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## Degradation of acetic acid with sulfate radical generated by persulfate ions photolysis

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26

27 **Keywords:** Sulfate radical, Mineralization, Carboxylic acids, Persulfate, Photolysis

28

## 29 1. Introduction

30

31 Advanced Oxidation Processes (AOPs) that usually involve ultraviolet irradiation,  
32 ozone, and/or hydrogen peroxide to generate hydroxyl radicals ( $\cdot\text{OH}$ ) are commonly used to  
33 destroy organic contaminants in various types of water. However oxidation by  $\cdot\text{OH}$  radicals is  
34 sometimes slow with some refractory pollutants as organic acids or can lead to harmful by-  
35 products.

36 The sulfate radical  $\text{SO}_4^{\cdot-}$  is known to be a very strong oxidant, i.e.  $E^\circ(\text{SO}_4^{\cdot-}/\text{SO}_4^{2-}) =$   
37  $2.43 \text{ V vs. NHE}$  (Stanbury, 1989). This radical could be generated by the scission of the  
38 peroxide bond of persulfate. In previous studies, the persulfate degradation has been  
39 performed by photolysis at wavelengths from 248 to 351 nm (Herrmann, 2007). The  
40 photolysis of  $\text{S}_2\text{O}_8^{2-}$  has been postulated to result in the formation of two  $\text{SO}_4^{\cdot-}$  radicals (Eq.  
41 1) (Tsao and Wilmarth, 1959).



43 The radical was identified from its optical absorption spectrum with a maximum at  
44 440-450 nm and a molar extinction coefficient between 460 and 1600  $\text{M}^{-1} \text{cm}^{-1}$  (Dogliotti and  
45 Hayon, 1967a; Chawla and Fessenden, 1975; McElroy and Waygood, 1990; Clarke et al.,  
46 2008). Alternatively, the sulfate radical was also formed by thermal (Huang et al., 2005;  
47 Johnson et al., 2008; Liang and Bruell, 2008; Mora et al., 2009), radiolytic (Chitose et al.,  
48 1999) or transition metal activation of persulfate (Anipsitakis and Dionysiou, 2004; Liang et  
49 al., 2009).

50 The sulfate radical was studied for the removal of refractory pollutants. Manoj et al.  
51 (2002) studied the cyanuric acid degradation by persulfate laser flash photolysis and steady  
52 state radiolysis; they determined a second order rate constant of  $1.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  by  
53 monitoring the decay of absorption of  $\text{SO}_4^{\cdot-}$  as a function of cyanuric acid concentration.  
54 Others (Hori et al., 2005; Hori et al., 2007) showed the photochemical decomposition of  
55 perfluorocarboxylic acids induced by persulfate as photochemical oxidant; these compounds  
56 were transformed to  $\text{F}^-$  and  $\text{CO}_2$  and small amounts of perfluorocarboxylic acids with shorter  
57 chain lengths. Liang et al. (Liang et al., 2004; Liang et al., 2006) described an application of  
58 *in situ* chemical oxidation for trichloroethylene oxidation by thermal or transition metal  
59 activation of persulfate. Moreover, Mora et al. (2009) showed the degradation of  
60 trichloroacetic acid by persulfate thermal activation in presence of formate as an additive to  
61 produce  $\text{CO}_2^{\cdot-}$  which are radicals available for degrading trichloroacetic acid by a reductive  
62 pathway.

63 The sulfate radical reacts in three different ways: electron transfer, addition or  
64 hydrogen abstraction (Chawla and Fessenden, 1975; Neta et al., 1977; Huie et al., 1991a).  
65 However a particular reaction occurs with carboxylic acids; whereas their reactions with  
66 hydroxyl radicals result in little decarboxylation, most aliphatic acids undergo efficient  
67 decarboxylation by  $\text{SO}_4^{\cdot-}$  (Madhavan et al., 1978; Davies et al., 1985).

68 Owing to its high redox potential, the sulfate radical produces radicals from many  
69 anions by electron transfer (Chawla and Fessenden, 1975). It makes the sulfate radical very  
70 reactive with many constituents of water such as chloride and bicarbonate ions. The reaction  
71 of sulfate radicals with chloride ions leads to the production of  $\text{Cl}^{\cdot}$  (McElroy, 1990). Then,  
72 competitive side reactions can result in scavenging of  $\text{SO}_4^{\cdot-}$  and could limit its oxidation  
73 efficiency.

74 The objective of this work was to investigate the sulfate radical reactivity towards  
75 acetic acid, a persistent by-product in numerous oxidation processes like O<sub>3</sub> and AOPs. The  
76 by-products formed from oxidation of acetic acid by the hydroxyl radicals are known; they  
77 consist mostly in oxalic and formic acids (Schuchmann et al., 1985; Leitner and Doré, 1997).  
78 Thus, this molecule was chosen to compare the action of SO<sub>4</sub><sup>•-</sup> and <sup>•</sup>OH radicals generated by  
79 two processes, S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and H<sub>2</sub>O<sub>2</sub> irradiation at 254 nm respectively. In addition, the influence  
80 of chloride and bicarbonate ions was examined for both conditions.

81

## 82 **2. Materials and methods**

### 83 **2.1. Experimental setup**

84 Irradiation experiments were conducted in a 5 L cylindrical batch reactor without  
85 headspace to prevent the loss of volatile by-products. This reactor is equipped with a low  
86 pressure mercury vapor lamp (Hanau NN/40/20) in the axial position with an optical width of  
87 6.3 cm. The lamp emits a monochromatic radiation at 253.7 nm. The incident photonic flux  
88 ( $I_0 = 9.9 \times 10^{-6} \text{ E s}^{-1}$ ) was determined by chemical actinometry using a  $4 \times 10^{-2} \text{ M}$  hydrogen  
89 peroxide solution (and with the quantum yield  $\Phi = 1$  for the overall reaction of H<sub>2</sub>O<sub>2</sub>  
90 photolysis). During all experiments the solutions were thermostated at 25±1 °C.

91 All reagents were reagent grade and were used without further purification: K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>  
92 (Aldrich), H<sub>2</sub>O<sub>2</sub> (30% Fulka), Acetic acid (> 99%, Riedel de Haën), NaCl and NaHCO<sub>3</sub> (>  
93 99%, Fischer).

94 All solutions were prepared in ultra pure water (MilliQ water; TOC < 0.2 mg L<sup>-1</sup>; 18  
95 MΩ cm). The pH was left uncontrolled or controlled during the course of the reaction by  
96 addition of sodium hydroxide or perchloric acid. Dissolved oxygen concentration was  
97 initially set at 20-30 mg L<sup>-1</sup> by bubbling O<sub>2</sub> to prevent the anoxic conditions due to oxygen

98 consumption during the experiments. The persulfate or hydrogen peroxide/acetic acid molar  
99 ratios used were approximately 4/1.

## 100 **2.2. Analysis**

101 Persulfate was determined using the Alcian Blue colorimetric method developed by  
102 Villegas et al. (1963). H<sub>2</sub>O<sub>2</sub> was determined iodometrically (for actinometry) and  
103 photometrically using the TiCl<sub>4</sub> method for [H<sub>2</sub>O<sub>2</sub>] < 2 mM as described previously (Leitner  
104 and Doré, 1997). pH and dissolved oxygen were measured with respectively a pH electrode  
105 Sentix 81 and an oxygen probe Cellox 325 (WTW), both inserted in the reactor.

106 Organic acids were determined by HPLC with an anionic column (Supelco C-610H)  
107 eluted with 0.1% of H<sub>3</sub>PO<sub>4</sub> in water. For the experiments performed with H<sub>2</sub>O<sub>2</sub>, organic acids  
108 were determined with an anionic column (Aminex HPX-87H) eluted with 5 mM H<sub>2</sub>SO<sub>4</sub>  
109 solution after H<sub>2</sub>O<sub>2</sub> neutralisation with sodium thiosulfate. Oxalic acid was determined with a  
110 Nucléosil C<sub>18</sub> column eluted with mixed (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, Acetonitrile and octylamine in water.  
111 Detection was performed with UV detector at 210 nm (Waters 486). The relative standard  
112 deviation was always below 3%. Quantification of TOC was performed with a TOC thermal  
113 analyser (Shimadzu V<sub>CSH</sub>).

114

## 115 **Results and Discussion**

### 116 **3.1. Comparison of acetic acid removal by S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/UV and H<sub>2</sub>O<sub>2</sub>/UV systems**

117 It was shown that without any solute, the decay of the sulfate radical concentration can  
118 be described by the following reactions: the bimolecular reaction (Eq. 2), the reaction with  
119 S<sub>2</sub>O<sub>8</sub><sup>2-</sup> (Eq. 3) and the reaction with the water molecule (Eq. 4) or hydroxide ions (Eq. 5)  
120 (Hayon et al., 1972; Neta et al., 1988; Schuchmann and Von Sonntag, 1988; McElroy and  
121 Waygood, 1990; Chitose et al., 1999; Herrmann et al., 2000).





126 In our study, the evolution of  $\text{S}_2\text{O}_8^{2-}$  concentration in pure water during the photolysis  
 127 at 254 nm wavelength has enabled the determination of the global quantum yield ( $\Phi_1$ ) value  
 128 of photodissociation equal to 0.7. The reaction system has been simulated with a deterministic  
 129 kinetic model (Software Copasi). The input to the kinetic model includes a list of all reacting  
 130 species, their initial concentration obtained from the experimental measurements and the rate  
 131 constants (Eqs. 1-5 with additional Eqs. 6-7). A good prediction of the experimental data was  
 132 obtained for the rate constants  $k_2 = 4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_3 = 6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_4 = 360 \text{ s}^{-1}$ ;  $k_5 =$   
 133  $6.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_6 = 8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_7 = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . The corresponding  $\Phi$ -value for  
 134 the formation of sulfate radical (Eq. 1) is estimated to be equal to 0.52. Literature data extend  
 135 from 0.5 to 1.4 (Ivanov et al., 2000; Hori et al., 2005; Herrmann, 2007).



138 The photodegradation of persulfate leads to the production of two mol of  $\text{SO}_4^{2-}$  per  
 139 mol of  $\text{S}_2\text{O}_8^{2-}$  removed. Moreover, a pH decrease and a formation of  $0.2 \text{ mol O}_2 \text{ mol}^{-1} \text{ S}_2\text{O}_8^{2-}$   
 140 were observed.  $\text{H}^+$  ion formation was studied and quantified by Mark et al. (1990a, 1990b);  
 141 they found a  $\text{H}^+$  quantum yield of 1.8.

142 Two series of UV irradiation experiments were carried out on aqueous solution of  
 143 acetic acid under similar initial conditions of pH, temperature and concentrations of solutes:  
 144 one in the presence of hydrogen peroxide for the generation of  $\cdot\text{OH}$  radicals and the other in  
 145 the presence of persulfate ions for the production of  $\text{SO}_4^{\cdot-}$  radicals.

146 Figures 1a and 1b show the evolution of the concentrations of acetic acid and TOC at an  
 147 uncontrolled pH. The quantification of persulfate and hydrogen peroxide consumption during

148 photolysis shows no difference between the two systems. Moreover, the evolution of  $S_2O_8^{2-}$   
149 was not significantly influenced by the presence of 500  $\mu M$  of acetic acid under the  
150 experimental conditions of Fig. 1 (not presented).

151 During the acetic acid removal in the  $S_2O_8^{2-}/UV$  system, the pH decreased  
152 dramatically from the initial value of 7 to 3.3 after 15 min of irradiation due to  $SO_4^{2-}$   
153 formation and more slowly down to a final value of 2.6 as reported by Neppolian et al.  
154 (2008). Without regulation, the rapid pH decrease converts acetate ion into acetic acid ( $pK_a =$   
155 4.76). The rate constant of the sulfate radical towards this latter form is smaller (Table 1).  
156 According to Fig. 1, the  $S_2O_8^{2-}/UV$  system led to a fast acetic acid degradation i.e. the acetic  
157 acid was almost totally removed after 60 min. During the photolysis, the oxygen  
158 concentration decreased from 1.1 to 0.7 mM after 60 min. This  $O_2$  evolution is the resultant of  
159 production and consumption in the reaction system and represents an apparent oxygen  
160 consumption of 0.8 mol mol<sup>-1</sup> acetic acid removed. Concurrently, the TOC removal measured  
161 during the persulfate photolysis is also fast and the mineralization by the sulfate radicals was  
162 found to be complete after 80 min. Only small amounts of carboxylic acids were formed in  
163 the  $S_2O_8^{2-}/UV$  system. Formic, glycolic and glyoxylic acids were identified and their  
164 concentrations were found to reach a maximum concentration of 14, 15 and 5  $\mu M$   
165 respectively.

166 During the acetic acid oxidation by the  $H_2O_2/UV$  system, only one pH unit decrease  
167 was observed. The oxygen consumed after 90 min irradiation time was 0.5 mM corresponding  
168 to 1 mol mol<sup>-1</sup> acetic acid removed. The rate of acetic acid degradation was similar to the  
169  $S_2O_8^{2-}/UV$  system (Fig. 1a). In the  $H_2O_2/UV$  system, oxalic acid was the main by-product  
170 with a maximum concentration of 140  $\mu M$  representing 30% of the acetic acid removed for 90  
171 min irradiation time. The data are consistent with the previous work of Leitner and Doré



172 (1997) where they detected the formation of approximately 20% of oxalic acid. In addition,  
173 traces of formic acid were detected and did not exceed 13  $\mu\text{M}$ .

174 Although similar initial concentrations of  $\text{S}_2\text{O}_8^{2-}$  and  $\text{H}_2\text{O}_2$  lead to the same rate of  
175 acetic acid degradation, the TOC evolution in the  $\text{H}_2\text{O}_2/\text{UV}$  and  $\text{S}_2\text{O}_8^{2-}/\text{UV}$  systems is very  
176 different. A greater TOC removal is observed during the persulfate photolysis. After 60 min,  
177 the mineralization by the sulfate radicals is complete, while more than 20% of the initial  
178 organic carbon is still present in solution after 180 min of hydrogen peroxide photolysis. In  
179 both systems, the carbon content from the products quantified i.e. the remaining acetic acid  
180 and the carboxylic acids analyzed (TOC calculated values), accounts for the TOC measured  
181 with a great accuracy (Fig. 1b). The carbon mass balance from TOC and inorganic carbon  
182 showed that no volatile compounds were formed. Most of the by-products were identified.  
183 Thus it appears that compared to the hydroxyl radical, the sulfate radical enables a direct  
184 mineralization of the acetic acid molecule without significant formation of intermediates. The  
185 presence of intermediates and the competitive reactions induced in the  $\text{H}_2\text{O}_2/\text{UV}$  system  
186 (including the consumption of  $\cdot\text{OH}$  by  $\text{H}_2\text{O}_2$ ) accounts for the similar evolution of acetic acid  
187 in the two systems despite the highest reactivity of the hydroxyl radicals.

188 The attack of the hydroxyl radical on acetic acid yields  $\cdot\text{CH}_2\text{COOH}/\cdot\text{CH}_2\text{COO}^-$   
189 radicals from H-abstraction (Eqs. 8-9). This radical is known to react rapidly with oxygen ( $k$   
190  $= 1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) to form the corresponding peroxy radicals  $\cdot\text{O}_2\text{CH}_2\text{COO}^-$  (Eq. 10) source of  
191 glyoxylic acid, glycolic acid and formaldehyde (Schuchmann et al., 1985). These by-products  
192 are then oxidized into oxalic acid and  $\text{CO}_2$  (Leitner and Doré, 1997).



196 According to Chawla and Fessenden (1975), the sulfate radical attack leads to the  
197 formation of the  $\text{H}_3\text{C}^\bullet$  radical (Eqs. 11-12) by electron transfer. This radical was detected by  
198 Gilbert and Stell (1990) after reaction between sulfate radical and acetic acid.



201 Under our experimental conditions, in the presence of oxygen in solution, the methyl  
202 radicals are subsequently converted into methylperoxyl radicals ( $^\bullet\text{OOCH}_3$ ). The reactions of  
203 the methylperoxyl radicals have already been investigated in detail (Schuchmann and Von  
204 Sonntag, 1984). They are known to decompose into methanol, formaldehyde and formic acid  
205 with formation of  $\text{H}_2\text{O}_2$ . These by-products are rapidly mineralized owing to their high rate  
206 constant values with  $\text{SO}_4^{\bullet-}$  and  $^\bullet\text{OH}$  radicals compared to acetic acid. Under our experimental  
207 conditions in the two systems, the solutions were neither anoxic and consequently by-products  
208 from dimerization of the primary radicals were not expected. This was confirmed by the  
209 almost complete carbon mass balance.

210

### 211 **3.2. Influence of pH**

212 A kinetic change with the pH is expected in the  $\text{SO}_4^{\bullet-}$  reaction system. Indeed (i) the  
213 rate constants of the sulfate radical on the acetic acid and acetate ion are different (1.4 to  
214  $20 \times 10^4$  and 4.3 to  $28 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  respectively; Table 1) and (ii) the increase of pH favors the  
215 contribution of the  $\text{SO}_4^{\bullet-}$  radical consumption from the reaction with the hydroxide ions to  
216 form the hydroxyl radical (Eq. 5). The rate constant for the reaction of  $^\bullet\text{OH}$  radicals with  
217 acetate ions is higher than the rate constant with acetic acid ( $8.5 \times 10^7$  and  $1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$   
218 respectively). Regarding the species present for different pH values and their reactivity, an  
219 improvement of the organic acid removal would be expected in the  $\text{S}_2\text{O}_8^{2-}/\text{UV}$  system when  
220 the pH is increased. Figure 2 confirms the better removal at pH 5 compared to pH 2 and 3 due

221 to the higher reactivity of the acetate ion. However, the kinetic of acetic acid removal is  
 222 slower at pH 7 than at pH 5 and decreases for higher pH values (Fig. 2). The pH influences  
 223 the formation of the active species ( $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$ ), the reaction of the active species with the  
 224 substrate (acetic acid and acetate ions) but also competitive reactions with the by-products  
 225 (organic acids, carbonic acid and bicarbonates). From the rate constants of the sulfate radical  
 226 with acetate and hydroxide ions ( $k_{12} = 4.3$  to  $28 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_5 = 1$  to  $7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$   
 227 respectively) and considering the reactivity of the hydroxyl radicals towards acetate ions ( $k_9 =$   
 228  $8.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) it can be calculated that the contribution of the  $\cdot\text{OH}$  radicals in the removal  
 229 of acetate becomes significant only for pH above 9. In a basic solution, the reaction of sulfate  
 230 radical with hydroxide ions becomes very significant. This reaction is considered as  
 231 predominant for a pH higher than 10.5. Chawla and Fessenden (1975) showed the radical  
 232 conversion in alkaline condition by electron spin resonance study.

233 In the pH range 2 to 7, i.e. when  $\text{SO}_4^{\cdot-}$  is the main active species, considering the  
 234 pseudo first order expression (Eq. 13), the constant  $k_{\text{app}}$  was found to increase up to pH 5 and  
 235 then decrease for higher pH values (Fig. 2).

$$236 \quad -\frac{d[\text{S}]}{dt} = (k_{11} [\text{CH}_3\text{COOH}] + k_{12} [\text{CH}_3\text{COO}^-]) [\text{SO}_4^{\cdot-}]$$

$$237 \quad -\frac{d[\text{S}]}{dt} = k_s [\text{S}] [\text{SO}_4^{\cdot-}]_{\text{ss}}$$

$$238 \quad -\frac{d[\text{S}]}{dt} = k_{\text{app}} [\text{S}] \tag{13}$$

$$239 \quad \text{with } [\text{S}] = [\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-]$$

$$240 \quad [\text{SO}_4^{\cdot-}]_{\text{ss}} = \text{Concentration of } \text{SO}_4^{\cdot-} \text{ at steady state}$$

$$241 \quad \text{and } k_s = \frac{k_{12} \text{Ka} + k_{11} [\text{H}^+]}{[\text{H}^+] + \text{Ka}}$$

242 The concentration of the  $\text{SO}_4^{\bullet-}$  radical (Eq. 16) is the resultant of the formation from  
 243  $\text{S}_2\text{O}_8^{2-}$  photolysis and the consumption by acetic acid, acetate ions, inorganic carbon (Eqs. 14-  
 244 15) and also by persulfate ions (Eq. 3).



$$247 \quad -\frac{d[\text{SO}_4^{\bullet-}]_{\text{ss}}}{dt} = \frac{\Phi_2 I_0 e^{(-\varepsilon l [\text{S}_2\text{O}_8^{2-}])}}{V} - (k_s[\text{S}] + k_l[\text{I}] + k_3[\text{S}_2\text{O}_8^{2-}])[\text{SO}_4^{\bullet-}]_{\text{ss}}$$

$$248 \quad -\frac{d[\text{SO}_4^{\bullet-}]_{\text{ss}}}{dt} = A - B [\text{SO}_4^{\bullet-}]_{\text{ss}} = 0 \quad (16)$$

249 with

250  $\Phi_2$ : quantum yield of sulfate radical formation (0.52)

251  $I_0$ : incident photonic flux ( $9.9 \times 10^{-6} \text{ E s}^{-1}$ )

252  $\varepsilon$ : molar absorption coefficient ( $19 \text{ mol}^{-1} \text{ cm}^{-1}$ )

253  $l$ : optical width (6.3 cm)

254  $V$ : reactor volume (5 L)

255  $k_3 = 6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$

256  $[\text{I}] = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-]$  for pH 2 to 7;  $\text{pK}_a (\text{H}_2\text{CO}_3/\text{HCO}_3^-) = 6.4$

$$257 \quad k_l = \frac{k_{15} \text{Ka} + k_{14}[\text{H}^+]}{[\text{H}^+] + \text{Ka}}$$

258 According to the  $\text{pK}_a$  values ( $\text{pK}_a (\text{HCO}_3^-/\text{CO}_3^{2-}) = 10.3$ ), at pH 9 (with  $[\text{I}] = [\text{HCO}_3^-]$   
 259  $+ [\text{CO}_3^{2-}]$ ), the expression  $k_l$  is calculated with the corresponding rate constants:  $k (\text{SO}_4^{\bullet-}$   
 260  $^{\bullet}/\text{CO}_3^{2-}) = 6.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{15}$ . From the analysis of persulfate ions, acetic acid and acetate  
 261 ions and from the TOC removed (i.e. I values), the concentration of  $\text{SO}_4^{\bullet-}$  radicals could be  
 262 determined from Eq. 16 at different irradiation times and pH values (Table 2). It is noted that

263 the evolution of  $S_2O_8^{2-}$  concentration is not influenced by the pH. In Table 2, for a given  
264 irradiation time, A doesn't vary with the pH.

265 The values of  $SO_4^{\cdot-}$  reported in Table 2 and the rate constants  $k_s$  enable the calculation  
266 of the apparent rate constants  $k_{app}$  for different irradiation times and pH. The data show that  
267 the values of  $k_{app}$  calculated from the kinetic expression are in accordance with the  
268 experimental values of Fig. 2. Data from kinetic expressions confirm that  $k_{app}$  increases from  
269 pH 2 to pH 5. From pH 5 to 9 data indicate that even if the global rate constant of acetic acid  
270 with  $SO_4^{\cdot-}$  radicals increases, the apparent constant  $k_{app}$  decreases. This is due to the smaller  
271  $SO_4^{\cdot-}$  concentrations at the highest pH values as a consequence of an increasing consumption  
272 by both the substrate and inorganic carbon as shown in Table 2. Thus, from pH 5 it was  
273 shown that the contribution of the inhibiting reactions with carbonic acid, bicarbonates and  
274 carbonates increases with regard to acetic acid degradation. These results explain the optimum  
275 rate of acetic acid removal observed at pH 5. Up to pH 9 the data processing is much more  
276 complex since  $\cdot OH$  radicals are involved from  $SO_4^{\cdot-}$  reaction with  $OH^-$  ions (Eq. 5).

277 The oxidation of acetic acid in the  $S_2O_8^{2-}/UV$  system was tentatively simulated at  
278 various pH using the previous kinetic model (Copasi) taking into consideration the photolysis  
279 of  $S_2O_8^{2-}$  (Eqs. 1-7) and the reactions with the sulfate and hydroxyl radicals (Eqs. 8-12, 14-15)  
280 (Fig. 3). This simulation predicts reliably the existing optimum pH value. However, at this pH  
281 (pH = 5) the initial rapid decrease of acetic acid concentration is badly described up to 20 min  
282 of irradiation.

283 The different by-products formed from the action of sulfate and hydroxyl radicals on  
284 acetic acid can be used to identify the nature of the active species in the  $S_2O_8^{2-}/UV$  system.  
285 Indeed in this system, the experiment carried out at pH 11 shows oxalic acid formation which  
286 is not found at lower pH levels. Same by-products are formed in the same order of

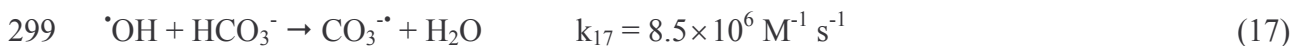
287 concentration from H<sub>2</sub>O<sub>2</sub>/UV and S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/UV at pH 11 (Fig. 4) which confirms the Eq. 5 and  
 288 the main contribution of the <sup>•</sup>OH radical.

289 However, in the S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/UV process the elimination of acetic acid is slowed down after  
 290 30 min of photolysis. This point could arise from the existing reaction between <sup>•</sup>OH and  
 291 persulfate (Chitose et al., 1999). This reaction depletes the persulfate concentration and could  
 292 produce other radical less reactive than the sulfate radical. The same reaction (Eq. 3) exists  
 293 between persulfate and sulfate radical but rate constants are lower than with <sup>•</sup>OH.

294

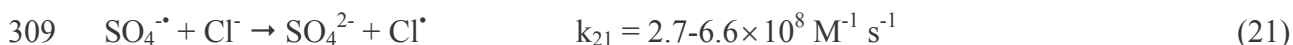
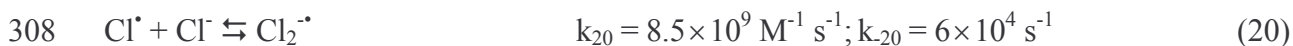
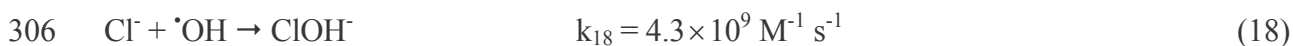
### 295 **3.3 Influence of chloride and bicarbonate ions**

296 Like the hydroxyl radical, the sulfate radical leads to the formation of radicals from  
 297 numerous anions. Both, hydroxyl and sulfate radicals can react with the bicarbonate ions to  
 298 produce the carbonate radical CO<sub>3</sub><sup>•-</sup> (Eqs. 15 and 17).



300 In the case of the chloride ion, <sup>•</sup>OH reacts with Cl<sup>-</sup> to give the chloride atom Cl<sup>•</sup> (Eqs. 18-19).

301 In the presence of an excess of Cl<sup>-</sup> ions, chlorine atoms are immediately scavenged to give  
 302 Cl<sub>2</sub><sup>•-</sup> (Eq. 20). Cl<sub>2</sub><sup>•-</sup> is believed to be relatively unreactive with aliphatic acids (Gilbert et al.,  
 303 1988). According to the intermediate reactions, <sup>•</sup>OH gives the Cl<sup>•</sup> and Cl<sub>2</sub><sup>•-</sup> radicals in acidic  
 304 conditions only. However the SO<sub>4</sub><sup>•-</sup> radical would react with Cl<sup>-</sup> to produce the Cl<sup>•</sup> radical  
 305 even in neutral solutions (Eq. 21).



310 The influence of the chloride and bicarbonate ions on the acetic acid degradation  
 311 during S<sub>2</sub>O<sub>8</sub><sup>2-</sup> photolysis was studied and compared with the H<sub>2</sub>O<sub>2</sub>/UV system. Experiments

312 were carried out in the presence of NaCl (500 or 5000  $\mu\text{M}$ ) or  $\text{NaHCO}_3$  (10 mM) at pH 7  
313 controlled with NaOH. The Fig. 5a illustrates the results.

314 Considering the rate constants for the reaction of  $\text{SO}_4^{\cdot-}$  radicals with acetate ions ( $k =$   
315  $5.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) and chloride ions ( $k = 3.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ), chloride ions concentrations of 500  
316 and 5000  $\mu\text{M}$  induce a consumption of  $\text{SO}_4^{\cdot-}$  radicals respectively 60 and 600 times greater  
317 than acetate. According to the Fig. 5a, although the reaction of  $\text{SO}_4^{\cdot-}$  with the chloride ion is  
318 dominating, the elimination of the acetic acid is faster in the presence of chloride ions in the  
319 persulfate/UV system. This acceleration can be explained considering that the Eq. 21 between  
320 the sulfate radical and the chloride ion which leads to the  $\text{Cl}^{\cdot}$  radical is followed by the  
321 reaction of this latter with acetate. The  $\text{Cl}^{\cdot}$  radical with a rate constant of  $3.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$   
322 (Buxton et al., 2000), i.e. three orders greater than the  $\text{SO}_4^{\cdot-}$  radical, (Table 1) is highly  
323 reactive with the acetate ion. Liang et al., (2006) showed an inhibition of trichloroethylene  
324 degradation for a chloride ion concentration higher than 0.2 M; no significant variation was  
325 observed for lower concentrations.

326 With equal concentrations of chloride and acetate used in this experiment, the  
327 formation of dichlorine radical ion is somewhat favored ( $k = 8.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) over the  
328 reaction of chlorine atom with acetate ( $k = 3.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). However, the dichlorine radical  
329 ion reacts slowly with acetate ( $k \approx 2.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ) compared to the chlorine atom and then  
330 the reaction of acetate with  $\text{Cl}^{\cdot}$  is believed to be significant (Gilbert et al., 1988). The  
331 experiment carried out with the highest chloride ions concentration (5000  $\mu\text{M}$ ) shows that the  
332 chloride ion concentration has no influence on the reactivity towards acetate. It reflects that  
333 increasing chloride ion concentration, the sulfate radical ion becomes the limiting reagent.

334 Concerning the mineralization of the carboxylic acid, the organic carbon removal is  
335 similar with or without chloride ions (Fig. 5b). The TOC balance including the formic acid

336 detected is incomplete in the presence of chloride ions. Unidentified by-products must be  
337 formed from the action of  $\text{Cl}^\bullet$  radicals on acetate.

338 As concerns the influence of the inorganic carbon, the concentration of bicarbonate  
339 ions was chosen in order to represent a competitive factor towards acetate ions close to the  
340 experiment with chloride ions (500  $\mu\text{M}$ ). Indeed, 10 mM of bicarbonate ions were introduced  
341 in the presence of the acetate ions in the  $\text{S}_2\text{O}_8^{2-}/\text{UV}$  system. Thus, the reaction of the sulfate  
342 radical with the bicarbonate ions ( $k_{15} = 9.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) was expected to be 30 times faster  
343 than the reaction with acetate ( $k_{12} = 5.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ). According to Fig. 5a, contrary to  
344 chloride ions, bicarbonate ions slow down dramatically the degradation of acetic acid in the  
345  $\text{S}_2\text{O}_8^{2-}/\text{UV}$  system. This inhibition is consistent with the low reactivity of the  $\text{CO}_3^{\bullet-}$  radical.

346 The influence of the two ions,  $\text{Cl}^-$  and  $\text{HCO}_3^-$  towards acetate removal, was also  
347 examined in the  $\text{H}_2\text{O}_2/\text{UV}$  system. Rate constants of reaction of hydroxyl radical with acetate  
348 and bicarbonate ions are respectively  $8.5 \times 10^7$  and  $8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . The experiment was  
349 carried out with a bicarbonate concentration of 0.18 M so as to obtain the same competitive  
350 factor ( $k_{17} [\text{HCO}_3^-]/k_9 [\text{CH}_3\text{COO}^-] = 30$ ) as in the persulfate/UV system. However in the case  
351 of the chloride ion, the rate constant with the  $^\bullet\text{OH}$  radical is known in acid media only. Since  
352 the rate constant of  $^\bullet\text{OH}$  with bicarbonate is close to the rate constant of  $\text{SO}_4^{\bullet-}$  with  
353 bicarbonate, it was assumed that the rate constant of  $^\bullet\text{OH}$  with  $\text{Cl}^-$  was similar to those  
354 between  $\text{SO}_4^{\bullet-}$  and  $\text{Cl}^-$  radical (i.e. about  $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ). Then, from an initial  $\text{Cl}^-$   
355 concentration of 5000  $\mu\text{M}$ , the rate constant  $k [\text{Cl}^-]$  was almost 35 times greater than the value  
356  $k_9 [\text{CH}_3\text{COO}^-]_0$ . The experiment about the influence of chloride ions in the  $\text{H}_2\text{O}_2/\text{UV}$  system  
357 was performed with a chloride ion concentration of 5000  $\mu\text{M}$ .

358 Figure 5a shows that the presence of chloride ions does not have any effect on acetic  
359 acid degradation in the  $\text{H}_2\text{O}_2/\text{UV}$  system. This result highlights that the rate constant of the  
360 hydroxyl radical with  $\text{Cl}^-$  ions at neutral pH is much smaller than the rate with the  $\text{SO}_4^{\bullet-}$



361 radical. Chloride ion does not compete for  $\cdot\text{OH}$  radical under pH conditions used in this study.  
362 By comparing the effect of bicarbonate ions addition in the  $\text{S}_2\text{O}_8^{2-}/\text{UV}$  and  $\text{H}_2\text{O}_2/\text{UV}$  systems,  
363 the inhibition appears to be greater in the  $\cdot\text{OH}$  radical generation process. As expected,  
364 bicarbonate ions addition in the  $\text{H}_2\text{O}_2/\text{UV}$  system leads to the total inhibition of acetic acid  
365 elimination and TOC removal by  $\cdot\text{OH}$ .

366

### 367 **3. Conclusions**

368 From this study it appears that the sulfate radical generated from the  $\text{S}_2\text{O}_8^{2-}/\text{UV}$  system  
369 (with a quantum yield of formation found to be 0.52) is of interest with regard to the  
370 mineralization of acetic acid in pure water. Under these conditions, at neutral pH or below,  
371 the persulfate photolysis could advantageously compete with the more common process based  
372 on hydrogen peroxide photolysis. The earlier by preventing the formation of by-products,  
373 favors the reaction of the active radical with the substrate. The promoting effect of the  
374 chloride ions could also render this advanced oxidation process attractive for the treatment of  
375 waters containing ions. However it was found that like  $\cdot\text{OH}$  radicals, the  $\text{SO}_4^{\cdot-}$  radicals are  
376 scavenged by bicarbonates. This inhibiting effect together with the conversion of  $\text{SO}_4^{\cdot-}$   
377 radicals into  $\cdot\text{OH}$  by reaction with  $\text{OH}^-$  ions is also responsible for the limited efficiency of the  
378  $\text{S}_2\text{O}_8^{2-}/\text{UV}$  process observed with the increase of pH.

379

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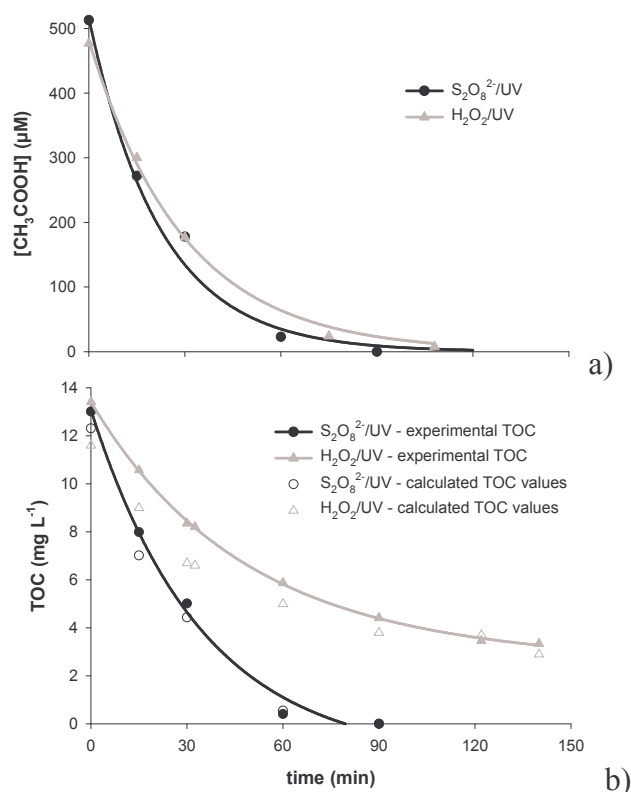
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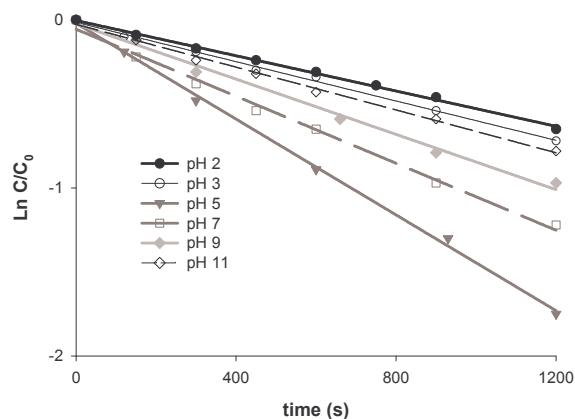
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 510 **Fig. 1. Acetic acid removal by persulfate and hydrogen peroxide photolysis**  
 511 **a)  $\text{CH}_3\text{COOH}$ ; b) TOC**

512  $\text{S}_2\text{O}_8^{2-}/\text{UV}$ :  $[\text{S}_2\text{O}_8^{2-}]_i = 1755 \mu\text{M}$ ;  $\text{pHi} = 7.05$ ;  $[\text{O}_2]_i = 1.1 \text{ mM}$

513  $\text{H}_2\text{O}_2/\text{UV}$ :  $[\text{H}_2\text{O}_2]_i = 1780 \mu\text{M}$ ;  $\text{pHi} = 6.93$ ;  $[\text{O}_2]_i = 1.0 \text{ mM}$ .

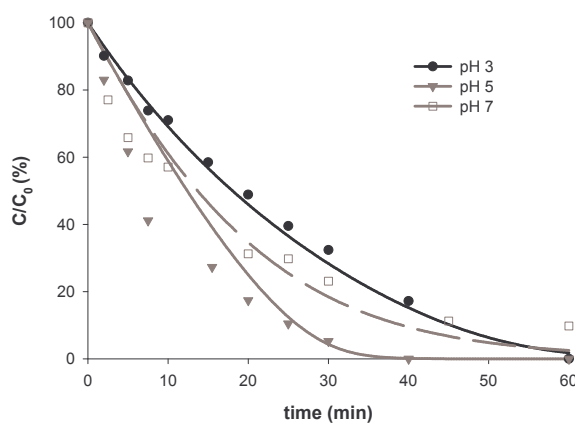
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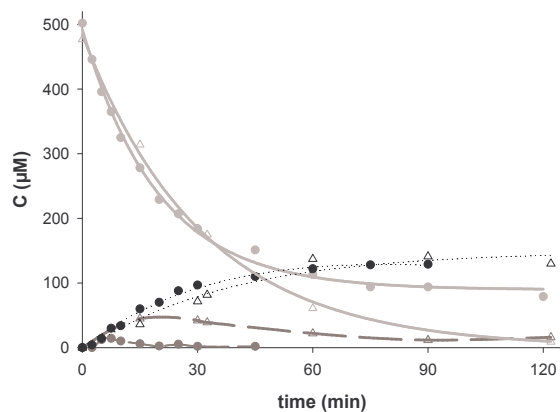
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517 **Fig. 2. Acetic Acid degradation in the  $S_2O_8^{2-}/UV$  system at 254 nm.**  
 518  $[CH_3COOH]_0 = 500 \mu M$ ;  $[S_2O_8^{2-}]_0 = 1800 \mu M$ . pH regulation with NaOH (1 M) or  
 519 perchloric acid (1 M) additions.  
 520



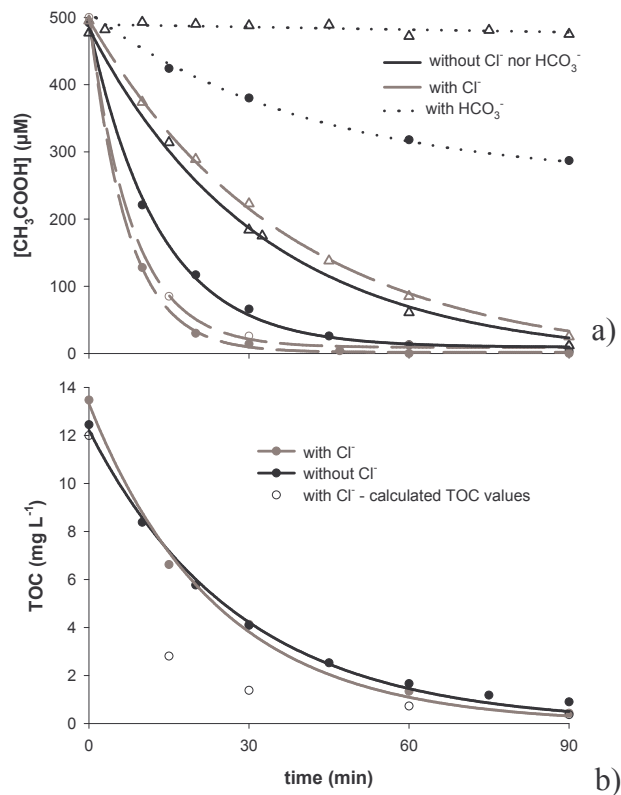
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522 **Fig. 3. Acetic acid degradation modelling at different pH.**  
 523 **Lines: simulation results; symbols: experimental data;  $[CH_3COOH]_0 = 500 \mu M$**   
 524 **(Rate constants used:  $k_2 = 4 \times 10^8 M^{-1} s^{-1}$ ;  $k_3 = 6 \times 10^4 M^{-1} s^{-1}$ ;  $k_4 = 360 s^{-1}$ ;**  
 525  **$k_5 = 6.5 \times 10^7 M^{-1} s^{-1}$ ;  $k_6 = 8 \times 10^4 M^{-1} s^{-1}$ ;  $k_7 = 1 \times 10^{10} M^{-1} s^{-1}$  and  $k_{12} = 2.8 \times 10^7 M^{-1} s^{-1}$ ).**  
 526  
 527



528

529 **Fig. 4. Acetic acid removal and by-products formation by H<sub>2</sub>O<sub>2</sub>/UV and S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/UV at pH**  
 530 **11 Δ H<sub>2</sub>O<sub>2</sub>/UV; ● S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/UV**  
 531 **H<sub>2</sub>O<sub>2</sub>/UV: [H<sub>2</sub>O<sub>2</sub>]<sub>i</sub> = 1780 μM; pH<sub>i</sub> = 6.9; [O<sub>2</sub>]<sub>i</sub> = 1.0 mM**  
 532 **S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/UV: [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>]<sub>i</sub> = 1650 μM; pH controlled at 11; [O<sub>2</sub>]<sub>i</sub> = 0.56 mM.**



533

534 **Fig. 5. a) Impact of Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> on the S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/UV and H<sub>2</sub>O<sub>2</sub>/UV systems**  
 535 **● S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/UV:**  
 536 **- without Cl<sup>-</sup> nor HCO<sub>3</sub><sup>-</sup>: [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>]<sub>i</sub> = 2030 μM; [O<sub>2</sub>]<sub>i</sub> = 0.56 mM; pH 7**  
 537 **- with Cl<sup>-</sup>: [Cl<sup>-</sup>] = 500 μM; [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>]<sub>i</sub> = 1740 μM; [O<sub>2</sub>]<sub>i</sub> = 0.66 mM; pH 7 (solid symbol)**  
 538 **- with Cl<sup>-</sup>: [Cl<sup>-</sup>] = 5000 μM; [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>]<sub>i</sub> = 1950 μM; [O<sub>2</sub>]<sub>i</sub> = 0.77 mM; pH 7 (open symbol)**  
 539 **- with HCO<sub>3</sub><sup>-</sup>: [HCO<sub>3</sub><sup>-</sup>] = 10 mM; [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>]<sub>i</sub> = 1830 μM; [O<sub>2</sub>]<sub>i</sub> = 0.64 mM; pH 8.2**  
 540 **Δ H<sub>2</sub>O<sub>2</sub>/UV:**  
 541 **- without Cl<sup>-</sup> nor HCO<sub>3</sub><sup>-</sup>: [H<sub>2</sub>O<sub>2</sub>]<sub>i</sub> = 1950 μM; [O<sub>2</sub>]<sub>i</sub> = 0.80 mM; pH 7**  
 542 **- with Cl<sup>-</sup>: [H<sub>2</sub>O<sub>2</sub>]<sub>i</sub> = 1750 μM; [Cl<sup>-</sup>] = 5000 μM; [O<sub>2</sub>]<sub>i</sub> = 0.68 mM; pH 7**  
 543 **- with HCO<sub>3</sub><sup>-</sup>: [H<sub>2</sub>O<sub>2</sub>]<sub>i</sub> = 1720 μM; [HCO<sub>3</sub><sup>-</sup>] = 0.18 M; [O<sub>2</sub>]<sub>i</sub> = 0.73 mM; pH 8.4**  
 544 **b) TOC Mineralization in the S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/UV system**  
 545 **- without Cl<sup>-</sup>: [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>]<sub>i</sub> = 1580 μM; pH 7; [O<sub>2</sub>]<sub>i</sub> = 0.68 mM**  
 546 **- with Cl<sup>-</sup>: [Cl<sup>-</sup>] = 500 μM; [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>]<sub>i</sub> = 1740 μM; [O<sub>2</sub>]<sub>i</sub> = 0.66 mM.**  
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**Table 1. Rate constants for the reaction of SO<sub>4</sub><sup>•-</sup>, <sup>•</sup>OH and Cl<sup>•</sup> radicals (M<sup>-1</sup> s<sup>-1</sup>).**

	SO <sub>4</sub> <sup>•-</sup>	<sup>•</sup> OH	Cl <sup>•</sup>
CH <sub>3</sub> COOH	<b>2.0 × 10<sup>5</sup></b> (Herrmann et al., 2000) 8.8 × 10 <sup>4</sup> (Dogliotti and Hayon, 1967b) 1.4 × 10 <sup>4</sup> (Buxton et al., 2000)	<b>1.5 × 10<sup>7</sup></b> (Buxton et al., 1988)	3.2 × 10 <sup>7</sup> (Buxton et al., 2000)
CH <sub>3</sub> COO <sup>-</sup>	5.06 × 10 <sup>6</sup> (Huie and Clifton, 1990) <b>5.0 × 10<sup>6</sup></b> (Chawla and Fessenden, 1975) 2.8 × 10 <sup>7</sup> (Herrmann et al., 2000) 4.3 × 10 <sup>6</sup> (Buxton et al., 2000)	<b>8.5 × 10<sup>7</sup></b> (Buxton et al., 1988)	3.7 ± 0.4 × 10 <sup>9</sup> (Buxton et al., 2000)
Cl <sup>•</sup>	2.7 × 10 <sup>8</sup> (Huie and Clifton, 1990) <b>3.1 × 10<sup>8</sup></b> (Chawla and Fessenden, 1975) 4.28 ± 0.05 × 10 <sup>8</sup> (George and Chovelon, 2002) 2.7-6.6 × 10 <sup>8</sup> (McElroy, 1990) 6.1 ± 0.2 × 10 <sup>8</sup> (Buxton et al., 1999) 4.7 × 10 <sup>8</sup> (Huie et al., 1991b)	4.3 × 10 <sup>9a</sup> (Buxton et al., 1988)	8.5 × 10 <sup>9</sup> (Buxton et al., 2000)
HCO <sub>3</sub> <sup>-</sup>	3.53 × 10 <sup>6</sup> (Huie and Clifton, 1990) <b>9.1 × 10<sup>6</sup></b> (Dogliotti and Hayon, 1967a) 1.6 ± 0.2 × 10 <sup>6</sup> (Zuo et al., 1999)	<b>8.5 × 10<sup>6</sup></b> (Buxton et al., 1988)	2.2 × 10 <sup>8</sup> (Mertens and Von Sonntag, 1995) 2.4 ± 0.5 × 10 <sup>9</sup> (Buxton et al., 2000)
CO <sub>3</sub> <sup>2-</sup>	<b>6.1 ± 0.4 × 10<sup>6</sup></b> (Zuo et al., 1999) 4.1 × 10 <sup>6</sup> (Padmaja et al., 1993)	<b>3.9 × 10<sup>8</sup></b> (Buxton et al., 1988)	5.0 × 10 <sup>8</sup> (Mertens and Von Sonntag, 1995)

552 bold characters : constants used for calculations

553 <sup>a</sup> at pH < 1

554 **Table 2. Experimental and calculated k<sub>app</sub> and SO<sub>4</sub><sup>•-</sup> radical concentrations calculated**  
555 **for different pH and different reaction times (steady state).**

pH	k <sub>s</sub> (M <sup>-1</sup> s <sup>-1</sup> )	k <sub>i</sub> (M <sup>-1</sup> s <sup>-1</sup> )	10 min (A = 8.8 × 10 <sup>-7</sup> )		20 min (A = 9.0 × 10 <sup>-7</sup> )		30 min (A = 9.2 × 10 <sup>-7</sup> )	
			1/B (s)	[SO <sub>4</sub> <sup>•-</sup> ] <sub>ss</sub> (M)	1/B (s)	[SO <sub>4</sub> <sup>•-</sup> ] <sub>ss</sub> (M)	1/B (s)	[SO <sub>4</sub> <sup>•-</sup> ] <sub>ss</sub> (M)
2	2.1 × 10 <sup>5</sup>	1.0 × 10 <sup>6</sup>	2.6 × 10 <sup>-3</sup>	2.3 × 10 <sup>-9</sup>	1.8 × 10 <sup>-3</sup>	1.6 × 10 <sup>-9</sup>	1.5 × 10 <sup>-3</sup>	1.4 × 10 <sup>-9</sup>
3	2.8 × 10 <sup>5</sup>	1.0 × 10 <sup>6</sup>	2.3 × 10 <sup>-3</sup>	2.0 × 10 <sup>-9</sup>	1.6 × 10 <sup>-3</sup>	1.4 × 10 <sup>-9</sup>	1.4 × 10 <sup>-3</sup>	1.3 × 10 <sup>-9</sup>
5	32 × 10 <sup>5</sup>	1.3 × 10 <sup>6</sup>	7.0 × 10 <sup>-4</sup>	6.1 × 10 <sup>-9</sup>	8.0 × 10 <sup>-4</sup>	7.2 × 10 <sup>-10</sup>	7.7 × 10 <sup>-4</sup>	7.5 × 10 <sup>-10</sup>
7	50 × 10 <sup>5</sup>	7.4 × 10 <sup>6</sup>	2.4 × 10 <sup>-4</sup>	2.1 × 10 <sup>-10</sup>	1.9 × 10 <sup>-4</sup>	1.8 × 10 <sup>-10</sup>	1.7 × 10 <sup>-4</sup>	1.6 × 10 <sup>-10</sup>
9	50 × 10 <sup>5</sup>	9.0 × 10 <sup>6</sup>	2.0 × 10 <sup>-4</sup>	1.7 × 10 <sup>-10</sup>	1.6 × 10 <sup>-4</sup>	1.5 × 10 <sup>-10</sup>	1.4 × 10 <sup>-4</sup>	1.3 × 10 <sup>-10</sup>

pH	Experimental k <sub>app</sub> (s <sup>-1</sup> )	k <sub>app</sub> (s <sup>-1</sup> )		
		10 min	20 min	30 min
2	5.3 × 10 <sup>-4</sup>	4.8 × 10 <sup>-4</sup>	3.3 × 10 <sup>-4</sup>	2.8 × 10 <sup>-4</sup>
3	6.0 × 10 <sup>-4</sup>	5.6 × 10 <sup>-4</sup>	4.0 × 10 <sup>-4</sup>	3.3 × 10 <sup>-4</sup>
5	1.4 × 10 <sup>-3</sup>	1.9 × 10 <sup>-3</sup>	2.3 × 10 <sup>-3</sup>	2.3 × 10 <sup>-3</sup>
7	1.0 × 10 <sup>-3</sup>	1.1 × 10 <sup>-3</sup>	8.8 × 10 <sup>-4</sup>	7.7 × 10 <sup>-4</sup>
9	8.5 × 10 <sup>-4</sup>	8.6 × 10 <sup>-4</sup>	7.4 × 10 <sup>-4</sup>	6.4 × 10 <sup>-4</sup>

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