Enhancement of carboxylic acid degradation with sulfate radical generated by persulfate activation

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ABSTRACT

The aim of this work was to investigate the generation of sulfate radical for the removal of two carboxylic acids in aqueous solution: acetic and citric acids. From photochemical and radiolytic processes, kinetics of the degradation of these two carboxylic acids was studied as a function of the pH of the solution. It was shown that the maximum of acetic acid degradation occurred at pH 5. Above this pH, competitive reactions with the carbon mineralized inhibit the reaction of with the solute. In the case of citric acid, pH has only a little effect on the kinetic of citric acid degradation. The determination of mineralization yields shows several differences depending on carboxylic acids and pH. The degradation of both carboxylic acids was also studied in the radiolysis process whether with or without persulfate addition. A comparison of the processes of sulfate radical production is presented.

Key words | acetic acid, citric acid, mineralization, oxidation, sulfate radical

INTRODUCTION

Activation of common oxidants (i.e. chlorine, permanganate, persulfate salts) for generating transient species which present much greater oxidizing strength than the parent oxidant is not extensively investigated. Advanced techniques such as photolysis and radiolysis are used for activating oxidants like ozone and hydrogen peroxide and thus provide a clean way for generating highly oxidizing radical species. Recently, it has been demonstrated that sulfate radicals are even more efficient oxidants than hydroxyl radicals for several compounds. The reactivity of the sulfate radical with different kinds of compounds has already been studied: e.g. 2,4-dichlorophenol (Anipsitakis & Dionysiou 2004), trichloroethylene (Liang et al. 2004), cyanuric acid, (Manoj et al. 2002, 2007), perfluorocarboxylic acids (Hori et al. 2005), PCB (Rastogi et al. 2009), organophosphorous insecticides (Eugenidou et al. 2007), hexachlorocyclohexane (Cao et al. 2008), dyes (Chen et al. 2007; Zhang et al. 2007).

Owing to its high redox potential of 2.43 V (Stanbury 1989), the sulfate radical is a very strong oxidant. Although the sulfate radical has the same reaction pathways than hydroxyl radical (addition, hydrogen abstraction or electron transfer) a particular reaction occurs with carboxylic acids. The hydroxyl radical reacts with carboxylic acids by H-abstraction in α-position, whereas the sulfate radical leads to the decarboxylated radical (Neta et al. 1977; Madhavan et al. 1978).

The objective of this study was to investigate the reactivity of sulfate radicals towards two different carboxylic acids: acetic and citric acids. The degradation and the mineralization of these two molecules were monitored and a comparison of two processes generating sulfate radicals i.e. photolysis and radiolysis, was performed.

METHODS

The sulfate radical was generated by $S_2O_8^{2-}$ photolysis which has been postulated to result in the formation of two $SO_4^{2-}$ radicals (Tsao & Wilmarth 1959). Irradiation experiments
were conducted in a 5 litres batch reactor equipped with a low pressure mercury vapour 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 with an incident photonic flux of $I_0 = 9.9 \times 10^{-6}$ E s$^{-1}$ (4.7 W). The pH was left uncontrolled or controlled by addition of sodium hydroxide or perchloric acid. Dissolved oxygen concentration was initially set at 20–30 mg L$^{-1}$ by bubbling to prevent the anoxic conditions due to oxygen consumption during the experiments. The persulfate/carboxylic acid ratios used were approximately 4/1. Persulfate was determined using the Alcian Blue colorimetric method developed by Villegas et al. (1963).

The two carboxylic acids studied were acetic acid (CH$_3$COOH; pKa = 4.76) and citric acid (C(OH)(COOH)(CH$_2$COOH)$_2$; pKa = 5.08; 4.74; 6.40). These organic acids were determined by HPLC with an anionic column (Supelco C-610H) eluted with 0.1% of H$_3$PO$_4$ in water. Detection was performed with UV detector at 210 nm (Waters 486). The Relative Standard Deviation (RSD) has always been below 3%. Quantification of Total Organic Carbon was performed with a TOC thermal analyser (Shimadzu VCSH).

The sulfate radical was also formed from the ionisation of aqueous solutions containing persulfate ions. The electron beam generator consists of a 3 MeV Van de Graaff accelerator which enables the treatment of a continuous flow up to 3,600 L h$^{-1}$. The irradiation of the solution is located in a plug-flow reactor of 15 mm depth. The reactor volume exposed to the beam was fixed to 0.045 L. For this present investigation, different doses ranging from 200 to 5,000 Gy were obtained by modifying the flow rate of the solution i.e. the residence time under the beam (Pellizzari et al. 2006).

**RESULTS AND DISCUSSION**

**Photochemical systems**

The photolysis of persulfate was performed to study the reactivity of the sulfate radical towards acetic and citric acids. SO$_4^{2-}$ is formed by the scission of the O-O bond of persulfate (Equation (1)).

$$\text{S}_2\text{O}_2^{2-} + h\nu \rightarrow 2\text{SO}_4^{2-}$$ (1)

Two series of UV irradiation experiments were carried out with similar initial conditions of pH, temperature and concentrations of solutes. The studies on acetic and citric acid aqueous solutions were performed separately. Figure 1 shows the evolution of the concentrations of the carboxylic acid and TOC in the S$_2$O$_2^{2-}$/UV system.

According to Figure 1, in the persulfate/UV system, at pH 7, 90% of the acetic acid is removed after about 30 min. At this reaction time, 70% of the mineralization is achieved. In the case of citric acid, the total degradation of citric acid is achieved within 100 min with a corresponding mineralization of 70%; after 4 hours, 15% of refractory carbon remains in solution.

Mineralization of solution for each carboxylic acid was studied at pH 7 and pH 3. Table 1 presents the values when 30, 50 and 70% of the acid has been removed.

According to the mineralization of the two carboxylic acid solutions shown in Table 1, the yield of acetic acid

![Figure 1](https://iwaponline.com/wst/article-pdf/61/5/1221/448122/1221.pdf)
mineralization is greater than the one of citric acid. Only small amounts of formic, glycolic and glyoxylic acids were detected from the acetic acid degradation in the \( \text{S}_2\text{O}_8^-/\text{UV} \) system. Moreover the yield of acetic acid mineralization decreases when the pH increases.

Experiments were conducted at different pH from 2 to 11. pH was regulated during irradiation by hydroxide or perchloric acid addition. The pseudo first order rate constant of acetic acid degradation was determined as a function of the pH of the solution (Figure 2).

According to this figure, an optimum pH for the acetic acid degradation in the persulfate/UV system is found around pH 5. \( k_{\text{app}} \) increases from pH 2 to 5 due to the rate constant of the sulfate radical with acetate higher than with acetic acid \((5.0 \times 10^6 \text{ M}^{-1} \text{s}^{-1})\) and \(2.0 \times 10^5 \text{ M}^{-1} \text{s}^{-1}\) respectively; pKa \((\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-) = 4.76\) (Equations (2) and (3)). Further increasing pH results in the formation of \( \cdot \text{OH} \) radicals from \( \text{SO}_4^- \) radicals (Equations (4)–(6)). Also, the results suggest that with the increase of pH, competitive reactions of the bicarbonate and carbonate formed inhibit the reaction of the solute with \( \text{SO}_4^- \) (Equations (7) and (8)) and also \( \cdot \text{OH} \) radicals (Equations (9) and (10)). However, in the case of citric acid, pH has only a little effect on the kinetics of the degradation (data not presented).

\[
\text{SO}_4^- + \text{CH}_3\text{COOH} \rightarrow \text{H}_3\text{C}^- + \text{CO}_2 + \text{H}^+ + \text{SO}_4^- \quad (2)
\]

\[
\frac{k}{8} = 2.0 \times 10^5 \text{ M}^{-1} \text{s}^{-1}
\]

\[
\text{SO}_4^- + \text{CH}_3\text{COO}^- \rightarrow \text{H}_3\text{C}^- + \text{CO}_2 + \text{SO}_4^- \quad (3)
\]

\[
\frac{k}{8} = 5.0 \times 10^5 \text{ M}^{-1} \text{s}^{-1}
\]

\[
\text{SO}_4^- + \cdot \text{OH} \rightarrow \text{SO}_4^- + \cdot \text{OH} \quad k = 1.4 \times 10^7 \text{ M}^{-1} \text{s}^{-1} \quad (4)
\]

\[
\cdot \text{OH} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_2\text{COOH} + \text{H}_2\text{O} \quad k = 1.5 \times 10^7 \text{ M}^{-1} \text{s}^{-1} \quad (5)
\]

\[
\cdot \text{OH} + \text{CH}_3\text{COO}^- \rightarrow \cdot \text{CH}_2\text{COO}^- + \text{H}_2\text{O} \quad k = 8.5 \times 10^7 \text{ M}^{-1} \text{s}^{-1} \quad (6)
\]

\[
\text{SO}_4^- + \text{HCO}_3^- \rightarrow \text{CO}_3^- + \text{HSO}_4^- \quad k = 9.1 \times 10^6 \text{ M}^{-1} \text{s}^{-1} \quad (7)
\]

\[
\text{SO}_4^- + \text{CO}_3^- \rightarrow \text{CO}_3^- + \text{SO}_4^- \quad k = 6.1 \times 10^6 \text{ M}^{-1} \text{s}^{-1} \quad (8)
\]

\[
\cdot \text{OH} + \text{HCO}_3^- \rightarrow \text{CO}_3^- + \text{H}_2\text{O} \quad k = 8.5 \times 10^6 \text{ M}^{-1} \text{s}^{-1} \quad (9)
\]

\[
\cdot \text{OH} + \text{CO}_3^- \rightarrow \text{CO}_3^- + \cdot \text{OH} \quad k = 3.9 \times 10^8 \text{ M}^{-1} \text{s}^{-1} \quad (10)
\]

### Radiolysis

Irradiation of aqueous solutions by ionizing radiations leads to the water radiolysis with formation of hydroxyl radicals, solvated electrons and hydrogen atoms as the main active entities (Equation (11)).

\[
\text{H}_2\text{O} \rightarrow \cdot \text{OH}, \cdot \text{e}_{\text{aq}}^-, \text{H}, \text{H}_3\text{O}^+, \text{H}_2, \text{H}_2\text{O}_2 \quad (11)
\]

The sulfate radical was studied by ionisation of aqueous solutions containing persulfate ions. \( \text{S}_2\text{O}_8^- \) reacts rapidly with solvated electrons to give the sulfate radical.

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**Table 1** | Mineralization of carboxylic acid solutions (TOC \( C \)/TOC \( C_0 \)) for 30, 50 and 70% of acetic or citric acid degradation in the \( \text{S}_2\text{O}_8^-/\text{UV} \) system (\( C_0 = 500 \text{ M} \)).

<table>
<thead>
<tr>
<th>pH</th>
<th>Acetic acid</th>
<th>Citric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>10</td>
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<tr>
<td>70</td>
<td>61</td>
<td>24</td>
</tr>
<tr>
<td>80</td>
<td>34</td>
<td>4</td>
</tr>
<tr>
<td>100</td>
<td>54</td>
<td>9</td>
</tr>
</tbody>
</table>

**Figure 2** | Apparent rate constant of acetic acid degradation as a function of the solution pH in the \( \text{S}_2\text{O}_8^-/\text{UV} \) system. \( [\text{CH}_3\text{COOH}]_0 = 500 \text{ M} \); \( [\text{S}_2\text{O}_8^-]_0 = 1.800 \text{ M} \).
\( \text{S}_2\text{O}_8^{2-} + e^- \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} \quad k = 1.1 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \) \( (12) \)

Differences were observed in the electron beam irradiation of the solutions of acetic acid or citric acid in the presence and in the absence of persulfate ions. According to the Figure 3a,c, the degradation of citric acid by radiolysis without persulfate addition requires less energy than acetic acid. This data is consistent with the rate constants of hydroxyl radical with citric acid (1 to 3 \( \times 10^{8} \) M\(^{-1}\) s\(^{-1}\)) compared to acetate (8 \( \times 10^{7} \) M\(^{-1}\) s\(^{-1}\)). Actually for a dose of 2,000 Gy, at pH 7, more than 80% of the citric acid is eliminated, while with the same absorbed dose, only 35% of the acetic acid is eliminated (Figure 3a,c). Regarding mineralization, the difference between the two carboxylic acids is less important with respectively 28% and 25% mineralization for citric and acetic acid at 2,000 Gy.

However, according to the Figure 3a,b, at pH 7, the acetic acid degradation is slightly improved in the presence of persulfate ions (at 5,000 Gy, 67% and 87% acetic acid removal respectively without and with persulfate addition). In the presence of \( \text{S}_2\text{O}_8^{2-} \), the mineralization is also improved (at 5,000 Gy, 55% and 80% respectively without and with persulfate addition, 25% and 45% for a dose of 2,000 Gy).

In the case of citric acid, the persulfate addition effect is very important (Figure 3c,d). While without persulfate,

| Mineralization of carboxylic acid solutions \( \frac{\text{TOC}_{0} - \text{TOC}}{\text{TOC}_{0}} \times 100 \) for a degradation of 30, 50 and 70% of acetic or citric acid in the radiolysis system, with or without persulfate addition (pH 7; \( C_0 = 100 \mu\text{M} \)) |
|-----------------|-----|-----|
| Acetic acid     |     |     |
| Without persulfate | 22  | 38  |
| With persulfate  | 28  | 45  |
| Citric acid     |     |     |
| Without persulfate | 7   | 14  |
| With persulfate  | 28  | 40  |
A dose of 2,000 Gy is necessary for the degradation of 80% of citric acid; in presence of persulfate, this same degradation is obtained with a dose smaller than 900 Gy. Moreover, the persulfate addition allows the enhancement of the mineralization. With a treatment dose of 2,000 Gy without persulfate, only 28% of mineralization is achieved; while 78% is achieved in presence of persulfate for the same dose. The better enhancement of mineralization by persulfate addition with citric acid compared to acetic acid could be explained by the three carbonyls contained in the first molecule which are the preferential targets of the sulfate radical.

The comparison of the mineralization yield obtained for a degradation of 50, 50 and 70% of both carboxylic acids with or without persulfate addition is shown in Table 2.

According to the results of Tables 1 and 2, carboxylic acids mineralization in the radiolysis system at pH 7 (especially with persulfate addition) is greater than that obtained in the S$_2$O$_8^{2-}$/UV system.

**Process comparison**

The different experiments performed under the same conditions of concentration ([carboxylic acid] = 500 µM; [S$_2$O$_8^{2-}$] = 2,000 µM; pH = 7; Citric acid: [citric acid] = 500 µM; [S$_2$O$_8^{2-}$] = 2,000 µM; pH uncontrolled.) allow us to compare the processes tested in terms of electrical energy consumption. The energy yield (i.e. energy absorbed by the solution) in the e-beam system was considered to be 80% of the electrical energy consumed (I.A.E.A. 2007) and the energy consumption of the UV lamp was obtained from the electric-power of 40 W. The results of all experiments were plotted as a function of the electrical energy dose.

According to Figure 4a, above 1,500 J/L$^{-1}$, the S$_2$O$_8^{2-}$/UV system consumes less energy compared to the other systems for the removal of acetic acid. However, when the aim is mineralization, the S$_2$O$_8^{2-}$/radiolysis system would be preferable (Figure 4b). On the other hand, in the case of citric acid, the S$_2$O$_8^{2-}$/radiolysis leads to a greater degradation and a better mineralization of this carboxylic acid (Figure 4c,d).
In the radiolysis system, the addition of persulfate induces the formation of sulfate radicals which lead to additive effects with hydroxyl radicals formed by the radiolysis of water. The combination of both radicals enhances the oxidative capacity of the process.

**CONCLUSIONS**

In conclusion, the sulfate radical SO$_4^{2-}$ is a very strong oxidant with interesting properties. The sulfate radical formed by persulfate photolysis enables a rapid mineralization of the two carboxylic acids studied. Moreover, persulfate addition induces the enhancement of acetic and citric acids degradation and mineralization in the water radiolysis process.

The combination of hydroxyl and sulfate radicals from addition of persulfate in radiolysis process makes this process more effective than S$_2$O$_8^{2-}$/UV for the degradation of citric acid and for the mineralization of both carboxylic acids.

**REFERENCES**


