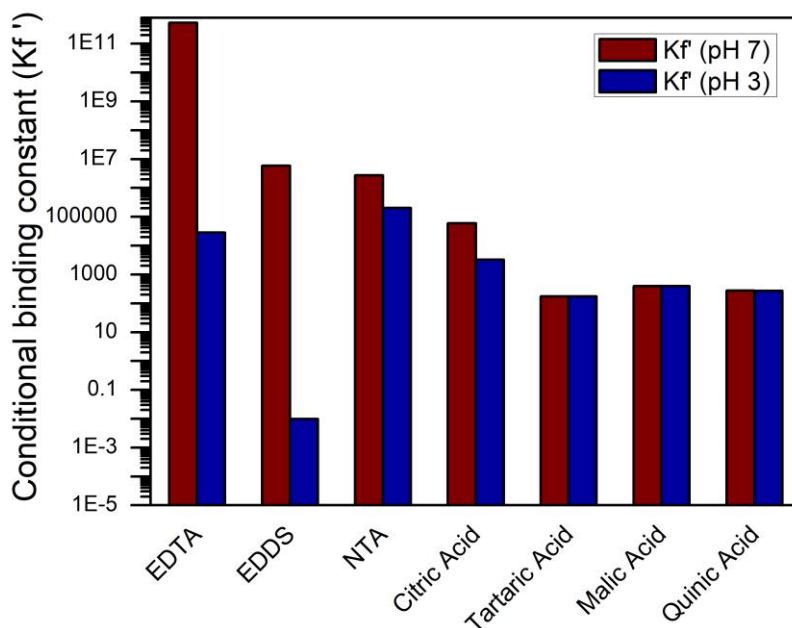
Figure S3. Conditional binding constant computed at pH 7 and pH 3 for a variety of ligands.

The conditional binding constants for the Fe(II) complexes $[FeL]^{(n-2)-}$ were computed as

$$K'_f = \alpha_n K_f$$

where:

K_f = binding constant for the ligand to metal complex with a 1 to 1 stoichiometry

α_n = molar fraction of the totally deprotonated ligand species computed as

$$\alpha_n = \frac{\prod_1^n K_i}{[H^+]^n + K_1[H^+]^{n-1} + K_1 K_2 [H^+]^{n-2} + \cdots + \prod_1^n K_i}$$

where

K_i = acid dissociation constant for the H_nL ligand

All the equilibrium constants were extracted from:

Arthur E. Martell and Robert M. Smith, NIST Standard Reference Database 46 Version 4.0, NIST critically selected constants of metal complexes, NIST Standard Reference Data, Gaithersburg, MD 20899 USA, 1997.

Table S4. Oxidation of cyclohexane with EDTA as iron ligand added at different concentrations, performed at pH 3 unless otherwise stated

[EDTA]/[Fe(II)]	A (M)	K (M)	A/K
0	4.86×10^{-10}	4.25×10^{-10}	1.14
0.25	7.32×10^{-10}	3.48×10^{-10}	2.10
0.375	1.24×10^{-9}	3.45×10^{-10}	3.60
0.5	1.29×10^{-8}	5.41×10^{-10}	23.80
0.75	9.87×10^{-9}	3.57×10^{-10}	27.61
1	9.10×10^{-9}	3.93×10^{-10}	23.13
1 (pH 7)	4.60×10^{-9}	1.20×10^{-10}	38.32

Reactants: cyclohexane (0.1 mM), hydrogen peroxide (0.001 mM), iron(II) (0.1 µM)

Table S5. Oxidation of cyclohexane with EDDS as iron ligand added at different concentrations, performed at pH 3 unless otherwise stated

[EDDS]/[Fe(II)]	A (M)	K (M)	A/K
0	4.86×10^{-10}	4.25×10^{-10}	1.14
0.25	7.88×10^{-10}	8.19×10^{-10}	0.96
0.375	8.76×10^{-10}	1.20×10^{-9}	0.73
0.5	1.14×10^{-9}	6.68×10^{-10}	1.71
0.75	5.81×10^{-10}	2.79×10^{-10}	2.08
1	6.41×10^{-10}	2.53×10^{-10}	2.53
1 (pH 7)	2.94×10^{-9}	6.41×10^{-11}	45.78

Reactants: cyclohexane (0.1 mM), hydrogen peroxide (0.001 mM), iron(II) (0.1 µM)