Supplementary Materials

Sulfate radical photogeneration using Fe-EDDS: Influence of critical parameters and naturally occurring scavengers

Yanlin Wu[a,b,c], Angelica Bianco[a,b], Marcello Brigante[a,b], Wenbo Dong[c], Pascal de Sainte-Claire[a,b], Khalil Hanna[d], Gilles Mailhot[a,b]

[a] Université Clermont Auvergne, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 CLERMONT-FERRAND, FRANCE

[b] CNRS, UMR 6296, ICCF, F-63171 AUBIERE, FRANCE

[c] Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, China

[d] Ecole Nationale Supérieure de Chimie de Rennes UMR CNRS 6226, 11 Allée de Beaulieu , CS 50837, F-35708 RENNES Cedex 7, France

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$Fe(III)\text{-}EDDS^{-} \xrightarrow{hv} Fe^{2+} + EDDS^{\bullet 3-}$	$k_1 = 3.9 \times 10^{-3}$ s^{-1} at pH 4.0 and 2.7×10^{-3} s^{-1} at pH 8.0 [a]	(K1)
$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet -}$	$k_2 = 27\ M^{-1}\ s^{-1}$	(K2)
$Fe^{2+} + SO_4^{\bullet -} \rightarrow Fe^{3+} + SO_4^{2-}$	$k_3 = 9.9 \times 10^{8}\ M^{-1}\ s^{-1}$ [1]	(K3)
$SO_4^{\bullet -} + H_2O \rightarrow SO_4^{2-} + H^{+} + HO^{\bullet}$	$k_4 = 11.92\ M^{-1}\ s^{-1}$ [1]	(K4)
$SO_4^{\bullet -} + HO^{-} \rightarrow SO_4^{2-} + HO^{\bullet}$	$k_5 = 7.3 \times 10^{7}\ M^{-1}\ s^{-1}$ [1]	(K5)
$2SO_4^{\bullet -} \rightarrow S_2O_8^{2-}$	$k_6 = 8.1 \times 10^{8}\ M^{-1}\ s^{-1}$ [1]	(K6)
$S_2O_8^{2-} + SO_4^{\bullet -} \rightarrow SO_4^{2-} + S_2O_8^{\bullet -}$	$k_7 = 1.2 \times 10^{6}\ M^{-1}\ s^{-1}$ [1]	(K7)
$HO^{\bullet} + S_2O_8^{2-} \rightarrow HO^{-} + S_2O_8^{\bullet -}$	$k_8 = 1.2 \times 10^{7}\ M^{-1}\ s^{-1}$ [2]	(K8)
$HO^{\bullet} + SO_4^{\bullet -} \rightarrow HSO_5^{-}$	$k_9 = 9.0 \times 10^{9}\ M^{-1}\ s^{-1}$ [3]	(K9)
$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + HO^{-}$	$k_{10} = 3.2 \times 10^{8}\ M^{-1}\ s^{-1}$ [2]	(K10)
$2HO^{\bullet} \rightarrow H_2O_2$	$k_{11} = 4.2 \times 10^{9}\ M^{-1}\ s^{-1}$ [4]	(K11)
$HO^{\bullet} + 4tBP \rightarrow 4tBP_{ox}^{+} + HO^{-}$	$k_{12} = 1.6 \times 10^{10}\ M^{-1}\ s^{-1}$ [a]	(K12)
$SO_4^{\bullet -} + 4tBP \rightarrow 4tBP_{ox}^{+} + SO_4^{2-}$	$k_{13} = 4.2 \times 10^{9}\ M^{-1}\ s^{-1}$ [a]	(K13)
$Fe^{III}\text{-}EDDS^{-} + HO^{\bullet} \rightarrow Fe^{III}\text{-}EDDS_{ox} + HO^{-}$	$k_{14} = 5.0 \times 10^{8}\ M^{-1}\ s^{-1}$ [a]	(K14)
$Fe^{III}\text{-}EDDS^{-} + SO_4^{\bullet -} \rightarrow Fe^{III}\text{-}EDDS_{ox} + SO_4^{2-}$	$k_{15} = 6.4 \times 10^{9}\ M^{-1}\ s^{-1}$ [a]	(K15)
$SO_4^{\bullet -} + H_2O_2 \rightarrow HO_2^{\bullet} + SO_4^{2-} + H^{+}$	$k_{16} = 1.2 \times 10^{7}\ M^{-1}\ s^{-1}$ [1]	(K16)
$HO_2^{\bullet} \rightleftharpoons O_2^{\bullet -} + H^{+}$	pka = 4.5	(EQ1)
$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2$	$k_{17} = 10^{10}\ M^{-1}\ s^{-1}$ [2]	(K17)

$O_2^{\bullet-} + HO^\bullet \rightarrow O_2 + HO^-$	$k_{18} = 10^{-10}$ M^{-1} s^{-1} [2]	(K18)
$HO^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O$	$k_{19} = 2.7 \times 10^7$ M^{-1} s^{-1} [5]	(K19)
$HO^\bullet + Cl^- \underset{k_{-20}}{\overset{k_{20}}{\rightleftarrows}} ClOH^{\bullet-}$	$k_{20} = 4.3 \times 10^9$ M^{-1} s^{-1} $k_{-20} = 6.1 \times 10^9$ M^{-1} s^{-1}	(K20)
$ClOH^{\bullet-} + H^+ \underset{k_{-21}}{\overset{k_{21}}{\rightleftarrows}} Cl^\bullet + H_2O$	$k_{21} = 2.1 \times 10^{10}$ M^{-1} s^{-1} $k_{-21} = 1.3 \times 10^3$ M^{-1} s^{-1}	(K21)
$Cl^\bullet + Cl^- \underset{k_{-22}}{\overset{k_{22}}{\rightleftarrows}} Cl_2^{\bullet-}$	$k_{22} = 2.1 \times 10^{10}$ M^{-1} s^{-1} $k_{-22} = 1.1 \times 10^5$ M^{-1} s^{-1}	(K22)
$SO_4^{\bullet-} + Cl^- \rightarrow Cl^\bullet + SO_4^{2-}$	$k_{23} = 2.0 \times 10^8$ M^{-1} s^{-1} [6]	(K23)
$Cl_2^{\bullet-} + HO^\bullet \rightarrow ClOH + Cl^-$	$k_{24} = 10^9$ M^{-1} s^{-1} [7]	(K24)
$ClOH^{\bullet-} + Cl^- \rightarrow Cl_2^{\bullet-} + HO^-$	$k_{25} = 10^4$ M^{-1} s^{-1} [8]	(K25)
$Cl^\bullet + H_2O \underset{k_{-26}}{\overset{k_{26}}{\rightleftarrows}} ClOH^{\bullet-} + H^+$	$k_{26} = 4.5 \times 10^3$ M^{-1} s^{-1} $k_{-26} = 2.1 \times 10^{10}$ M^{-1} s^{-1}	(K26)
$Cl^\bullet + HO^- \rightarrow HO^\bullet + Cl^-$	$k_{27} = 1.8 \times 10^8$ M^{-1} s^{-1} [9]	(K27)
$Cl_2^{\bullet-} + H_2O \rightarrow ClOH^{\bullet-} + Cl^- + H^+$	$k_{28} = 23.49$ M^{-1} s^{-1} [10]	(K28)
$2Cl_2^{\bullet-} \rightarrow Cl_2 + 2Cl^-$	$k_{29} = 2.1 \times 10^9$ M^{-1} s^{-1} [11]	(K29)
$Cl_2^{\bullet-} + HO^- \rightarrow ClOH^{\bullet-} + Cl^-$	$k_{30} = 4.5 \times 10^7$ M^{-1} s^{-1}	(K30)
$Fe^{2+} + Cl^\bullet \rightarrow Fe^{3+} + Cl^-$	$k_{31} = 1.3 \times 10^{10}$ M^{-1} s^{-1} [12]	(K31)
$Fe^{2+} + Cl_2^{\bullet-} \rightarrow Fe^{3+} + 2Cl^-$	$k_{32} = 10^7$ M^{-1} s^{-1} [13]	(K32)
$Cl_2^{\bullet-} + 4tBP \rightarrow 4tBP_{ox}^+ + 2Cl^-$	$k_{33} = 2.8 \times 10^8$ M^{-1} s^{-1} [a]	(K33)

$Fe^{III}\text{-}EDDS^{-} + Cl_2^{\bullet -} \rightarrow Fe^{III}\text{-}EDDS_{ox} + 2Cl^{-}$	$k_{36} = 5.2 \times 10^{7}\ M^{-1}\ s^{-1}$ [a]	(K34)

Table S1: Kinetic constants considered in the model. [a:] this work

References

1. Neta, P.; Hule, R. E.; Ross, A. B., Rate constant for reactions of inorganic radicals in aqueous solution. *J. Phys. Chem. Ref. Data* **1988,** *17*, (3), 1027-1284.
2. Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B., Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($^{\bullet}OH/^{\bullet}O^{-}$) in aqueous solution. *J. Phys. Chem. Ref. Data* **1988,** *17*, 513-886.
3. Klaning, U. K.; Sehested, K.; Appelman, E. H., Laser flash photolysis and pulse radiolysis of aqueous solutions of the fluoroxysulfate ion, SO_4F. *Inorg. Chem.* **1991,** *30*, (18), 3582-3584.
4. Elliot, A. J.; McCracken, D. R.; Buxton, G. V.; Wood, N. D., Estimation of rate constants for near-diffusion-controlled reactions in water at high temperatures. *J. Chem. Soc., Faraday Trans.* **1990,** *86*, (9), 1539-1547.
5. Christensen, H.; Sehested, K.; Corfitzen, H., Reactions of hydroxyl radicals with hydrogen peroxide at ambient and elevated temperatures. *J. Phys. Chem.* **1982,** *86*, (9), 1588-1590.
6. Padmaja, S.; Neta, P.; Huie, R. E., Rate constants for some reactions of inorganic radicals with inorganic ions. Temperature and solvent dependence. *Int. J. Chem. Kinet.* **1993,** *25*, (6), 445-455.
7. Wagner, I.; Karthauser, J.; Strehlow, H., On the decay of the dichloride anion Cl_2^{-} in aqueous solution. *Ber. Bunsen-Ges. Phys. Chem.* **1986,** *90*, 861-867.
8. Grigor'ev, A. E.; Makarov, I. E.; Pikaev, A. K., Formation of Cl_2^{-} in the bulk of solution during radiolysis of concentrated aqueous solutions of chlorides. *Journal High Energy Chemistry* **1987,** *21*, (2), 123-126.
9. Kläning, U. K.; Wolff, T., Laser Flash Photolysis of HClO, ClO−, HBrO, and BrO− in Aqueous Solution. Reactions of Cl- and Br-Atoms. *Berichte der Bunsengesellschaft für physikalische Chemie* **1985,** *89*, (3), 243-245.
10. McElroy, W. J., A laser photolysis study of the reaction of SO_4^{-} with Cl^{-} and the subsequent decay of Cl_2^{-} in aqueous solution. *J. Phys. Chem.* **1990,** *94*, (6), 2435-2441.
11. Navaratnam, S.; Parsons, B. J.; Swallow, A. J., Some reactions of the dichloride anion radical. *Radiation Physics and Chemistry (1977)* **1980,** *15*, (2â€“3), 159-161.
12. Bjergbakke, E.; Navaratnam, S.; Parsons, B. J.; Swallow, A. J., A quantitative description of the action of high-dose pulses of radiation on aerated acid solutions containing ferrous and chloride ions. *Int. J. Radiat. Appl.* **1987,** *30*, (1), 59-62.
13. Thornton, A. T.; Laurence, G. S., Kinetics of oxidation of transition-metal ions by halogen radical anions. Part I. The oxidation of iron(II) by dibromide and dichloride ions generated by flash photolysis. *Journal of the Chemical Society, Dalton Transactions* **1973**, (8), 804-813.

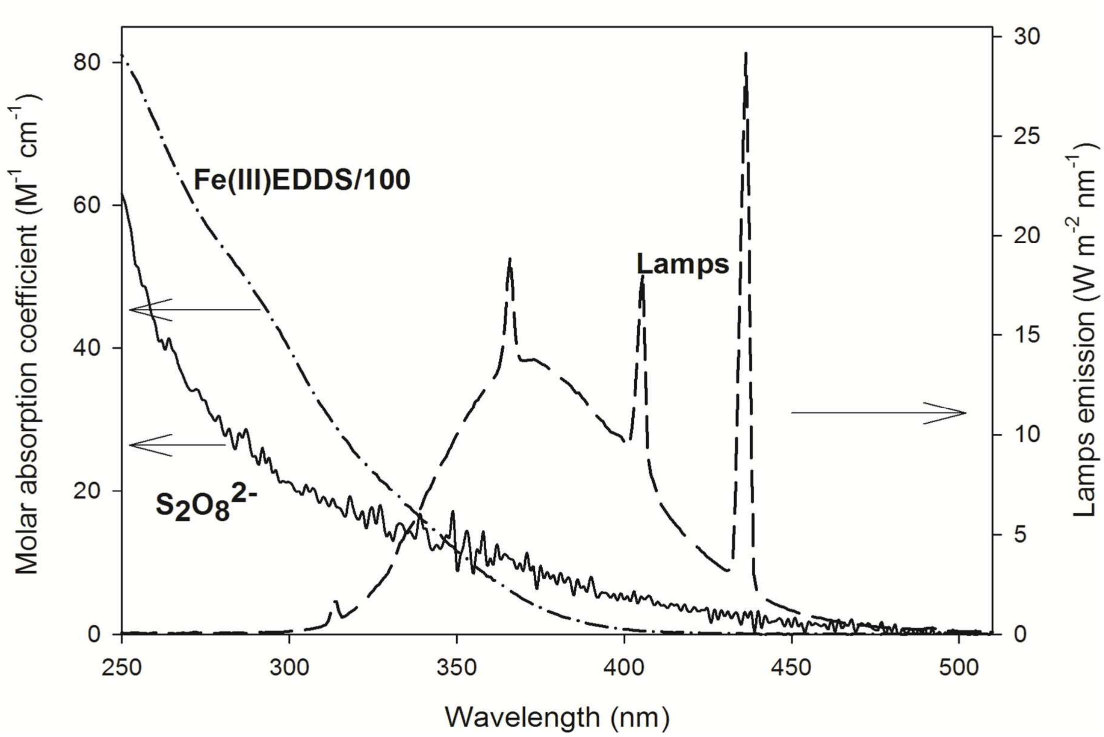

Figure S1. Molar absorption spectra of $S_2O_8^{2-}$ solution at pH 5.1 (solid line) and Fe(III)-EDDS complex at pH 4.0 (dot and dashed line) and emission spectrum of the irradiation system reaching the solution (dashed line).

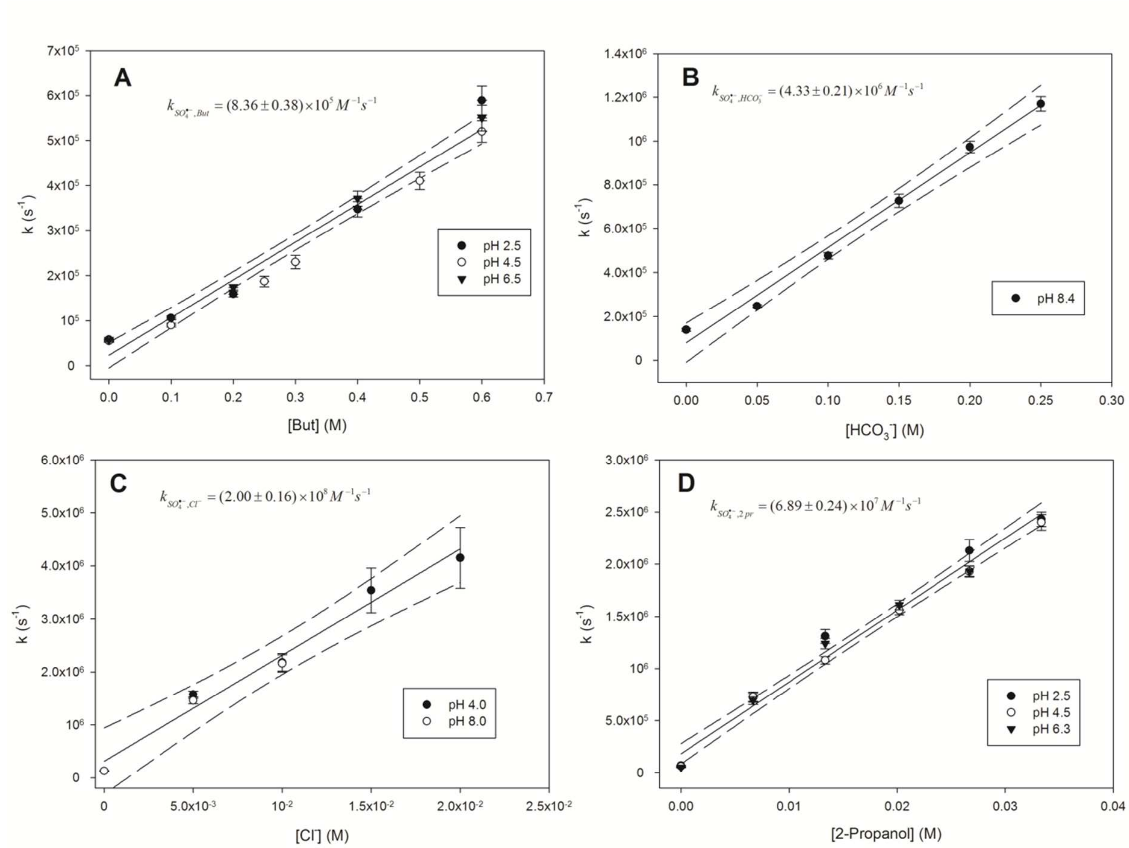

Figure S2. Pseudo-first order rate constant of $SO_4^{\bullet-}$ decay, as a function of tert-butanol (**A**), HCO_3^-(**B**), Cl^- (**C**) and 2-propanol (**D**) concentrations at different pH. Excitation is fixed at 266 nm and laser pulse energy is 45 mJ. The solid line represents the linear fit of the experimental data considering all pH values. The dashed line denotes the 95% confidence interval of this fit.

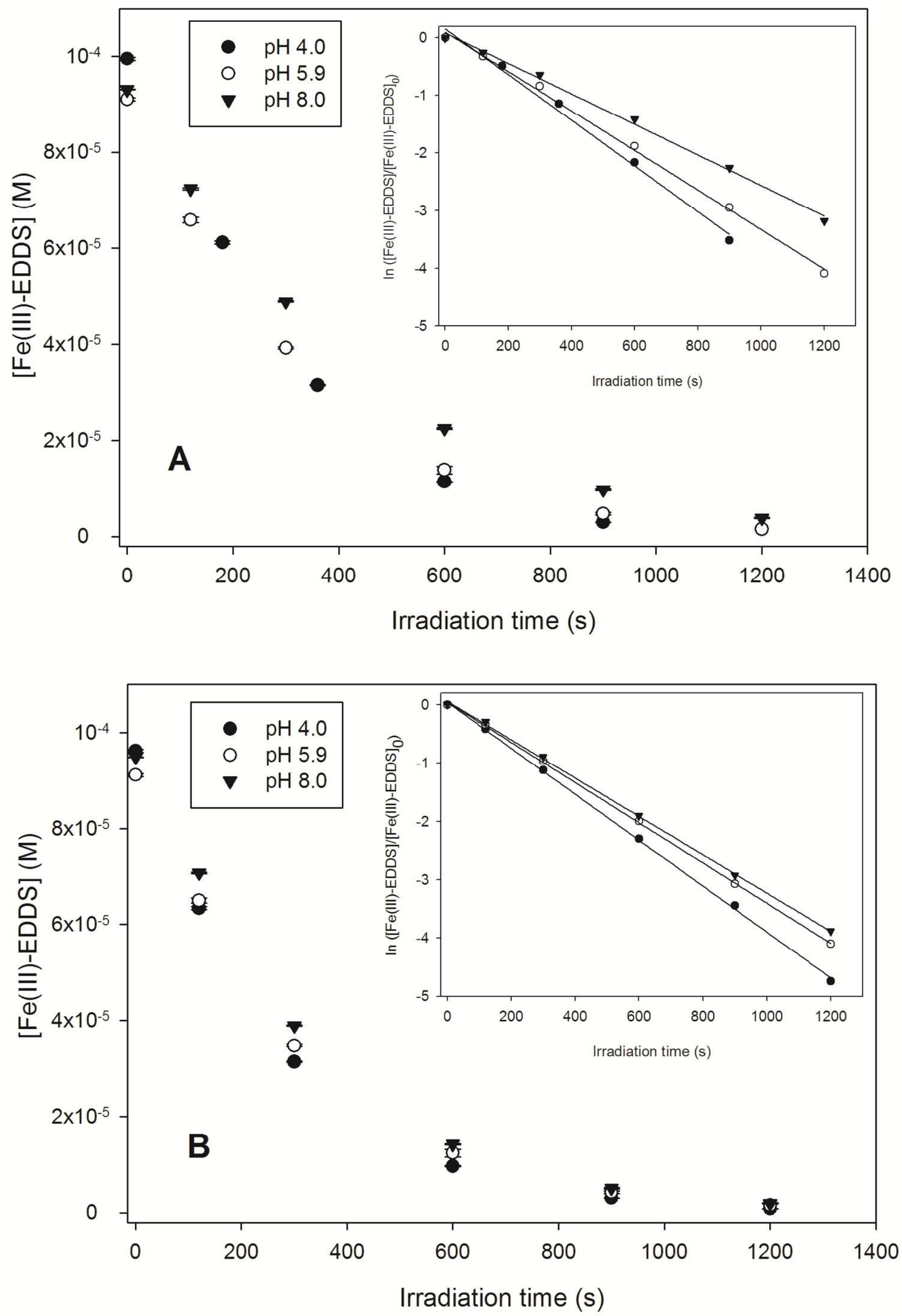

Figure S3. Degradation of 100 µM Fe(III)-EDDS as a function of pH value without (A) and with (B) addition of $S_2O_8^{2-}$ 500 µM .

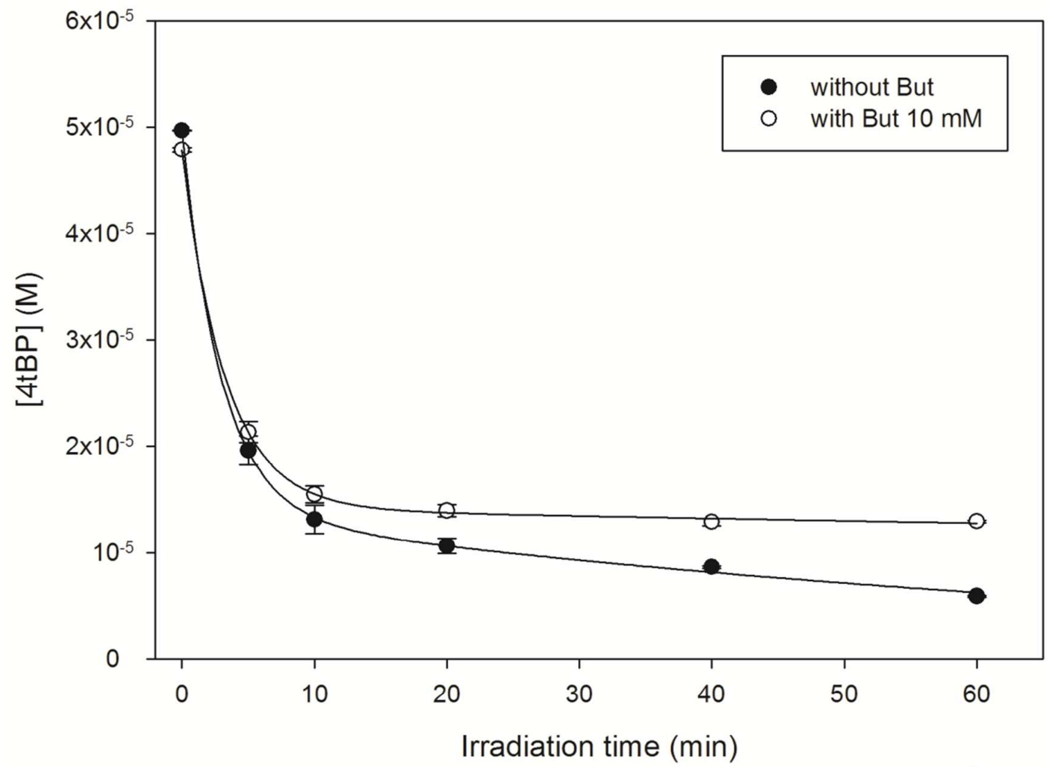

Figure S4. 4tBP degradation using 100 µM of Fe(III)-EDDS + 500 µM of $S_2O_8^{2-}$ with (empty circle) and without (filled circle) 10 mM of Butanol (But) addition under polychromatic irradiation at pH 4.0.

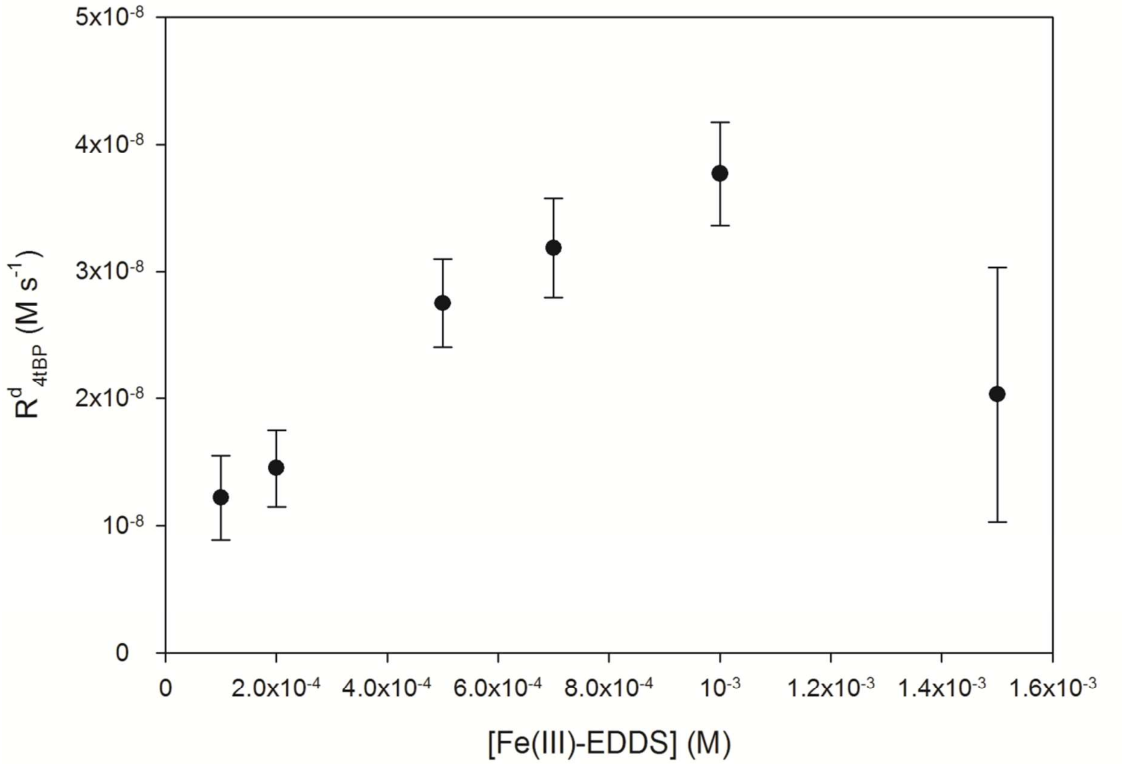

Figure S5. 4tBP degradation rate (R^d_{4tBP}) in the presence of 500 µm of $S_2O_8^{2-}$ and different Fe(III)-EDDS concentrations at pH 4.5 and 293 ± 2 K under polychromatic irradiation.

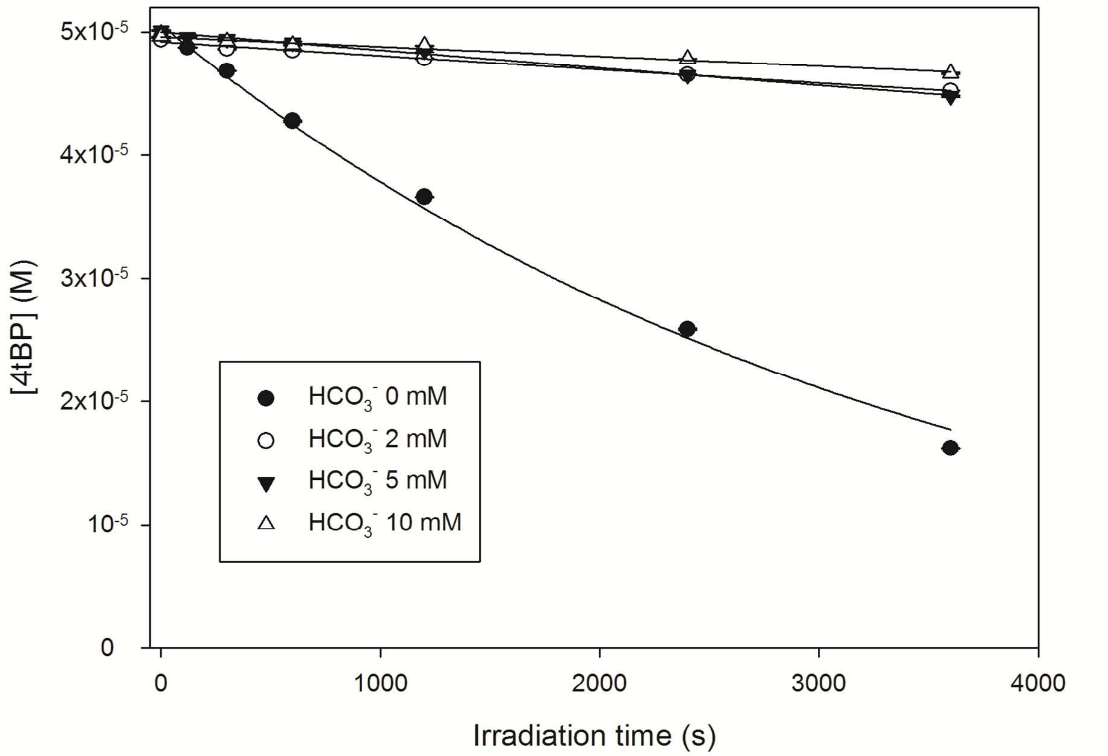

Figure S6. 4tBP degradation with and without carbonates at pH 8.2 in the system Fe(III)-EDDS 100 µM + 500 µM of $S_2O_8^{2-}$ under polychromatic irradiation.