Oxidative Degradation of 2,4-Dihydroxybenzoic Acid by the *Fenton* and Photo-*Fenton* Processes: Kinetics, Mechanisms, and Evidence for the Substitution of H_2O_2 by O_2

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The kinetics and mechanisms of the oxidative degradation of 2,4-dihydroxybenzoic acid (2,4-DHBA) by the *Fenton* and photo-*Fenton* processes were investigated in detail by a combination of HPLC, IC, and TOC analyses. The formation of 2,3,4-trihydroxybenzoic acid (2,3,4-THBA) at an early oxidation stage shows that hydroxylation of the aromatic ring is the first step of the process. This intermediate was able to reduce Fe^{III} and to contribute to the recycling of Fe^{II}. Complete mineralization could only be achieved under irradiation (photo-*Fenton*). A detailed study of the dependence of the rate of mineralization on the concentration of H_2O_2 and dissolved O_2 was carried out. It was found that, even at a low initial concentration of H_2O_2, mineralization by the photo-*Fenton* process was complete in a relatively short time, provided that the O_2 concentration was high enough, indicating that O_2 may, at least in part, substitute H_2O_2. Channeling reaction pathways toward O_2 rather than H_2O_2 consumption is of particular interest for the technical development of the photo-*Fenton* process.

Introduction. – Advanced Oxidation Processes (AOPs) are gaining in importance as alternatives to conventional methods of water treatment, especially for wastewaters containing non-biodegradable and/or toxic pollutants. The AOPs are generally based on the catalytic, electrochemical, and/or photochemical generation of hydroxyl radicals ($HO^•$), strong oxidizing species known to initiate the oxidative degradation of a variety of organic contaminants in aqueous solutions [1–3]. Among AOPs, the *Fenton* and especially the photochemically enhanced *Fenton* (photo-*Fenton*) processes are considered to be among the most efficient for the remediation of wastewaters from chemical, pharmaceutical, and textile industries [4–6]. The *Fenton* reaction efficiently produces $HO^•$ from hydrogen peroxide (H_2O_2) and Fe^{II} salts in a pH range from 2.5 to 4 (*Reaction 1*), $[Fe(H_2O)_5(HO)]^+$ being the dominant aqua complex at pH 2.5–3 [7][8].

$$[Fe(H_2O)_5(HO)]^+ + H_2O_2 \rightarrow [Fe(H_2O)_5(HO)]^{2+} + HO^- + HO^• \qquad (1)$$

$$(k = 53-76\ l\ mol^{-1}\ s^{-1})$$

The Fe^{III} ions produced in *Reaction 1* are recycled to Fe^{II} by reaction with H_2O_2 (*Reactions 2* and *3*, simplified notation for the Fe^{II}/Fe^{III} aqua complexes), leading to a catalytic cycle for Fe^{II} and $HO^•$ production as long as H_2O_2 is present (see, *e.g.*, [9]).

Therefore, Fe^{II} may be used at a concentration below $[H_2O_2]/[Fe^{II}]$ 1:1 stoichiometric ratio required by *Reaction 1.*

$$Fe^{3+} + H_2O_2 \rightleftarrows [Fe{-}OOH]^{2+} + H^+ \tag{2}$$

$$[Fe{-}OOH]^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \tag{3}$$

However, the overall rate constant of these two reactions is small, and, if complexation of Fe^{III} by H_2O_2 (*Reaction 2*) is inhibited, the *Fenton* process is slowed down and may completely stop. It has been demonstrated that reduction of Fe^{III} to Fe^{II} may be enhanced, and a higher efficiency of the *Fenton* process can be achieved, when the reaction system is irradiated by near-UV and VIS (visible) light (photo-*Fenton* reaction). The photochemical reduction of Fe^{III} takes place with different efficiencies from aqua complexes, complexes containing H_2O_2 or various organic ligands (*e.g.*, carboxylic acids, amines). Therefore, the photo-*Fenton* process is generally more effective for the abiotic treatment of wastewater than the corresponding thermal process [6][10][11].

Hydroxylated benzoic acid derivatives are used as intermediates for the synthesis of pharmaceuticals and organic mass products, such as resins, polyesters, plasticizers, dyestuffs, preservatives, and are, therefore, often found in industrial wastewaters, including those of paper and olive-oil processing industries. Investigations on their oxidative degradation by the *Fenton* and/or photo-*Fenton* processes have been reported in the literature, but most studies were limited to the consumption of the initial pollutant [12–17]. In this work, we have investigated the kinetics and mechanisms of the oxidation and mineralization of 2,4-dihydroxybenzoic acid (β-resorcylic acid, 2,4-DHBA) by the *Fenton* and photo-*Fenton* processes. Moreover, we have carried out a detailed study of the dependence of the rate of mineralization on the concentration of dissolved O_2, particularly under conditions of sub-stoichiometric concentrations of H_2O_2 (relative to the initial substrate concentration).

Results and Discussion. – *Depletion of 2,4-DHBA by the* Fenton *Process.* At the initial concentration used in this work ($[2,4\text{-DHBA}]_0 = 2.6$ mM), the natural pH of the aqueous solution was 2.5, within the optimal pH range for the *Fenton* reaction [6]. *Fig. 1* shows the evolution of the concentration of 2,4-DHBA under various initial conditions of the *Fenton* reagent (two levels of $[Fe^{II}]_0$: 0.5 and 1 mM, resp., and three levels of $[H_2O_2]_0$: 6, 12.5, and 25 mM, resp.) in air-equilibrated aqueous solutions.

In all cases, the initial decay of 2,4-DHBA was fast (within a few min), due to the initial production of $HO^{\bullet}$ by *Reaction 1.* However, as expected, the percent of substrate oxidized depended on the molar ratio $[H_2O_2]_0/[2,4\text{-DHBA}]_0$ (R) employed. The stoichiometric ratio required to mineralize 2,4-DHBA by H_2O_2-mediated oxidation is 13, as calculated according to *Reaction 4*. In this work, the H_2O_2 amount was kept below this limit in all experiments.

$$C_7O_4H_6 + 13\,H_2O_2 \rightarrow 7\,CO_2 + 16\,H_2O \tag{4}$$

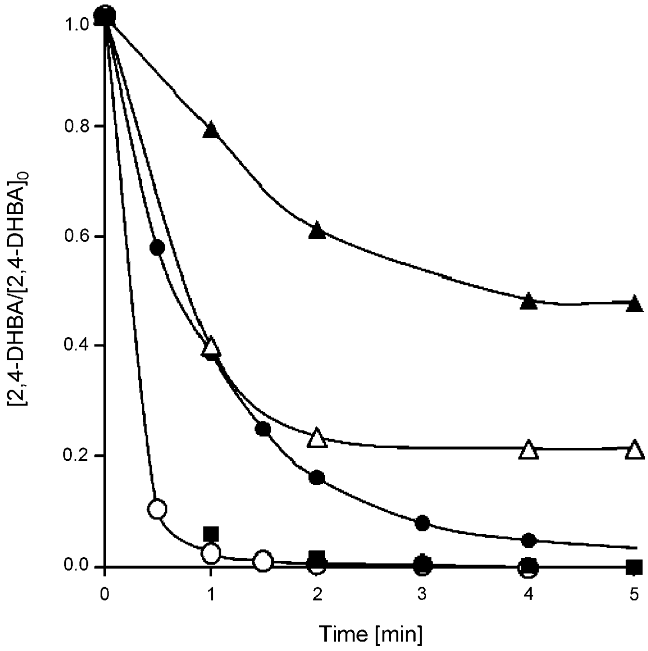


Fig. 1. *Effect of the initial concentrations of Fe^{II} and H_2O_2 on the consumption of 2,4-DHBA by the* Fenton *process in air-equilibrated aqueous solution.* [Fe^{II}]$_0$: 0.5 mM (full symbols), 1 mM (open symbols); [H_2O_2]$_0$: 6 mM (triangles), 12.5 mM (circles), and 25 mM (squares); [2,4-DHBA]$_0$ = 2.6 mM (2,4-DHBA was almost completely consumed within 1 min using the combination 1mM for [Fe^{II}]$_0$ and 25 mM for [H_2O_2]$_0$).

At the lowest [H_2O_2]$_0$ used (6 mM, $R = 2.3$), only partial consumption of 2,4-DHBA was observed, and a plateau was reached at 55 and 75% depending on [Fe^{II}]$_0$ (*Fig. 1*). When [H_2O_2]$_0$ was increased to 12.5 mM ($R = 5$), 2,4-DHBA depletion reached its maximum value of 92% within 5 min, whereas no 2,4-DHBA could be detected after less than 2 min for a [H_2O_2]$_0$ of 25 mM ($R = 10$). These results could be explained by following the evolution of the H_2O_2 concentration during the *Fenton* process (*Fig. 2*). Using a ratio R of 5, H_2O_2 was completely consumed after *ca.* 5 min, whereas, at $R = 10$, 35% of the initial amount of H_2O_2 was still present at that time. Increasing the [Fe^{II}]$_0$ from 0.5 mM to 1 mM resulted in a significant increase of the oxidation rate for $R = 2.3$ and 5 ([H_2O_2]$_0$ = 6 mM and 12.5 mM, *Fig. 1*), but did not affect the reaction at $R = 10$. In the latter case, the amount of H_2O_2 was high enough to ensure a more efficient recycling of Fe^{II} (*Reactions 2* and *3*), even at a lower [Fe^{II}]$_0$.

The role of H_2O_2 for Fe^{II} recycling during the *Fenton* oxidation of 2,4-DHBA was demonstrated by following the evolution of the concentration of Fe^{III} by titration using thiocyanate as a complexing agent. The experiment was started with a [H_2O_2]$_0$ of 12.5 mM (*Fig. 3,a*). As expected, very fast formation of Fe^{III} was observed at first due to the *Fenton* reaction (*Reaction 1*). Then, as long as H_2O_2 was present (*Fig. 2*), Fe^{III} was reduced, and its concentration decreased, the reaction coming to a halt when H_2O_2 was consumed. After a second addition of H_2O_2 (12.5 mM), *Reaction 1* produced again a

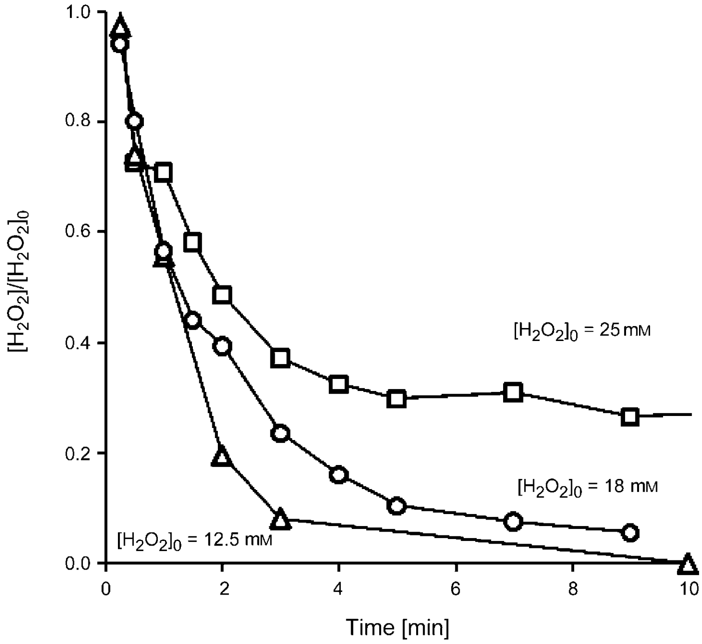


Fig. 2. *Evolution of the concentration of H_2O_2 during the oxidation of 2,4-DHBA by the* Fenton *process in air-equilibrated solutions using different $[H_2O_2]_0$.* $[Fe^{II}]_0 = 0.5$ mM, $[2,4\text{-DHBA}]_0 = 2.6$ mM.

fast increase in the Fe^{III} concentration with the formation of further oxidation products (*Fig. 3,a*), then, the concentration of Fe^{III} decreased to reach a plateau in spite of remaining H_2O_2 (*vide infra*, discussion on 2,4-DHBA mineralization).

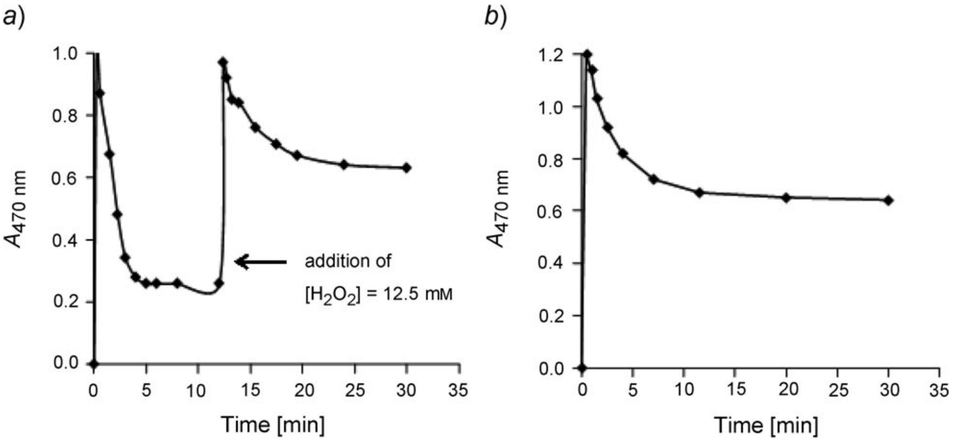


Fig. 3. *Evolution of the Fe^{III} concentration measured by the absorbance at λ_{max} 470 nm of $[Fe(SCN)_2]^+$ during the* Fenton *process at different H_2O_2 concentrations. a*) $[H_2O_2]_0$: 12.5 mM and second addition of 12.5 mM H_2O_2; *b*) $[H_2O_2]_0 = 25$ mM; $[Fe^{II}]_0 = 0.5$ mM, air-equilibrated solution.

Depletion of 2,4-DHBA by the Photo-Fenton *Process.* Irradiations were performed at wavelengths above 300 nm to minimize the photolysis of 2,4-DHBA. At a $[H_2O_2]_0$ of 25 mM ($R = 10$), no significant difference could be observed between *Fenton* and photo-*Fenton* experiments: 2,4-DHBA was depleted after 2 min of reaction in both cases. Under these conditions, $HO^•$ radicals were produced at the same rate in both processes (*Reaction 1*), and irradiation did not play a significant role in the 2,4-DHBA oxidation. At a lower $[H_2O_2]_0$, oxidation was slower but complete consumption of the substrate could be observed in contrast to the *Fenton* process. For example, for $R = 5$, the dark process left *ca.* 8% of $[2,4\text{-DHBA}]_0$ unreacted due to the lack of H_2O_2 (*Figs. 1* and *2*). Under irradiation, however, 2,4-DHBA was totally consumed within 5 min in spite of the absence of H_2O_2 (data not shown), most probably due to the production of $HO^•$ concomitant to the photochemical reduction of Fe^{III} to Fe^{II} in the electronically excited ferric aqua complex (*Reaction 5*) [6][18][19].

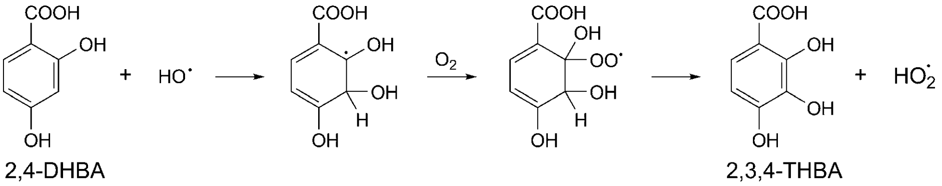
$$[Fe(H_2O)_5(OH)]^{2+} + H_2O + h\nu \rightarrow [Fe(H_2O)_5(OH)]^{+} + HO^• + H^+ \quad (5)$$

Photochemical control experiments were performed in the absence of Fe^{II} and/or H_2O_2 (irradiation at wavelengths above 300 nm; see *Exper. Part*). In all cases, the oxidation of 2,4-DHBA proceeded at a much slower rate than in the *Fenton* experiments described above. Photolysis of 2,4-DHBA (excitation in its lowest energy absorption band (λ_{max} 292 nm)), in the absence of *Fenton* reagent, led to 15% depletion after 6 h. The photolysis of H_2O_2 produces $HO^•$ radicals (UV/H_2O_2 process), but the molar absorption coefficient of H_2O_2 at wavelengths > 300 nm as used in this work is very low [20]), and only 10% depletion of 2,4-DHBA was observed after 2 h of irradiation in the presence of 25 mM H_2O_2.

Considering the short reaction times involved, *Fenton* and photo-*Fenton* processes are very efficient for the oxidation of 2,4-DHBA, as reported for other hydroxylated benzoic acid derivatives (*e.g.*, [14]). It should be noted that these processes are more efficient than TiO_2 photocatalysis and hybrid techniques [21–23].

Mechanism of 2,4-DHBA Oxidation. During the *Fenton* and photo-*Fenton* oxidation of 2,4-DHBA, 2,3,4-trihydroxybenzoic acid (2,3,4-THBA) was the first and the only aromatic intermediate detected in significant concentration by HPLC analysis. Therefore, it may be assumed that the first step of the oxidation was the electrophilic addition of $HO^•$ to the aromatic ring (*Scheme*). Considering the electronic effects of the COOH and OH groups, it would be expected that electrophilic attack of $HO^•$ on the aromatic system of 2,4-DHBA would occur preferentially at C(3) and C(5). However, C(3) lies in *ortho* position relative to both OH groups, and $HO^•$ attack at C(3) could be

Scheme. *Mechanism of the First Step of the Oxidation of 2,4-DHBA*



favoured. Alternatively, the rate of oxidation of 2,4,5-THBA could be faster than that of the 2,3,4-trihydroxy derivative, preventing its detection.

Fig. 4 shows the evolution of the 2,3,4-THBA concentration during the oxidative degradation of 2,4-DHBA using a $[H_2O_2]_0$ of 12.5 mM. During both *Fenton* and photo-*Fenton* processes, 2,3,4-THBA was formed at about the same rate as 2,4-DHBA was consumed and underwent a first step of fast oxidation. Then, in the case of the *Fenton* process, the concentration of 2,3,4-THBA reached a plateau as H_2O_2 was consumed. Formation and oxidation of 2,3,4-THBA was faster under photo-*Fenton* conditions. Moreover, this intermediate was slowly depleted even after H_2O_2 was consumed, as observed for 2,4-DHBA. At higher H_2O_2 concentration (25 mM), formation and oxidation of 2,3,4-THBA were so fast that its detection by HPLC was hardly possible.

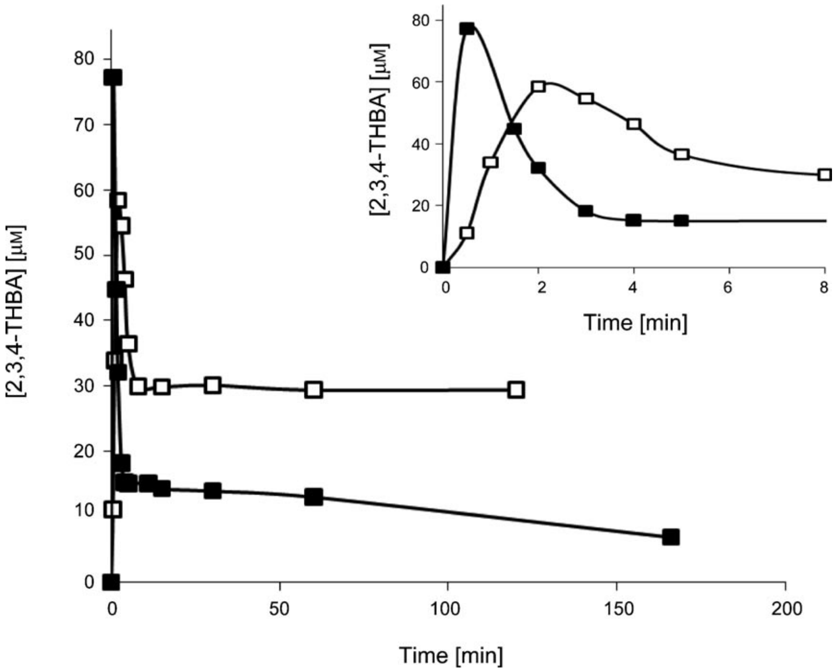


Fig. 4. *Evolution of the concentration 2,3,4-THBA during the oxidation of 2,4-DHBA in air-equilibrated aqueous solutions by the* Fenton (open squares) *and photo-*Fenton (full squares) *processes.* Inset: expanded scale up to 8 min of reaction time. $[Fe^{II}]_0 = 0.5$ mM, $[H_2O_2]_0 = 12.5$ mM, and $[2,4\text{-DHBA}]_0 = 2.6$ mM.

It has been shown previously that compounds such as *ortho*- or *para*-dihydroxybenzenes (hydroquinones) could reduce very efficiently Fe^{III} and be oxidized to quinones, by two successive one-electron transfer steps *via* the semiquinone radical and contribute to Fe^{II} recycling [6] [23–25]. We have shown that 2,3,4-THBA was also able to reduce efficiently Fe^{III} in the dark. The two compounds were mixed in various proportions in aqueous solution at pH 2.5, and the formation of Fe^{II} was followed by complexation with 1,10-phenanthroline (*Exper. Part*). Reduction was complete within a few seconds. Therefore, 2,3,4-THBA may contribute to the recycling of Fe^{II} during the

Fenton oxidation of 2,4-DHBA. This would explain the fast consumption of 2,3,4-THBA following its formation. Decarboxylated derivatives of 2,4-DHBA and its hydroxylation products (polyphenols) could not be detected in the case of *Fenton* and photo-*Fenton* processes, in contrast to the degradation by vacuum-ultraviolet (V-UV) photolysis of H_2O [26]. When formed, most of these compounds would reduce efficiently Fe^{III} and would probably not accumulate in detectable amounts in the reaction system.

Effects of Concentrations of H_2O_2 and O_2 on the Mineralization of 2,4-DHBA by the Fenton *Process.* The normalized profiles of the evolution of the total organic carbon (TOC) are represented in *Fig. 5* and show that the efficiency of 2,4-DHBA mineralization by both *Fenton* and photo-*Fenton* processes strongly depends on the experimental conditions.

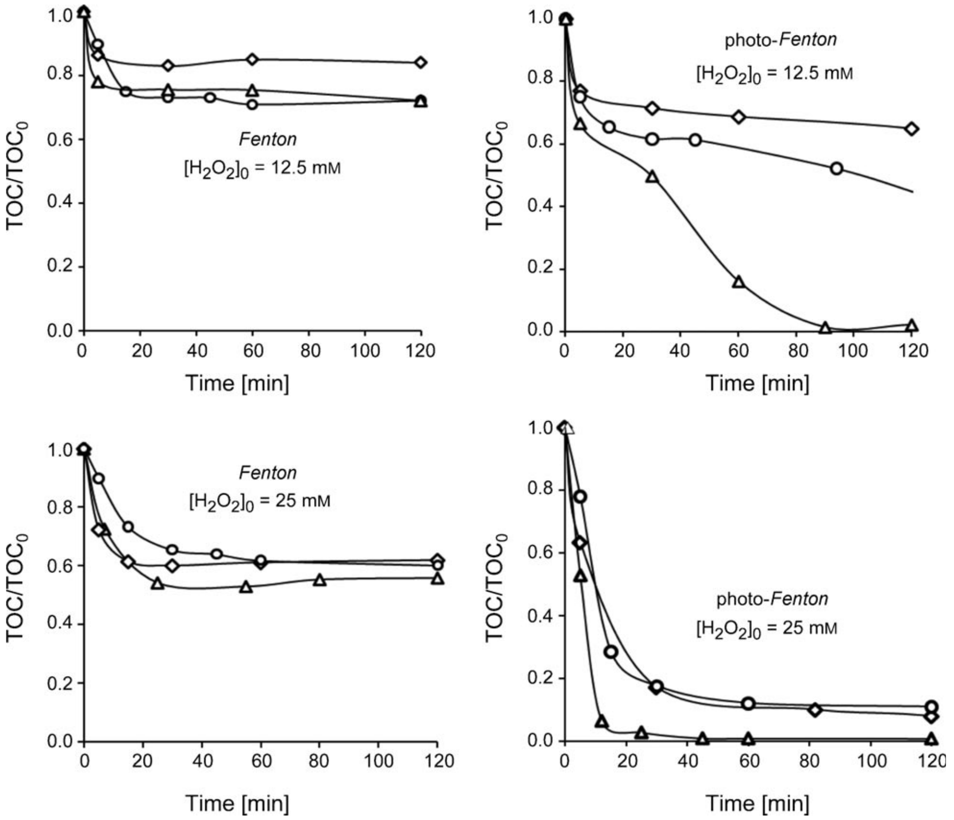


Fig. 5. *Evolution of TOC during the oxidative degradation of 2,4-DHBA in aqueous solution by the* Fenton *and photo-*Fenton *processes under different conditions of oxygenation.* ◇: air-equilibrated solution; ○: air-saturated solution; △: O_2-saturated solution; $[H_2O_2]_0 = 12.5$ mM or 25 mM, $[Fe^{II}]_0 = 0.5$ mM, $[TOC]_0$: 218 mg l^{-1} ($[2,4\text{-DHBA}]_0 = 2.6$ mM).

Besides H_2O_2, O_2 plays an important role in the mineralization process. Indeed, the reaction of $HO^•$ with organic compounds (*e.g.*, hydrogen abstraction, addition to C=C bonds) leads to the production of C-centered radicals, subsequently trapped by O_2 to yield peroxyl radicals (*Reaction 6*).

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \quad (6)$$

(k in the order of 10^9 M^{-1} s^{-1})

Subsequent reactions of the latter lead to the formation of intermediate oxidized products that in turn undergo oxidation. Depending on the conditions, the manifold of reactions may result in the complete mineralization of the organic pollutant (to CO_2, H_2O, and inorganic acids if heteroatoms are present in the molecule). In this respect, the effect of different oxygenation conditions (air-equilibrated, air-saturated, or O_2-saturated solutions) on the degradation of 2,4-DHBA were investigated at two different $[H_2O_2]_0$ values (12.5 and 25 mM, resp.).

In the case of the *Fenton* oxidation of 2,4-DHBA, a plateau was reached in all cases after less than 20 min of reaction, and TOC conversion did not exceed 45% under the best condition. The plateau of TOC conversion was found to be significantly affected by the concentration of H_2O_2. In fact, for $[H_2O_2]_0 = 12.5$ mM, mineralization did not exceed 15% in air-equilibrated aqueous solution, but reached 40% under the same oxygenation conditions for $[H_2O_2]_0 = 25$ mM. Evolution of the absorption spectra during the reaction (*Fig. 6,a*) and analysis of the low-molecular-weight carboxylic acids (*Fig. 7*) by ion chromatography (IC) showed that complete mineralization was prevented, even at relatively high $[H_2O_2]_0$, by the formation of stable complexes of Fe^{III} with the intermediates of substrate oxidative degradation. As the absorption bands of 2,4-DHBA at 250 and 292 nm decreased rapidly in agreement with the fast oxidation of the acid, the absorbance at wavelengths > 340 nm (a spectral region where 2,4-DHBA

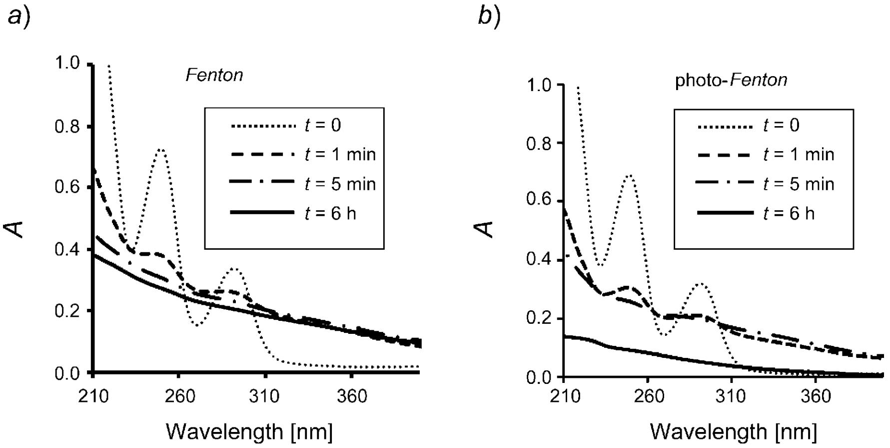


Fig. 6. *Evolution of the UV/VIS absorption spectra of the aqueous solution during the oxidative degradation of 2,4-DHBA by the* Fenton *and photo-*Fenton *processes* (total reaction time: 6 h). $[Fe^{II}]_0 = 0.5$ mM, $[H_2O_2]_0 = 12.5$ mM, $[\text{2,4-DHBA}]_0 = 2.6$ mM; air-equilibrated conditions (optical pathlength of spectroscopic cell: 1 cm, reaction mixture dilution: 1:40).

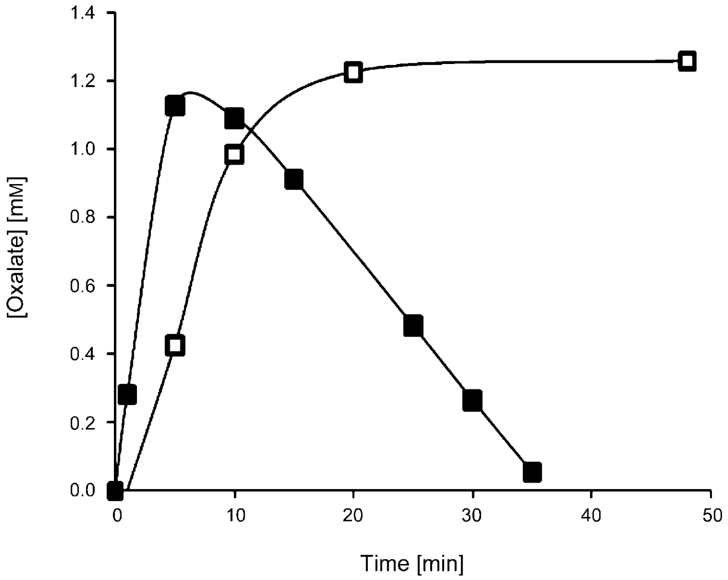


Fig. 7. *Evolution of the concentration of oxalic acid during the oxidative degradation of 2,4-DHBA in air-saturated aqueous solutions by the* Fenton (□) *and photo-*Fenton (■) *processes.* $[Fe^{II}]_0 = 0.5$ mm, $[H_2O_2]_0 = 25$ mm, and $[2,4\text{-DHBA}]_0 = 2.6$ mm.

does not absorb) increased to reach a plateau (at approximately the same time as the TOC plateau).

The reaction mixture changed from colorless to violet and finally to brown, an indication of the formation and accumulation of compounds absorbing in the VIS-spectral region. In particular, carboxylate ions, especially those derived from low-molecular-weight carboxylic acids, are known to form complexes with Fe^{III} [23][27–29].

Goi et al. [15] reported the formation of a dark-violet complex between salicylic acid (or its by-products) and Fe^{III} during the *Fenton* process. We have shown that 2,4-DHBA itself forms a violet 1:1 complex, with an absorption maximum of the charge transfer band at 514 nm [30]. We have observed that 2,3,4-THBA also forms a violet complex with Fe^{III}, followed by fast bleaching; indeed, as in the case of most catechols [23][25], the complex is not stable in the dark, electron transfer between Fe^{III} and the ligand leading to fast reduction of Fe^{III} and formation of the semiquinone (*vide supra*). Moreover, IC analysis during the *Fenton* and photo-*Fenton* degradation of 2,4-DHBA showed that, among low-molecular-weight carboxylic acids, HCOOH was formed in very low amount, whereas oxalic acid reached a concentration close to 50% of $[2,4\text{-DHBA}]_0$ (*Fig. 7*).

Therefore, oxalic acid was the most important intermediate in the 2,4-DHBA mineralization. In the case of the *Fenton* process, the concentration of oxalic acid increased to reach a plateau after *ca.* 20 min, as observed for the TOC under the same conditions. Ferrioxalate complexes are stable in the dark, and the *Fenton* process comes to a halt at that stage. Even in the presence of enough H_2O_2, ligand exchange by H_2O_2 is unfavorable in these complexes, and the recycling of Fe^{II} by reduction of Fe^{III} (*Reaction 3*) cannot take place [6]. This is confirmed by the evolution of the concentration of Fe^{III} during the oxidative degradation of 2,4-DHBA (*Fig. 3*): even in presence of an excess of H_2O_2, the concentration of Fe^{III} reaches a plateau (corresponding to the formation of stable ferrioxalate complexes; *Fig. 3,a*, after second addition of H_2O_2, and *Fig. 3,b*).

Within experimental error, the conditions of oxygenation had a relatively small effect on the mineralization induced by the *Fenton* reaction. This is most likely due to the early halt of the global process of oxidative degradation.

*Effects of Concentrations of H_2O_2 and O_2 on the Mineralization of 2,4-DHBA by the Photo-*Fenton *Process.* In this case, no plateau was observed for the mineralization, although it proceeded at a slow rate under the least favorable conditions of O_2 and H_2O_2 concentrations (*Fig. 5*). The complexes formed between the intermediates of the oxidative degradation of the substrate and Fe^{III} did not stop the degradation process, as they were more or less efficiently photolyzed. This was shown by the evolution of the absorption spectra (*e.g.*, *Fig. 6,b*), the solution changing from colorless to brown to become again colorless at longer irradiation times. Under irradiation, even in the absence of H_2O_2, the photochemical reaction of Fe^{III}–carboxylate complexes may lead to decarboxylation of the acid and Fe^{II} formation (*Reaction 7*), with variable efficiencies [27–29]. The photolysis of such complexes has, therefore, been used for enhancing the degradation of pollutants (see, *e.g.*, [23][28][31]).

$$[Fe^{III}(RCOO)] + h\nu \rightarrow Fe^{II} + CO_2 + R^{\bullet} \qquad (7)$$

Ferrioxalate complexes are photochemically labile (ferrioxalate is used as a chemical actinometer [32]), and the global reaction leads to the formation of CO_2 and the reduction of Fe^{III} to Fe^{II} with a quantum yield higher than 1. Accordingly, during the photo-*Fenton* degradation of 2,4-DHBA, the concentration of oxalic acid went through a maximum before decreasing to negligible values (*Fig. 7*).

The effect of $[H_2O_2]_0$ was even more pronounced than in the *Fenton* process. A $[H_2O_2]_0$ value of 25 mM was high enough: *i*) to contribute to the (thermal) regeneration of Fe^{II} (*Reactions 2* and *3*), *ii*) to maintain *Reaction 1*, as Fe^{II} was photochemically recycled, leading to the complete or almost complete mineralization of 2,4-DHBA (*Fig. 5*). For experiments with $[H_2O_2]_0 = 12.5$ mM, H_2O_2 was already totally consumed after *ca.* 5 min (as in the case of the *Fenton* reaction, *Fig. 2*). The observed decrease of the TOC after the reaction time for complete consumption of H_2O_2 was, therefore, due to the photolysis of ferric aqua complexes (*Reaction 5*, *vide supra*) and of intermediate oxidation products (mainly Fe^{III}–carboxylate complexes, *e.g.*, *Reaction 7*).

The conditions of oxygenation of the aqueous reaction system drastically influenced the photo-*Fenton* process. *Fig. 8* summarizes the corresponding results.

The importance of the concentration of dissolved O_2 was most remarkable in experiments with a $[H_2O_2]_0$ value of 12.5 mM (grey bars in *Fig. 8*). After a reaction time of 120 min, the mineralization was limited to 57 and 35% for air-saturated and air-equilibrated solutions, respectively, but mineralization was practically complete under O_2-saturated conditions within 30 min. These results of the photo-*Fenton* experiments emphasize the important role of O_2 in the mineralization process. One of the reasons is

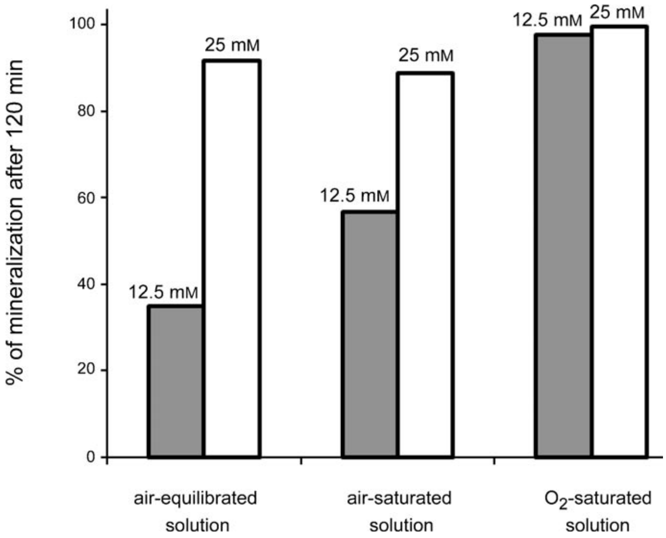


Fig. 8. *Percent of mineralization of 2,4-DHBA in aqueous solution by the photo-*Fenton *process after 2 h of reaction time in air-equilibrated, and air- and O_2-saturated solutions, respectively.* $[H_2O_2]_0 = 12.5$ mM (grey bars) or 25 mM (white bars); $[Fe^{II}]_0 = 0.5$ mM, $[TOC]_0 = 218$ mg l^{-1}.

that the C-centered radicals $R^\bullet$ produced photochemically, *e.g.*, in *Reaction 7*, are more efficiently trapped at higher O_2 concentrations (*Reaction 6*). Depending on the nature of $R^\bullet$, an electron-transfer reaction between $R^\bullet$ and O_2 may also occur (*Reaction 8*).

$$R^\bullet + O_2 \rightarrow R^{\bullet +} + O_2^{\bullet -} \tag{8}$$

It may be also assumed that O_2 replaces H_2O_2 as an electron acceptor, when the latter is rapidly depleted (low $[H_2O_2]_0$). The effect being more pronounced with increasing concentration of dissolved O_2 and decreasing $[H_2O_2]$, experimental conditions may yield a kinetic control on competing *Reactions 1* and *9*.

$$Fe^{II} + O_2 \rightleftarrows Fe^{III} + O_2^{\bullet -} \tag{9}$$

Superoxide anion ($O_2^{\bullet -}$) formed in *Reactions 8* and *9* disproportionates with its conjugated acid, the perhydroxyl radical ($HO_2^\bullet$), to yield HO_2^-/H_2O_2 and O_2 (*Reactions 10–12*).

$$O_2^{\bullet -} + H_3O^+ \rightleftarrows HO_2^\bullet + H_2O \tag{10}$$

$$O_2^{\bullet -} + HO_2^\bullet \rightarrow HO_2^- + O_2 \tag{11}$$

$$HO_2^- + H_3O^+ \rightleftarrows H_2O_2 + H_2O \tag{12}$$

Furthermore, the oxidation of the carboxylate radical anion generated by the photolysis of ferrioxalates (*Reaction 13*) may be enhanced with an increased concentration of dissolved O_2 (*Reaction 14*) leading again to the production of HO_2^-/H_2O_2 and O_2.

$$[Fe(C_2O_4)_3]^{3-} + h\nu \rightarrow [Fe(C_2O_4)_2(H_2O)_2]^{2-} + CO_2 + CO_2^{\bullet -} \qquad (13)$$

$$CO_2^{\bullet -} + O_2 \rightarrow CO_2 + O_2^{\bullet -} \qquad (14)$$

These mechanistic hypotheses are of fundamental as well economic importance for the large-scale application of the photo-*Fenton* process to the degradation of organic pollutants. Replacement of H_2O_2 by O_2 was previously reported in the case of the degradation of aniline by the *Fenton* and photo-*Fenton* processes [33]. However, all experiments were performed under O_2 saturation, and large degrees of replacement were only achieved when the relative TOC mineralization was low (10%). Further investigations to elucidate the alternative pathways are of interest in order to find generally applicable experimental conditions under which the overall process may be mainly channeled toward O_2 rather than H_2O_2 consumption.

Conclusions. – The efficiency of *Fenton* and photo-*Fenton* processes for the oxidative degradation of a 2,4-dihydroxybenzoic acid (2,4-DHBA) was demonstrated. The evolution of the main (hydroxylated) intermediate, 2,3,4-trihydroxybenzoic acid (2,3,4-THBA), shows that hydroxylation of the aromatic ring is the first step of the process. 2,3,4-THBA contributes to the reduction of Fe^{III} and, therefore, to the recycling of Fe^{II} required for the catalytic decomposition of H_2O_2 and the production of $HO^\bullet$ radicals (*Fenton* reaction). Complete mineralization (albeit not always desirable, if the intermediates are not toxic and biodegradable) can only be reached under irradiation (photo-*Fenton*). Only under these conditions, the various complexes formed between Fe^{III} and the intermediates of oxidative degradation (especially oxalic acid) may be decomposed. The conditions of oxygenation are crucial for the mineralization of 2,4-DHBA, particularly when $[H_2O_2]_0$ is low, and H_2O_2 is rapidly depleted. These results suggest that O_2 may replace H_2O_2 acting as an electron acceptor. The resulting superoxide radical anion ($O_2^{\bullet -}$) and perhydroxyl radical ($HO_2^\bullet$) would subsequently produce H_2O_2 that is necessary for the generation of hydroxyl radicals ($HO^\bullet$) needed in turn to initiate the oxidative degradation of the organic pollutant. The important effect of oxygenation conditions on the efficiency of the photo-*Fenton* process, at low H_2O_2 concentration, may have a cost-determining impact for the treatment of industrial wastewaters. This phenomenon should be more generally investigated for various types of pollutants.

Experimental Part

Reagents. 2,4-Dihydroxybenzoic acid (2,4-DHBA, $\varepsilon_{250\,nm}$ 10400 ($\pm$100) M^{-1} cm^{-1}, $\varepsilon_{292\,nm}$ 4680 ($\pm$50) M^{-1} cm^{-1}) and 2,3,4-trihydroxybenzoic acid (2,3,4-THBA, 98%) were purchased from *Fluka*. H_2O_2 (35% (*w*/*v*)) was bought from *Acros*. Peroxidase (type II, 191 purpurogallin units/mg), 4-aminoantipyrine, phenol, $FeSO_4 \cdot 7\,H_2O$, NaI, Na_2HPO_4, KH_2PO_4, H_3PO_4, KOH, HCOOH, Na_2SO_3, oxalic acid, MeCN, and MeOH were supplied by *Sigma-Aldrich*. All these chemicals and solvents were of *ACS* grade and used without further purification. H_2O was of bi-distilled quality.

Fenton *and Photo*-Fenton *Processes.* The experiments were carried out in a *DEMA 13/12* glass annular photochemical reactor (*Mangels*, D-Bornheim-Roisdorf) containing 350 ml of soln. A medium-pressure Hg lamp (*Philips HPK*; 125 W) was positioned in the axis of the reactor (optical pathlength: 1.1 cm). Cooled water was circulated in the *Pyrex* lamp jacket, maintaining a temp. of 20° in the reaction mixture. The soln. was continuously magnetically stirred before and during the degradation processes. Different conditions of oxygenation of the reaction mixture were used: air equilibration (the reactor was open to ambient atmosphere), and air or O_2 saturation by continuous bubbling with the appropriate gas. The initial concentration of 2,4-DHBA ($[2,4\text{-DHBA}]_0$) was 2.6 mM. The total amount of $FeSO_4$ (0.5 or 1 mM) was dissolved in the aq. soln. of 2,4-DHBA before adding H_2O_2 (6 to 25 mM). The same volume of an aq. soln. of H_2O_2 at the required concentration for each molar ratio ($[H_2O_2]_0/[2,4\text{-DHBA}]_0$) was added at once. It should be noted that the continuous addition of the same total amount of H_2O_2 using a peristatic pump did not significantly modify the results. In the case of the photo-*Fenton* process, irradiation was started 10 min before H_2O_2 addition for stabilizing the lamp emission. The natural pH of the reaction system was 2.5. Samples (1 ml) were taken from the reaction mixture at various time intervals and analyzed by UV/VIS spectrophotometry, HPLC, IC, and TOC measurements.

Treatment of Samples Prior to Analysis. Before analysis, the samples were treated for stopping the oxidative degradation. For IC, HPLC, and UV/VIS analyses, an equal volume of MeOH was added to the samples to trap $HO^{\bullet}$ radicals. For TOC measurements, an equivalent volume of a reductive and precipitation agent, composed of NaI (0.1M), Na_2SO_3 (0.1M), KH_2PO_4 (0.05M), and Na_2HPO_4 (0.1M) [34], was added to each sample to stop the reaction, as MeOH could not be used in this case. This procedure led to a complete reduction of the residual H_2O_2 as well as to the removal of the iron by precipitation. The samples were filtered using *Durapore* 0.45-μm filters prior to analysis. Within experimental error, both treatments led to the same results as checked by HPLC.

Analyses. The concentration of H_2O_2 was measured by an enzymatic-colorimetric method using the peroxidase enzyme [35]. The reagent was composed of phenol (0.025M), 4-aminoantipyrine (5 mM), and peroxidase (10 mM) in a NaH_2PO_4/H_3PO_4 buffer, pH 6.9. In the presence of H_2O_2, a quinoneimine is formed that may be analyzed spectrophotometrically at λ_{max} 505 nm. For the analysis of Fe^{III}, 1 ml of a soln. of 0.30M of aq. KSCN and of 0.05M of H_2SO_4 was added to the sample (1 ml) to obtain the complex $[Fe(SCN)_2(H_2O)]^+$, which was analyzed by its absorption at λ_{max} 470 nm (ε_{470} 7200 ± 30 M^{-1} cm^{-1}) [36]. For the analysis of Fe^{II}, 1 ml of a reagent consisting of AcONa (0.4M), 1,10-phenanthroline (0.018M), and KF (0.02M) was added to 1 ml of the sample [37]. The concentration of Fe^{II} was determined by measuring the absorbance of the $[Fe(phen)_3]^{2+}$ complex at 510 nm (ε_{510} 11000 ± 50 M^{-1} cm^{-1}).

The degree of mineralization was determined by TOC analysis, with a *Shimadzu TOC-V CSN* analyzer. The aromatic intermediates were analyzed by HPLC, using a *Waters 2695 Separation Module*, equipped with a diode array detection system and a reversed-phase column (*Waters X-Bridge Shield RP 18*; length, 100 mm; diameter 2.1 mm; particle size, 3.5 μm). As eluent, a mixture of acidified H_2O (0.1% HCOOH) and MeCN was chosen (with a gradient from 100 to 60% of H_2O). The flow rate was 0.35 ml min^{-1}. The evolution of the concentration of low-molecular-weight acids (oxalic and formic acids) was followed by IC (*Dionex DX-500* with refractometric detector *ED 40*). A *Dionex IonPac AS 11-HC* column (2 × 250 mm) was employed. The eluent was an aq. KOH soln. (the gradient applied was from 0.2 to 35 mM KOH within 25 min at a flow rate of 1 ml min^{-1}). The integrated peaks were compared with the corresponding values of a previously established calibration curve. The experimental errors did not exceed 5, 9, and 8% for H_2O_2, TOC, and HPLC/IC analyses, resp.

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