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Justine Criquet, Nathalie Karpel Vel Leitner.
radical generated by persulfate ions photolysis.
10.1016/j.chemosphere.2009.07.040 . hal-02592931

Degradation of acetic acid with sulfate
Chemosphere, 2009, 77 (2), pp.194-200.

HAL Id: hal-02592931

<https://hal.science/hal-02592931>

Submitted on 15 May 2020

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Degradation of Acetic Acid with Sulfate Radical Generated by persulfate ions photolysis

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Abstract

The photolysis of $S_2O_8^{2-}$ was studied for the removal of acetic acid in aqueous solution and compared with the H_2O_2 /UV system. The $SO_4^{\bullet-}$ radicals generated from the UV irradiation of $S_2O_8^{2-}$ ions yield a greater mineralization of acetic acid than the $\bullet OH$ radicals. Acetic acid is oxidized by $SO_4^{\bullet-}$ radicals without significant formation of intermediate by-products. Increasing system pH results in the formation of $\bullet OH$ radicals from $SO_4^{\bullet-}$ radicals. Maximum acetic acid degradation occurred at pH 5. The results suggest that above this pH, competitive reactions with the carbon mineralized inhibit the reaction of the solute with $SO_4^{\bullet-}$ and also $\bullet OH$ radicals. Scavenging effects of two naturally occurring ions were tested; in contrast to HCO_3^- ions, the presence of Cl^- ions enhances the efficiency of the $S_2O_8^{2-}$ /UV process towards the acetate removal. It is attributed to the formation of the $Cl^{\bullet}$ radical and its great reactivity towards acetate.

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

1. Introduction

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

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

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

The sulfate radical was studied for the removal of refractory pollutants. Manoj et al. (2002) studied the cyanuric acid degradation by persulfate laser flash photolysis and steady state radiolysis; they determined a second order rate constant of $1.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ by monitoring the decay of absorption of $\text{SO}_4^{\cdot-}$ as a function of cyanuric acid concentration. Others (Hori et al., 2005; Hori et al., 2007) showed the photochemical decomposition of perfluorocarboxylic acids induced by persulfate as photochemical oxidant; these compounds were transformed to F^- and CO_2 and small amounts of perfluorocarboxylic acids with shorter chain lengths. Liang et al. (Liang et al., 2004; Liang et al., 2006) described an application of *in situ* chemical oxidation for trichloroethylene oxidation by thermal or transition metal activation of persulfate. Moreover, Mora et al. (2009) showed the degradation of trichloroacetic acid by persulfate thermal activation in presence of formate as an additive to produce $\text{CO}_2^{\cdot-}$ which are radicals available for degrading trichloroacetic acid by a reductive pathway.

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

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

The objective of this work was to investigate the sulfate radical reactivity towards acetic acid, a persistent by-product in numerous oxidation processes like O₃ and AOPs. The by-products formed from oxidation of acetic acid by the hydroxyl radicals are known; they consist mostly in oxalic and formic acids (Schuchmann et al., 1985; Leitner and Doré, 1997). Thus, this molecule was chosen to compare the action of SO₄^{•-} and [•]OH radicals generated by two processes, S₂O₈²⁻ and H₂O₂ irradiation at 254 nm respectively. In addition, the influence of chloride and bicarbonate ions was examined for both conditions.

2. Materials and methods

2.1. Experimental setup

Irradiation experiments were conducted in a 5 L cylindrical batch reactor without headspace to prevent the loss of volatile by-products. This reactor is equipped with a low pressure mercury vapor lamp (Hanau NN/40/20) in the axial position with an optical width of 6.3 cm. The lamp emits a monochromatic radiation at 253.7 nm. The incident photonic flux ($I_0 = 9.9 \times 10^{-6} \text{ E s}^{-1}$) was determined by chemical actinometry using a $4 \times 10^{-2} \text{ M}$ hydrogen peroxide solution (and with the quantum yield $\Phi = 1$ for the overall reaction of H₂O₂ photolysis). During all experiments the solutions were thermostated at 25±1 °C.

All reagents were reagent grade and were used without further purification: K₂S₂O₈ (Aldrich), H₂O₂ (30% Fulka), Acetic acid (> 99%, Riedel de Haën), NaCl and NaHCO₃ (> 99%, Fischer).

All solutions were prepared in ultra pure water (MilliQ water; TOC < 0.2 mg L⁻¹; 18 MΩ cm). The pH was left uncontrolled or controlled during the course of the reaction by addition of sodium hydroxide or perchloric acid. Dissolved oxygen concentration was initially set at 20-30 mg L⁻¹ by bubbling O₂ to prevent the anoxic conditions due to oxygen

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

2.2. Analysis

Persulfate was determined using the Alcian Blue colorimetric method developed by Villegas et al. (1963). H_2O_2 was determined iodometrically (for actinometry) and photometrically using the TiCl_4 method for $[\text{H}_2\text{O}_2] < 2 \text{ mM}$ as described previously (Leitner and Doré, 1997). pH and dissolved oxygen were measured with respectively a pH electrode Sentix 81 and an oxygen probe Cellox 325 (WTW), both inserted in the reactor.

Organic acids were determined by HPLC with an anionic column (Supelco C-610H) eluted with 0.1% of H_3PO_4 in water. For the experiments performed with H_2O_2 , organic acids were determined with an anionic column (Aminex HPX-87H) eluted with 5 mM H_2SO_4 solution after H_2O_2 neutralisation with sodium thiosulfate. Oxalic acid was determined with a Nucléosil C_{18} column eluted with mixed $(\text{NH}_4)_2\text{HPO}_4$, Acetonitrile and octylamine in water. Detection was performed with UV detector at 210 nm (Waters 486). The relative standard deviation was always below 3%. Quantification of TOC was performed with a TOC thermal analyser (Shimadzu V_{CSH}).

Results and Discussion

3.1. Comparison of acetic acid removal by $\text{S}_2\text{O}_8^{2-}/\text{UV}$ and $\text{H}_2\text{O}_2/\text{UV}$ systems

It was shown that without any solute, the decay of the sulfate radical concentration can be described by the following reactions: the bimolecular reaction (Eq. 2), the reaction with $\text{S}_2\text{O}_8^{2-}$ (Eq. 3) and the reaction with the water molecule (Eq. 4) or hydroxide ions (Eq. 5) (Hayon et al., 1972; Neta et al., 1988; Schuchmann and Von Sonntag, 1988; McElroy and 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 (Φ_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 Φ -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 $\text{SO}_4^{\cdot-}$ 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. H^+ ion formation was studied and quantified by Mark et al. (1990a, 1990b);
 141 they found a 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

photolysis shows no difference between the two systems. Moreover, the evolution of $\text{S}_2\text{O}_8^{2-}$ was not significantly influenced by the presence of 500 μM of acetic acid under the experimental conditions of Fig. 1 (not presented).

During the acetic acid removal in the $\text{S}_2\text{O}_8^{2-}/\text{UV}$ system, the pH decreased dramatically from the initial value of 7 to 3.3 after 15 min of irradiation due to SO_4^{2-} formation and more slowly down to a final value of 2.6 as reported by Neppolian et al. (2008). Without regulation, the rapid pH decrease converts acetate ion into acetic acid ($\text{pK}_a = 4.76$). The rate constant of the sulfate radical towards this latter form is smaller (Table 1). According to Fig. 1, the $\text{S}_2\text{O}_8^{2-}/\text{UV}$ system led to a fast acetic acid degradation i.e. the acetic acid was almost totally removed after 60 min. During the photolysis, the oxygen concentration decreased from 1.1 to 0.7 mM after 60 min. This O_2 evolution is the resultant of production and consumption in the reaction system and represents an apparent oxygen consumption of 0.8 mol mol^{-1} acetic acid removed. Concurrently, the TOC removal measured during the persulfate photolysis is also fast and the mineralization by the sulfate radicals was found to be complete after 80 min. Only small amounts of carboxylic acids were formed in the $\text{S}_2\text{O}_8^{2-}/\text{UV}$ system. Formic, glycolic and glyoxylic acids were identified and their concentrations were found to reach a maximum concentration of 14, 15 and 5 μM respectively.

During the acetic acid oxidation by the $\text{H}_2\text{O}_2/\text{UV}$ system, only one pH unit decrease was observed. The oxygen consumed after 90 min irradiation time was 0.5 mM corresponding to 1 mol mol^{-1} acetic acid removed. The rate of acetic acid degradation was similar to the $\text{S}_2\text{O}_8^{2-}/\text{UV}$ system (Fig. 1a). In the $\text{H}_2\text{O}_2/\text{UV}$ system, oxalic acid was the main by-product with a maximum concentration of 140 μM representing 30% of the acetic acid removed for 90 min irradiation time. The data are consistent with the previous work of Leitner and Doré

(1997) where they detected the formation of approximately 20% of oxalic acid. In addition, traces of formic acid were detected and did not exceed 13 μM .

Although similar initial concentrations of $\text{S}_2\text{O}_8^{2-}$ and H_2O_2 lead to the same rate of 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 different. A greater TOC removal is observed during the persulfate photolysis. After 60 min, the mineralization by the sulfate radicals is complete, while more than 20% of the initial organic carbon is still present in solution after 180 min of hydrogen peroxide photolysis. In both systems, the carbon content from the products quantified i.e. the remaining acetic acid and the carboxylic acids analyzed (TOC calculated values), accounts for the TOC measured with a great accuracy (Fig. 1b). The carbon mass balance from TOC and inorganic carbon showed that no volatile compounds were formed. Most of the by-products were identified. Thus it appears that compared to the hydroxyl radical, the sulfate radical enables a direct mineralization of the acetic acid molecule without significant formation of intermediates. The presence of intermediates and the competitive reactions induced in the $\text{H}_2\text{O}_2/\text{UV}$ system (including the consumption of $\cdot\text{OH}$ by H_2O_2) accounts for the similar evolution of acetic acid in the two systems despite the highest reactivity of the hydroxyl radicals.

The attack of the hydroxyl radical on acetic acid yields $\cdot\text{CH}_2\text{COOH}/\cdot\text{CH}_2\text{COO}^-$ radicals from H-abstraction (Eqs. 8-9). This radical is known to react rapidly with oxygen ($k = 1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) to form the corresponding peroxy radicals $\cdot\text{O}_2\text{CH}_2\text{COO}^-$ (Eq. 10) source of glyoxylic acid, glycolic acid and formaldehyde (Schuchmann et al., 1985). These by-products are then oxidized into oxalic acid and CO_2 (Leitner and Doré, 1997).

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

Under our experimental conditions, in the presence of oxygen in solution, the methyl radicals are subsequently converted into methylperoxyl radicals ($^\bullet\text{OOCH}_3$). The reactions of the methylperoxyl radicals have already been investigated in detail (Schuchmann and Von Sonntag, 1984). They are known to decompose into methanol, formaldehyde and formic acid with formation of H_2O_2 . These by-products are rapidly mineralized owing to their high rate constant values with $\text{SO}_4^{\bullet-}$ and $^\bullet\text{OH}$ radicals compared to acetic acid. Under our experimental conditions in the two systems, the solutions were neither anoxic and consequently by-products from dimerization of the primary radicals were not expected. This was confirmed by the almost complete carbon mass balance.

3.2. Influence of pH

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

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

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

$$\begin{aligned}
 -\frac{d[\text{S}]}{dt} &= (k_{11} [\text{CH}_3\text{COOH}] + k_{12} [\text{CH}_3\text{COO}^-]) [\text{SO}_4^{\cdot-}] \\
 -\frac{d[\text{S}]}{dt} &= k_s [\text{S}] [\text{SO}_4^{\cdot-}]_{\text{ss}} \\
 -\frac{d[\text{S}]}{dt} &= k_{\text{app}} [\text{S}]
 \end{aligned} \tag{13}$$

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

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

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

242 The concentration of the $\text{SO}_4^{\cdot-}$ 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).

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

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

249 with

250 Φ_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 ϵ : 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; $\text{pKa} (\text{H}_2\text{CO}_3/\text{HCO}_3^-) = 6.4$

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

258 According to the pKa values ($\text{pKa} (\text{HCO}_3^-/\text{CO}_3^{2-}) = 10.3$), 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: $k (\text{SO}_4^{\cdot-}$
 260 $^{\cdot-}/\text{CO}_3^{2-}) = 6.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ 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 $\text{SO}_4^{\cdot-}$ radicals could be
 262 determined from Eq. 16 at different irradiation times and pH values (Table 2). It is noted that

the evolution of $\text{S}_2\text{O}_8^{2-}$ concentration is not influenced by the pH. In Table 2, for a given irradiation time, A doesn't vary with the pH.

The values of $\text{SO}_4^{\cdot-}$ reported in Table 2 and the rate constants k_s enable the calculation of the apparent rate constants k_{app} for different irradiation times and pH. The data show that the values of k_{app} calculated from the kinetic expression are in accordance with the experimental values of Fig. 2. Data from kinetic expressions confirm that k_{app} increases from pH 2 to pH 5. From pH 5 to 9 data indicate that even if the global rate constant of acetic acid with $\text{SO}_4^{\cdot-}$ radicals increases, the apparent constant k_{app} decreases. This is due to the smaller $\text{SO}_4^{\cdot-}$ concentrations at the highest pH values as a consequence of an increasing consumption by both the substrate and inorganic carbon as shown in Table 2. Thus, from pH 5 it was shown that the contribution of the inhibiting reactions with carbonic acid, bicarbonates and carbonates increases with regard to acetic acid degradation. These results explain the optimum rate of acetic acid removal observed at pH 5. Up to pH 9 the data processing is much more complex since $\cdot\text{OH}$ radicals are involved from $\text{SO}_4^{\cdot-}$ reaction with OH^- ions (Eq. 5).

The oxidation of acetic acid in the $\text{S}_2\text{O}_8^{2-}/\text{UV}$ system was tentatively simulated at various pH using the previous kinetic model (Copasi) taking into consideration the photolysis of $\text{S}_2\text{O}_8^{2-}$ (Eqs. 1-7) and the reactions with the sulfate and hydroxyl radicals (Eqs. 8-12, 14-15) (Fig. 3). This simulation predicts reliably the existing optimum pH value. However, at this pH (pH = 5) the initial rapid decrease of acetic acid concentration is badly described up to 20 min of irradiation.

The different by-products formed from the action of sulfate and hydroxyl radicals on acetic acid can be used to identify the nature of the active species in the $\text{S}_2\text{O}_8^{2-}/\text{UV}$ system. Indeed in this system, the experiment carried out at pH 11 shows oxalic acid formation which is not found at lower pH levels. Same by-products are formed in the same order of

concentration from H₂O₂/UV and S₂O₈²⁻/UV at pH 11 (Fig. 4) which confirms the Eq. 5 and the main contribution of the [•]OH radical.

However, in the S₂O₈²⁻/UV process the elimination of acetic acid is slowed down after 30 min of photolysis. This point could arise from the existing reaction between [•]OH and persulfate (Chitose et al., 1999). This reaction depletes the persulfate concentration and could produce other radical less reactive than the sulfate radical. The same reaction (Eq. 3) exists between persulfate and sulfate radical but rate constants are lower than with [•]OH.

3.3 Influence of chloride and bicarbonate ions

Like the hydroxyl radical, the sulfate radical leads to the formation of radicals from numerous anions. Both, hydroxyl and sulfate radicals can react with the bicarbonate ions to produce the carbonate radical CO₃^{•-} (Eqs. 15 and 17).

In the case of the chloride ion, [•]OH reacts with Cl⁻ to give the chloride atom Cl[•] (Eqs. 18-19). In the presence of an excess of Cl⁻ ions, chlorine atoms are immediately scavenged to give Cl₂^{•-} (Eq. 20). Cl₂^{•-} is believed to be relatively unreactive with aliphatic acids (Gilbert et al., 1988). According to the intermediate reactions, [•]OH gives the Cl[•] and Cl₂^{•-} radicals in acidic conditions only. However the SO₄^{•-} radical would react with Cl⁻ to produce the Cl[•] radical even in neutral solutions (Eq. 21).

The influence of the chloride and bicarbonate ions on the acetic acid degradation during S₂O₈²⁻ photolysis was studied and compared with the H₂O₂/UV system. Experiments

were carried out in the presence of NaCl (500 or 5000 μM) or NaHCO_3 (10 mM) at pH 7 controlled with NaOH. The Fig. 5a illustrates the results.

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

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

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

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

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

The influence of the two ions, Cl^- and HCO_3^- towards acetate removal, was also examined in the $\text{H}_2\text{O}_2/\text{UV}$ system. Rate constants of reaction of hydroxyl radical with acetate and bicarbonate ions are respectively 8.5×10^7 and $8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. The experiment was carried out with a bicarbonate concentration of 0.18 M so as to obtain the same competitive factor ($k_{17} [\text{HCO}_3^-]/k_9 [\text{CH}_3\text{COO}^-] = 30$) as in the persulfate/UV system. However in the case of the chloride ion, the rate constant with the $^\bullet\text{OH}$ radical is known in acid media only. Since the rate constant of $^\bullet\text{OH}$ with bicarbonate is close to the rate constant of $\text{SO}_4^{\bullet-}$ with bicarbonate, it was assumed that the rate constant of $^\bullet\text{OH}$ with Cl^- was similar to those between $\text{SO}_4^{\bullet-}$ and Cl^- radical (i.e. about $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). Then, from an initial Cl^- concentration of 5000 μM , the rate constant $k [\text{Cl}^-]$ was almost 35 times greater than the value $k_9 [\text{CH}_3\text{COO}^-]_0$. The experiment about the influence of chloride ions in the $\text{H}_2\text{O}_2/\text{UV}$ system was performed with a chloride ion concentration of 5000 μM .

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

radical. Chloride ion does not compete for $\cdot\text{OH}$ radical under pH conditions used in this study. 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, the inhibition appears to be greater in the $\cdot\text{OH}$ radical generation process. As expected, bicarbonate ions addition in the $\text{H}_2\text{O}_2/\text{UV}$ system leads to the total inhibition of acetic acid elimination and TOC removal by $\cdot\text{OH}$.

3. Conclusions

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

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Fig. 1. Acetic acid removal by persulfate and hydrogen peroxide photolysis

a) CH_3COOH ; b) TOC

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

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

Fig. 2. Acetic Acid degradation in the $\text{S}_2\text{O}_8^{2-}$ /UV system at 254 nm. $[\text{CH}_3\text{COOH}]_0 = 500 \mu\text{M}$; $[\text{S}_2\text{O}_8^{2-}]_0 = 1800 \mu\text{M}$. pH regulation with NaOH (1 M) or perchloric acid (1 M) additions.

Fig. 3. Acetic acid degradation modelling at different pH. Lines: simulation results; symbols: experimental data; $[\text{CH}_3\text{COOH}]_0 = 500 \mu\text{M}$ (Rate constants used: $k_2 = 4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$; $k_3 = 6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$; $k_4 = 360 \text{ s}^{-1}$; $k_5 = 6.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$; $k_6 = 8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$; $k_7 = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $k_{12} = 2.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$).

Fig. 4. Acetic acid removal and by-products formation by $\text{H}_2\text{O}_2/\text{UV}$ and $\text{S}_2\text{O}_8^{2-}/\text{UV}$ at pH 11
 Δ $\text{H}_2\text{O}_2/\text{UV}$; $\bullet$ $\text{S}_2\text{O}_8^{2-}/\text{UV}$
 $\text{H}_2\text{O}_2/\text{UV}$: $[\text{H}_2\text{O}_2]_i = 1780 \mu\text{M}$; $\text{pH}_i = 6.9$; $[\text{O}_2]_i = 1.0 \text{ mM}$
 $\text{S}_2\text{O}_8^{2-}/\text{UV}$: $[\text{S}_2\text{O}_8^{2-}]_i = 1650 \mu\text{M}$; pH controlled at 11; $[\text{O}_2]_i = 0.56 \text{ mM}$.

Fig. 5. a) Impact of Cl^- and HCO_3^- on the $\text{S}_2\text{O}_8^{2-}/\text{UV}$ and $\text{H}_2\text{O}_2/\text{UV}$ systems
 $\bullet$ $\text{S}_2\text{O}_8^{2-}/\text{UV}$:
- without Cl^- nor HCO_3^- : $[\text{S}_2\text{O}_8^{2-}]_i = 2030 \mu\text{M}$; $[\text{O}_2]_i = 0.56 \text{ mM}$; $\text{pH } 7$
- with Cl^- : $[\text{Cl}^-] = 500 \mu\text{M}$; $[\text{S}_2\text{O}_8^{2-}]_i = 1740 \mu\text{M}$; $[\text{O}_2]_i = 0.66 \text{ mM}$; $\text{pH } 7$ (solid symbol)
- with Cl^- : $[\text{Cl}^-] = 5000 \mu\text{M}$; $[\text{S}_2\text{O}_8^{2-}]_i = 1950 \mu\text{M}$; $[\text{O}_2]_i = 0.77 \text{ mM}$; $\text{pH } 7$ (open symbol)
- with HCO_3^- : $[\text{HCO}_3^-] = 10 \text{ mM}$; $[\text{S}_2\text{O}_8^{2-}]_i = 1830 \mu\text{M}$; $[\text{O}_2]_i = 0.64 \text{ mM}$; $\text{pH } 8.2$
 Δ $\text{H}_2\text{O}_2/\text{UV}$:
- without Cl^- nor HCO_3^- : $[\text{H}_2\text{O}_2]_i = 1950 \mu\text{M}$; $[\text{O}_2]_i = 0.80 \text{ mM}$; $\text{pH } 7$
- with Cl^- : $[\text{H}_2\text{O}_2]_i = 1750 \mu\text{M}$; $[\text{Cl}^-] = 5000 \mu\text{M}$; $[\text{O}_2]_i = 0.68 \text{ mM}$; $\text{pH } 7$
- with HCO_3^- : $[\text{H}_2\text{O}_2]_i = 1720 \mu\text{M}$; $[\text{HCO}_3^-] = 0.18 \text{ M}$; $[\text{O}_2]_i = 0.73 \text{ mM}$; $\text{pH } 8.4$
b) TOC Mineralization in the $\text{S}_2\text{O}_8^{2-}/\text{UV}$ system
- without Cl^- : $[\text{S}_2\text{O}_8^{2-}]_i = 1580 \mu\text{M}$; $\text{pH } 7$; $[\text{O}_2]_i = 0.68 \text{ mM}$
- with Cl^- : $[\text{Cl}^-] = 500 \mu\text{M}$; $[\text{S}_2\text{O}_8^{2-}]_i = 1740 \mu\text{M}$; $[\text{O}_2]_i = 0.66 \text{ mM}$.

Table 1. Rate constants for the reaction of $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$ and $\text{Cl}^{\cdot}$ radicals ($\text{M}^{-1} \text{s}^{-1}$).

	$\text{SO}_4^{\cdot-}$	$\cdot\text{OH}$	$\text{Cl}^{\cdot}$
CH_3COOH	2.0×10^5 (Herrmann et al., 2000) 8.8×10^4 (Dogliotti and Hayon, 1967b) 1.4×10^4 (Buxton et al., 2000)	1.5×10^7 (Buxton et al., 1988)	3.2×10^7 (Buxton et al., 2000)
CH_3COO^-	5.06×10^6 (Huie and Clifton, 1990) 5.0×10^6 (Chawla and Fessenden, 1975) 2.8×10^7 (Herrmann et al., 2000) 4.3×10^6 (Buxton et al., 2000)	8.5×10^7 (Buxton et al., 1988)	$3.7 \pm 0.4 \times 10^9$ (Buxton et al., 2000)
Cl^-	2.7×10^8 (Huie and Clifton, 1990) 3.1×10^8 (Chawla and Fessenden, 1975) $4.28 \pm 0.05 \times 10^8$ (George and Chovelon, 2002) $2.7\text{--}6.6 \times 10^8$ (McElroy, 1990) $6.1 \pm 0.2 \times 10^8$ (Buxton et al., 1999) 4.7×10^8 (Huie et al., 1991b)	4.3×10^{9a} (Buxton et al., 1988)	8.5×10^9 (Buxton et al., 2000)
HCO_3^-	3.53×10^6 (Huie and Clifton, 1990) 9.1×10^6 (Dogliotti and Hayon, 1967a) $1.6 \pm 0.2 \times 10^6$ (Zuo et al., 1999)	8.5×10^6 (Buxton et al., 1988)	2.2×10^8 (Mertens and Von Sonntag, 1995) $2.4 \pm 0.5 \times 10^9$ (Buxton et al., 2000)
CO_3^{2-}	$6.1 \pm 0.4 \times 10^6$ (Zuo et al., 1999) 4.1×10^6 (Padmaja et al., 1993)	3.9×10^8 (Buxton et al., 1988)	5.0×10^8 (Mertens and Von Sonntag, 1995)

bold characters : constants used for calculations

^a at pH < 1

Table 2. Experimental and calculated k_{app} and $\text{SO}_4^{\cdot-}$ radical concentrations calculated for different pH and different reaction times (steady state).

pH	k_s ($\text{M}^{-1} \text{s}^{-1}$)	k_i ($\text{M}^{-1} \text{s}^{-1}$)	10 min ($A = 8.8 \times 10^{-7}$)		20 min ($A = 9.0 \times 10^{-7}$)		30 min ($A = 9.2 \times 10^{-7}$)	
			1/B (s)	$[\text{SO}_4^{\cdot-}]_{\text{ss}}$ (M)	1/B (s)	$[\text{SO}_4^{\cdot-}]_{\text{ss}}$ (M)	1/B (s)	$[\text{SO}_4^{\cdot-}]_{\text{ss}}$ (M)
2	2.1×10^5	1.0×10^6	2.6×10^{-3}	2.3×10^{-9}	1.8×10^{-3}	1.6×10^{-9}	1.5×10^{-3}	1.4×10^{-9}
3	2.8×10^5	1.0×10^6	2.3×10^{-3}	2.0×10^{-9}	1.6×10^{-3}	1.4×10^{-9}	1.4×10^{-3}	1.3×10^{-9}
5	32×10^5	1.3×10^6	7.0×10^{-4}	6.1×10^{-9}	8.0×10^{-4}	7.2×10^{-10}	7.7×10^{-4}	7.5×10^{-10}
7	50×10^5	7.4×10^6	2.4×10^{-4}	2.1×10^{-10}	1.9×10^{-4}	1.8×10^{-10}	1.7×10^{-4}	1.6×10^{-10}
9	50×10^5	9.0×10^6	2.0×10^{-4}	1.7×10^{-10}	1.6×10^{-4}	1.5×10^{-10}	1.4×10^{-4}	1.3×10^{-10}
pH	Experimental k_{app} (s^{-1})	k_{app} (s^{-1})						
		10 min	20 min	30 min				
2	5.3×10^{-4}	4.8×10^{-4}	3.3×10^{-4}	2.8×10^{-4}				
3	6.0×10^{-4}	5.6×10^{-4}	4.0×10^{-4}	3.3×10^{-4}				
5	1.4×10^{-3}	1.9×10^{-3}	2.3×10^{-3}	2.3×10^{-3}				
7	1.0×10^{-3}	1.1×10^{-3}	8.8×10^{-4}	7.7×10^{-4}				
9	8.5×10^{-4}	8.6×10^{-4}	7.4×10^{-4}	6.4×10^{-4}				