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EDTA destruction using the solar ferrioxalate advanced oxidation technology (AOT) Comparison with solar photo-Fenton treatment

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Abstract

Degradation of ethylenediaminetetraacetic acid (EDTA; in the mmol/l range) at pH 3 was studied by the ferrioxalate/H_2O_2 process under solar irradiation. A rapid total organic carbon (TOC) removal was attained in all cases, reaching almost 100% after 1 h solar exposure under the best conditions. In order to attain a high TOC removal yield, the pH must be rigorously controlled. The reaction rate increased with H_2O_2 concentration; but its effect was not very marked. The final extent of degradation was found to decrease with higher ferrioxalate concentrations, probably by competition of oxalate with EDTA or its degradation products. In the absence of oxalate, EDTA could also be degraded to a reasonably good extent, with a TOC removal only slightly lower than when using ferrioxalate, which constitutes a good advantage from the economical point of view. The intensity of solar light was found to be a very important factor to improve the reaction.
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Keywords: EDTA; Ferrioxalate; Photo-Fenton; Solar light; Advanced oxidation technologies (AOTs)

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1. Introduction

Removal of ethylenediaminetetraacetic acid (EDTA), a common industrial and domestic water contaminant, has been attempted by different methods ([1,2] and references therein). EDTA is not easily biodegradable [3], it is scarcely degradable by chlorine [4], hardly retained by activated carbon filters and resistant to ozone treatment [5,6]. EDTA degradation has been tried by UV/oxidants [7,8], radiolysis [9], heterogeneous photocatalysis [10–20] and radiophotocatalysis [21]. Results have been variable. Advanced oxidation processes (AOPs) or advanced oxidation technologies (AOTs) are promising treatments owing to their ability to destroy a large variety of organic pollutants, including recalcitrant chemical species. UV/H_2O_2 treatments were studied in detail at the very low EDTA concentrations found in drinking water, including evaluating the influence of Fe^{3+} [22–24]. The mechanisms associated to EDTA degradation by TiO_2 heterogeneous photocatalysis (including results in the presence of Fe(III) and/or H_2O_2) have recently been elucidated by us, and several resistant intermediates formed in the course of the reaction before total mineralization have been identified [1,2,25].

Fe(II/III) based methods to destroy pollutants in water are increasingly used. In particular, Fenton and Fenton-like reagents are composed of a hydrogen peroxide solution and a metal transition salt (Fe^{2+}, Fe^{3+} or Cu^{2+}) in acid medium. H_2O_2 decomposition catalyzed by the metal ion generates a hydroxyl radical ($HO^\bullet$), as shown for Fe^{2+} in the following simplified equations ([26–30] and references therein):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\bullet \tag{1}$$

Fe^{3+} (added or generated from Fe^{2+}) gives rise to a radical chain mechanism:

$$Fe^{3+} + H_2O_2 \rightleftarrows Fe\text{–}OOH^{2+} + H^+ \tag{2}$$

$$Fe\text{–}OOH^{2+} \rightarrow Fe^{2+} + HO_2^\bullet \tag{3}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\bullet \tag{1}$$

$$Fe^{2+} + HO_2^\bullet + H^+ \rightarrow Fe^{3+} + H_2O_2 \tag{4}$$

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$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \qquad (5)$$

In the presence of oxygen, $HO^{\bullet}$ radicals attack the organic molecule by several degradative mechanisms:

$$HO^{\bullet} + \text{organic reactants} \xrightarrow{O_2} \text{degradation products} \qquad (6)$$

Under light irradiation, Fe^{3+} is continuously reduced to Fe^{2+}:

$$FeOH^{2+} + h\nu \rightarrow Fe^{2+} + HO^{\bullet} \qquad (7)$$

and the Fenton reaction (1) is enhanced by the participation of photogenerated Fe^{2+}.

On the other hand, Fe(III) complexes of oligocarboxylic acids that absorb in the UV–VIS range are photolyzed through a ligand to metal charge transfer (LMCT) reaction, yielding Fe^{2+} and $HO^{\bullet}$ with good quantum yields, even in the absence of H_2O_2:

$$Fe(III)(RCO_2)^{2+} + h\nu \xrightarrow{LMCT} Fe(II) + CO_2 + R^{\bullet} \qquad (8)$$

In the presence of O_2, the radicals $R^{\bullet}$ produced contribute to the cycle:

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \xrightarrow{Fe^{3+}} \text{oxygenated products} \rightarrow HO^{\bullet} + Fe^{2+} \qquad (9)$$

Of course, in the presence of H_2O_2, the photo-Fenton reaction is continuously promoted. The most representative of these complexes is potassium ferrioxalate (FeOx), widely used as an actinometer [31]. Fe(III)–oxalate complexes in acid medium absorb strongly from 250 to 480 nm. Irradiation of these species generates Fe(II) and CO_2, according to the following reactions, written for the trisoxalatoferrate complex [32]:

$$[Fe(C_2O_4)_3]^{3-} + h\nu \rightarrow [Fe(C_2O_4)]^{2-} + C_2O_4^{\bullet -} \qquad (10)$$

$$C_2O_4^{\bullet -} + [Fe(C_2O_4)_3]^{3-} \rightarrow [Fe(C_2O_4)_2]^{2-} + C_2O_4^{2-} + 2CO_2 \qquad (11)$$

$$C_2O_4^{\bullet -} + O_2 \rightarrow O_2^{\bullet -} + 2CO_2 \qquad (12)$$

Potassium ferrioxalate as a source of Fe(II), in combination with H_2O_2, then results in the continuous formation of the Fenton reagent, according to reaction (1). This combination has been adopted as an AOT and was found recently to be very efficient for the photodegradation of organic pollutants, including the use of solar light for irradiation (with a profit of about 18% of the incident energy) [33,34]. Also, this combined AOT results in a high quantum yield of Fe^{2+} production, $\phi_{Fe}{}^{2+}$, close to or higher than the unity and, consequently, in a high quantum yield of the oxidizing species, either $HO^{\bullet}$ or another oxygenated radical.

Apart from oxalate, other iron carboxylates have been considered potential agents to be used in photo-Fenton related processes [30,33,35]. For example, Fe(III) complexes of EDTA and their degradation products absorb in the UV–VIS range and can be photolyzed through a LMCT reaction like (8) [36]. It has been proposed that, in addition to $HO^{\bullet}$, a nucleophilic adduct of Fe(II)–EDTA with H_2O_2 can be an additional oxidizing species [37]. Of course, as in the case of oxalic acid, EDTA auto-oxidation through (9) or other oxidative pathways can also take place. Thus, Fe(III)–EDTA and its degradation products (which include oxalic acid), can operate similarly to oxalate, and it can be proposed that the external addition of this reagent would not be essential for the oxidation. Recently, it has been reported that azo dyes can be oxidized with good yields using a Fe(III)–EDTA–H_2O_2 reagent, although it was not indicated if the reaction was performed in the dark or under illumination [35].

In the present work, the efficiency of the solar ferrioxalate/H_2O_2 process for EDTA mineralization was evaluated. The influence of parameters such as pH control, and H_2O_2 and ferrioxalate demand in the system were investigated and the results compared with those of a solar photo-Fenton process, i.e. in the absence of oxalate.

2. Experimental

2.1. Materials and methods

All chemicals were at least of reagent grade and used without purification. Na_2EDTA (Merck) was dissolved in deionized water to the desired concentration, and the pH was adjusted to 3 with 3 mol/l nitric acid. H_2O_2 (Merck) was a 29–31% (w/w) solution (Dinâmica Reagentes Analíticos, São Paulo, density = 1.1 g/ml). Potassium ferrioxalate was obtained by mixing one volume of a 0.75 mol/l solution of $Fe(NO_3)_3 \cdot 9H_2O$ (Mallinckrodt) with three volumes of a $(COOK)_2 \cdot H_2O$ (Carlo Erba) solution of the same concentration. Millipore Milli-Q water was used.

2.2. EDTA degradation experiments under solar light

Experiments were carried out in glass vessels (100 ml) containing 50 ml (ca. 60 mm height) of the system solution. Direct exposure solar light was performed on the campus of the University of Campinas, Brazil (23°S, 47°W). In a typical experiment, the corresponding volumes of aqueous EDTA and ferrioxalate (or iron nitrate) solutions were mixed and H_2O_2 at the desired concentration was carefully added. The pH was controlled by diluted nitric acid addition. Samples (500 μl) were taken periodically and the extent of photodegradation immediately analyzed by total organic carbon (TOC) measurements using a Shimadzu TOC 5000 apparatus. Losses of water by evaporation were evaluated in parallel experiments by weighing the vessel containing the solution before and after the exposure.

When possible, sets of experiments were performed simultaneously to assure the same photon flux and ambient

Table 1
Extent of TOC removal after 60 min exposure to sun light for 5 mmol/l EDTA degradation experiments in the presence of FeOx/H_2O_2 or Fe^{3+}/H_2O_2[a]

Experiment	$[H_2O_2]$ (mol/l)	$[Fe^{3+}]$ (mmol/l)	H_2O_2:Fe^{3+}:EDTA (molar ratio)	P_0 (mW/cm^2)[b]	TOC removal with EDTA (%)	TOC removal without EDTA (%)
1[c]	0.5	20[d]	500:20:1	1.1–0.2	20.5	–
2[c]	0.5	20[d]	500:20:1	0.7–0.2	78.7	54.8
3	0.58	10[d]	116:2:1	1.8–2.1	72.9	81.6
4	1.18	10[d]	236:2:1	1.8–2.1	72.9	100
5	1.75	10[d]	350:2:1	1.8–2.1	73.2	100
6	2.32	10[d]	464:2:1	1.9–2.1	94.2	100
7	2.32	2.5[d]	464:0.5:1	1.9–2.1	99.7	100
8	2.32	5[d]	464:1:1	1.9–2.1	85.1	100
9	2.32	10[d]	464:2:1	1.9–2.1	86.4	92.6
10	2.32	15[d]	464:3:1	1.9–2.1	72.1	85.9
11	0.66	5[e]	132:1:1	1.7–2.0	62.6	–
12	1.00	5[e]	200:1:1	1.7–2.0	78.8	–
13	1.33	5[e]	266:1:1	1.7–2.0	77.2	–
14	1.66	5[e]	332:1:1	1.7–2.0	81.9	–
15	2.32	5[e]	464:1:1	1.7–2.0	88.7	–
16	5	5[e]	1000:1:1	0.7–1.3	77.3 (48.1)[f]	–

[a] All experiments under pH control except Experiment 1.
[b] Initial and final photon fluxes during the experiment (60 min solar irradiation).
[c] [EDTA] = 1 mmol/l and TOC removal after 120 min.
[d] Fe^{3+} added as ferrioxalate.
[e] No FeOx; Fe^{3+} added as nitrate.
[f] In the dark.

conditions, together with control experiments in the absence of EDTA. In some cases, blanks in the dark were also evaluated.

The incident photon flux (P_0) was measured with a Cole Parmer radiometer (365 nm) every 30 min, positioning the sensor in a flat position on the ground.

3. Results and discussion

In the present work, ferrioxalate was produced in situ simply by mixing appropriate amounts of iron and oxalate solutions, avoiding the use of the solid compound, of laborious preparation; previous experiments performed in other chemical systems have shown no difference between both techniques [38]. In the presence of ferrioxalate, solutions exhibited the characteristic green color of the complex, which faded during the course of the experiment. On the other hand, in the absence of ferrioxalate, solutions presented a pale yellow color, typical of the Fe(III)–EDTA complex [39]. Table 1 presents the conditions and the results of the experiments. As the objective was to evaluate the degree of mineralization of samples, only TOC was measured and no efforts to measure EDTA concentration were made. Plots of TOC removal versus time have been obtained. Only experiments performed under similar photon flux and ambient conditions can be compared and, in each series the influence of different parameters on the extent of the TOC removal can be assessed. Evaporation losses after 120 min ranged from 3.7 to 8.9%; therefore, results are affected by this evaporation, as can be seen in some plots.

3.1. Preliminary experiments: influence of pH (Experiments 1–2)

Preliminary experiments were conducted using 1 mmol/l EDTA and a 500:20:1 H_2O_2:FeOx:EDTA molar ratio, adjusting the initial pH to 3. This ratio of reagents was chosen tentatively, as no previous knowledge existed about the system. Fig. 1 shows the time course of Experiments 1 and 2, together with controls in the dark. Experiment 1 was performed without pH control and, after 120 min of solar exposure, TOC removal reached 20.5%, with a concomitant pH increase up to ca. 7. This increase has been attributed to the formation of amino compounds as EDTA is degraded [1,2]. After 10 min, the green color of the solution disappeared and a brown precipitate of Fe(III)-oxo and -hydroxo species could be observed. A qualitative $KMnO_4$ test at the end of the experiment (120 min) showed the complete depletion of H_2O_2 in the illuminated vessel, but not in the dark control. Experiment 2 was performed under the same conditions, but at controlled pH (2–3) by periodical addition of 3 mol/l HNO_3. Neither color changes nor a precipitate were observed in this case, with the exception of a slight bleaching of the solution after 2 h of illumination. Percentage of TOC removal was remarkably higher than that in Experiment 1, in spite of a lower photon flux (Table 1), reaching 78.7% after 120 min. It can be proposed that the decreased yield when pH is not controlled arises from the increasing heterogeneity of the system, due to precipitation of iron (hydro)oxides as the pH increases, which causes alterations in light absorption. TOC removal takes place even in the absence of light, although to a much lower extent. Solutions stayed green

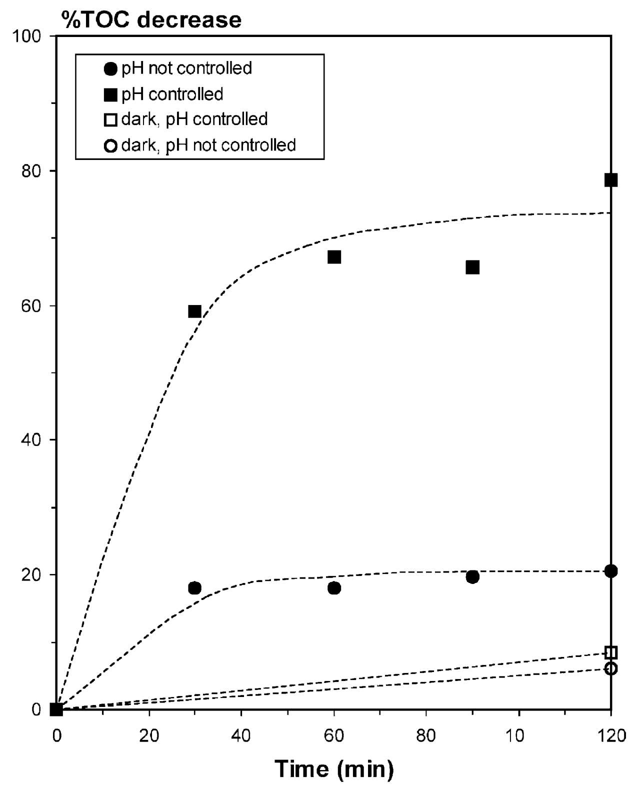

Fig. 1. Profiles of TOC removal as a function of time for EDTA degradation experiments with ferrioxalate/H_2O_2. [EDTA] = 1 mmol/l; [FeOx] = 20 mmol/l; $[H_2O_2]$ = 0.5 mol/l; initial pH 3; solar irradiation. (●) Without control of pH, $P_0 = 1.1$–$0.2\,\mathrm{mW/cm^2}$; (■) with control of pH, $P_0 = 0.7$–$0.2\,\mathrm{mW/cm^2}$. Filled symbols, under light; open symbols, controls in the dark.

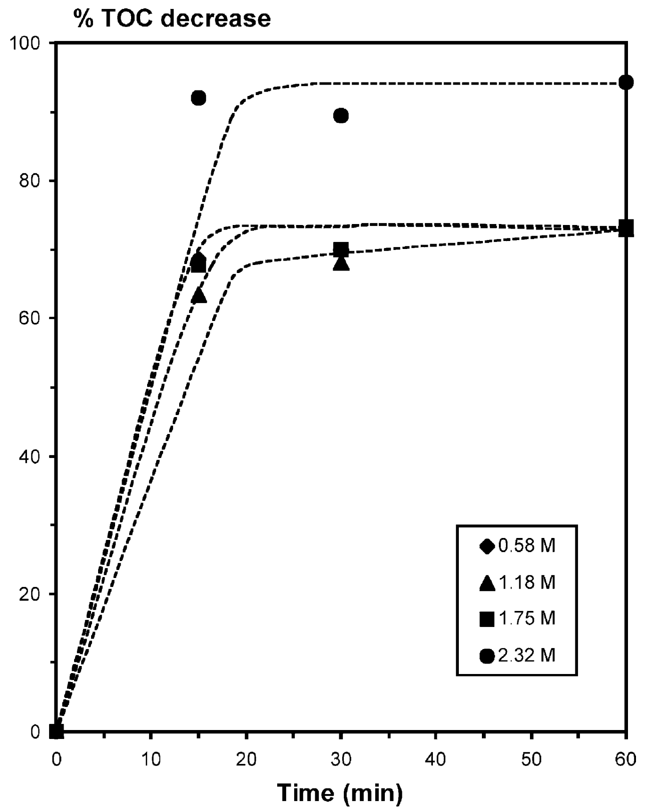

Fig. 2. Profiles of TOC removal as a function of time for EDTA degradation experiments with ferrioxalate/H_2O_2 performed at different H_2O_2 concentrations. [EDTA] = 5 mmol/l; [FeOx] = 10 mmol/l; pH 3 (controlled); solar irradiation, $P_0 = 1.8$–$2.1\,\mathrm{mW/cm^2}$. The H_2O_2 concentrations are in the legends.

and H_2O_2 was not totally consumed; TOC removal was also somewhat more important under pH control. The low reactivity in the dark is due not only to the lower efficiency of the Fenton reaction in the absence of light, as indicated before, but also because of the thermal stability of Fe(III) complexes.

3.2. Influence of H_2O_2 concentration (Experiments 3–6)

The following experiments were carried out at 5 mmol/l EDTA. Irradiations lasted only 60 min as TOC removal did not vary very much in the second hour and to reduce evaporation problems. The experiments were performed simultaneously to assure equal photon flux and ambient conditions, together with the corresponding control without EDTA. Different H_2O_2 concentrations at a constant FeOx concentration were tested. Percentage of TOC removal versus time profiles, shown in Fig. 2, indicate a similar conversion at the three lowest H_2O_2 concentrations and an almost total mineralization at the highest concentration (2.32 mol/l). However, some values can be affected by evaporation, as mentioned earlier. Although, there are no values at very early irradiation times, Fig. 2 also shows an important deceleration of the reaction after the first 15 min, which can indicate depletion of some reagent as it is consumed, probably H_2O_2 (see following sections), or another inhibitory process. For example, formation of very resistant compounds or a change in the kinetic regime can be suspected. This indicates that at low H_2O_2, an upper limit of degradation is attained in approximately 10 min, beyond which degradation is much more difficult. In all controls, except for that performed at the lowest H_2O_2 concentration (0.58 mol/l), oxalate was totally mineralized after 60 min (Table 1), with a rapid complete discoloration of the solution in less than 25 min.

3.3. Influence of ferrioxalate concentration (Experiments 7–10)

Further experiments were carried out at the highest H_2O_2 concentration (2.32 mol/l), and with different FeOx concentrations (i.e. different amounts of Fe(III), Fig. 3). A good mineralization was observed in all cases (nearly 100% at 2.5 mmol/l FeOx, Experiment 7), but the efficiency decreased as the FeOx concentrations increased. This is remarkable at 15 mmol/l FeOx. It is important to note that in the controls without EDTA no organic carbon remained at 30 min at the two lowest FeOx concentrations (2.5 and 5 mmol/l, Table 1). The results of EDTA mineralization suggest that an excess of oxalate competes with EDTA or

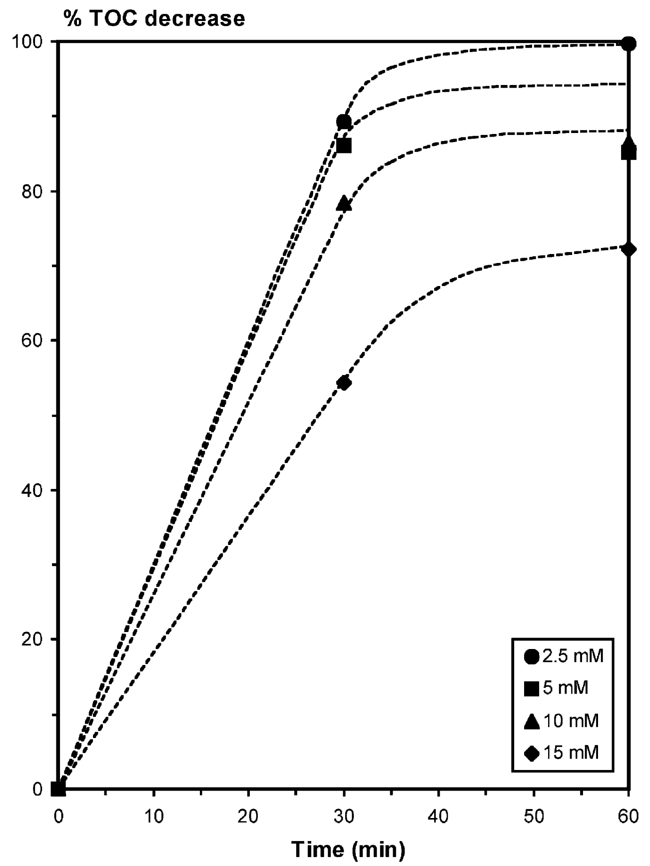

Fig. 3. Profiles of TOC removal in function of time for EDTA degradation experiments with ferrioxalate/H_2O_2 performed at different ferrioxalate concentrations. [EDTA] = 5 mmol/l; [H_2O_2] = 2.32 mol/l; pH 3 (controlled); solar irradiation, P_0 = 1.9–2.1 mW/cm^2. The FeOx concentrations are in the legends.

its degradation products for the oxidizing agents, either HO$^\bullet$ or species coming from processes (8)–(9). This effect has also been observed recently for atrazine [40].

3.4. *Experiments without oxalate (Experiments 11–15): auto-oxidation of EDTA*

The following series of experiments were performed to comparatively evaluate a solar photo-Fenton procedure, i.e. TOC removal of the EDTA solution in the absence of oxalate, and were carried out at different H_2O_2 concentrations in the presence of a fixed Fe^{3+} concentration (5 mmol/l, i.e. EDTA:Fe^{3+} molar ratio 1:1). Results are depicted in Fig. 4 and Table 1, and show a lower but still effective mineralization degree compared with experiments performed with oxalate under similar conditions. Experiments 8 and 15, for example, show a very similar TOC removal after 60 min irradiation (85.1 and 88.7%, respectively), indicating a very good efficiency at the highest H_2O_2 concentration. A slight dependence of conversion degrees on H_2O_2 concentration can be seen in this case (Fig. 4, inset), although a saturation with H_2O_2 concentration seems to begin beyond 1.0 mol/l H_2O_2. Again, deceleration after 30 min occurs in all curves, and suggests an insufficient amount of hydrogen peroxide or another inhibitory process at long reaction times.

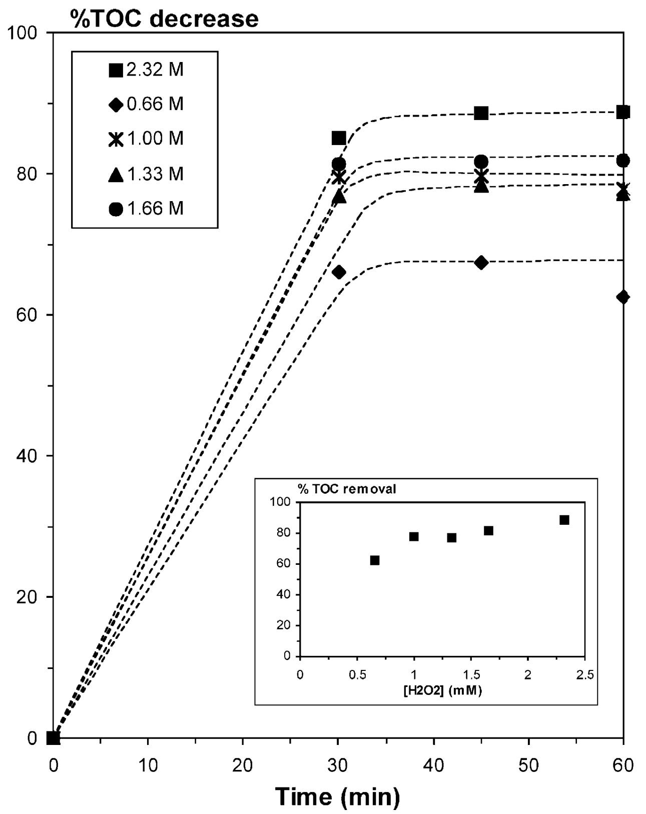

Fig. 4. Profiles of TOC removal as a function of the irradiation time for EDTA degradation experiments performed in the presence of Fe^{3+}/H_2O_2 at different H_2O_2 concentrations. [EDTA] = 5 mmol/l; [Fe^{3+}] = 5 mmol/l (as nitrate); pH 3 (controlled); solar irradiation, P_0 = 1.7–2.0 mW/cm^2. The H_2O_2 concentrations are in the legends. Inset: dependence of percent TOC removal with [H_2O_2].

Comparison of experiments performed with EDTA/Fe(III) and ferrioxalate (no EDTA) in similar conditions (cf. control without EDTA of Experiments 8 and 15, Table 1), indicates that oxalic acid auto-oxidation is easier than that of EDTA. This could be explained by: (i) a higher rate of reaction of the complex with HO$^\bullet$; (ii) a higher absorption coefficient in the solar range; (iii) a higher quantum yield of the photolysis of the Fe(III)–L complex, i.e. of reaction (8). The constant rate for Fe(III)–EDTA with HO$^\bullet$ is around two orders of magnitude higher than the corresponding one for oxalic acid [9,41], which does not explain the experimental result. On the other hand, although the absorption coefficient of both complexes in the near UV–VIS range is very similar [23,36], the quantum yield of reaction (8) differs by more than one order of magnitude [31,36], and this can be the reason for a faster degradation rate for oxalate compared with EDTA. This indicates the relevance of reaction (8) in these photo-Fenton related processes. The relative reactivity of EDTA (or its degradation products) and oxalate to other active forms generated in the Fenton systems can be also involved.

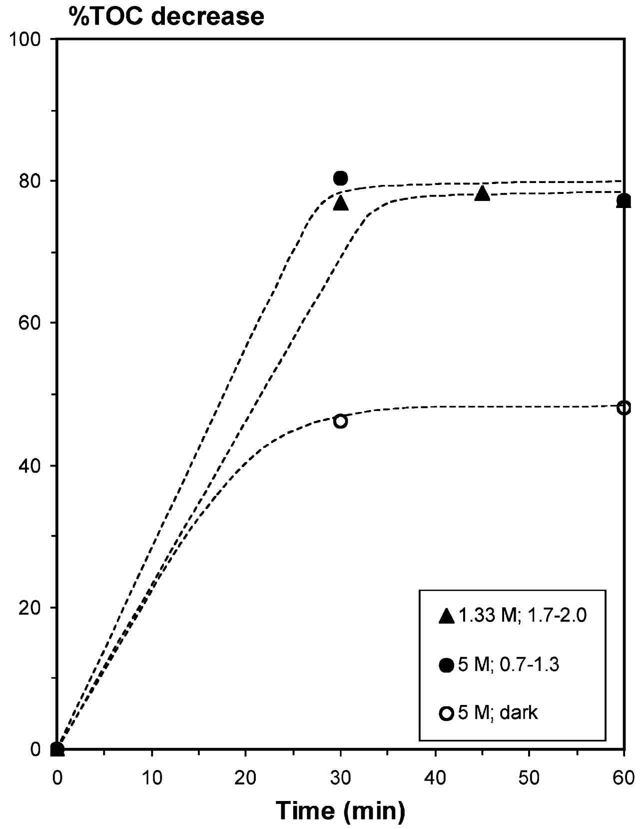

Fig. 5. Profiles of TOC removal as a function of the irradiation time for EDTA degradation experiments performed in the presence of Fe^{3+}/H_2O_2 at different H_2O_2 concentrations and different light intensities. [EDTA] = 5 mmol/l; $[Fe^{3+}]$ = 5 mmol/l (as nitrate); pH 3 (controlled); solar irradiation. The legends indicate the H_2O_2 concentrations and the incident photon fluxes in mW/cm^2.

3.5. *Influence of the light (Experiment 16)*

Experiment 16 was performed in a cloudy day but with a very large excess of H_2O_2 (1000:1:1 H_2O_2:FeOx:EDTA molar ratio). At a so high an oxidant concentration, H_2O_2 is surely no longer the limiting reagent, and the dark reaction was very important, allowing the evaluation of the influence of light intensity. In Fig. 5, Experiments 13, 16 and 16 in the dark are compared. Under solar light, similar profiles were obtained in spite of very different conditions: an almost doubled intensity and a H_2O_2 concentration four-fold lower, which without any doubt indicates the important effect of the light intensity.

4. Conclusions

A very rapid mineralization of EDTA takes place by the use of the ferrioxalate:H_2O_2 process under solar light for aqueous EDTA solutions. The pH must be controlled to achieve a good yield. Hydrogen peroxide is the limiting reagent, and the conversion degree increases somewhat with the concentration of the oxidant, although its effect is not remarkable. The amount of oxalic acid must be also controlled because it competes with EDTA or its degradation products for the oxidizing system, causing its own degradation. In the absence of oxalic acid, EDTA degradation also takes place, the extent of mineralization being only slightly lower. Our results indicate that the use of oxalate is not essential, and point to the important contribution to mineralization by the photolysis of Fe(III)–EDTA complexes or other intermediates involved in photo-Fenton cycles. Thus, pollutants which form complexes with Fe(III), of high absorption coefficient in the UV–VIS range and able to react according to Eq. (8) could be auto-oxidized in these conditions; they could even serve as advanced oxidation reagents for mineralization of other organic compounds, especially those not forming Fe(III) complexes, such as most aromatic compounds.

In this work, no effort to attain the optimum ratio of reagents has been made. As H_2O_2 concentration does not produce a very important effect, it is possible that a lower amount can be used, decreasing costs and avoiding safety cares. Although Fe(III) must be present in the system, it is also possible that a lower concentration can be employed. Moreover, many industrial and domestic effluents contain some Fe(III), which would make the external addition of this reagent unnecessary. Further experiments are underway to find the best compromise between the amount of oxidants and economic costs.

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