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Destruction of EDTA using Fenton and photo-Fenton-like reactions under UV-A irradiation

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Abstract

Degradation experiments using 5 mmol/l ethylenediaminetetraacetic acid (EDTA) solutions at pH 3 were performed in the presence of H_2O_2 and metals such as Fe^{2+}, Fe^{3+}, Cu^{2+} and mixtures of Fe^{2+}/Cu^{2+} and Fe^{3+}/Cu^{2+} under UV-A irradiation (366 nm)—photo-Fenton and photo-Fenton-like reactions—at different metal/EDTA concentration ratios in order to determine the best conditions for EDTA photochemical removal. Analogous dark reactions were performed for comparison. The reaction course was monitored by both EDTA and TOC determinations. Hydrogen peroxide demand was also evaluated in all cases. In terms of TOC removal, photo-Fenton-like reactions were remarkably more efficient than the analogous Fenton-like reactions. When EDTA was monitored, Fenton-like reactions showed variable performances, being more efficient with EDTA:Fe^{2+} and EDTA:Fe^{3+} ratios of 1:1. However, in these both cases, reaction rates were lower than the ones obtained under irradiation. Total mineralization ranged from 31% (Cu^{2+} system) to 92% (Fe^{2+}, Fe^{3+}, $Fe^{3+} + Cu^{2+}$ and $Fe^{2+} + Cu^{2+}$ systems) after 4 h of irradiation. Percentage of TOC removal was higher in the presence of iron because some photoactive intermediates were probably formed during EDTA degradation.

Keywords: Advanced oxidation technologies; EDTA destruction; Iron; Copper; Fenton; Photo-Fenton

1. Introduction

Ethylenediaminetetraacetic acid (EDTA) is a common chelating agent used in many different industrial applications for sequestration of metal ions. Thus, it is employed in the photographic industry, in textile and paper manufacturing, in the metal industry and in chemical cleaning processes but, because of its metal binding and metal solubilizing properties, it may produce deleterious effects when released into the environment [1–3]. For example, EDTA can make difficult the removal of heavy metals present in water and wastewaters by conventional precipitation processes mainly because of the dramatic increase in the solubility of heavy metal ions. In addition, the presence of organic chelating agents such as EDTA may also cause some metal-laden wastewater discharges to violate the COD requirement for effluent discharge, because the toxicity of heavy metal complexes prevents the reduction of COD by most biological treatment processes [3–8]. Removal of EDTA from wastewaters by conventional techniques is not simple because it is not easily biodegradable, and several recalcitrant compounds are formed during the degradation [1,3,5,7,9].

Advanced oxidation processes or techniques (AOPs, AOTs) have been proposed in recent years as an attractive alternative for the treatment of matrices contaminated by highly toxic, refractory or biologically resistant substances. The common characteristic of all AOPs is the use of very reactive free radicals, mainly hydroxyl radicals, which may be generated by various methods including thermal processes with H_2O_2 or ozone, and light-induced reactions such as direct homogeneous photolysis. These hydroxyl radicals attack organic molecules by abstracting a hydrogen atom or by adding to the double bonds. Organic molecules are then totally mineralized to carbon dioxide, inorganic ions and water. Usually, UV-C (wavelength between 200 and 280 nm) and UV-A (wavelength between 315 and 400 nm),

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also called long-wave radiation or black light, are employed as radiation sources. Transition metals and their complexes are also used in these processes as catalysts and/or mediators, especially iron salts in their various oxidation states [10–16].

Methods based on use of the redox pair Fe(II/III) to destroy pollutants in water are increasingly reported. In particular, Fenton's reagent is composed of a solution containing hydrogen peroxide and a Fe^{2+} salt, in an acid medium. Ferric and Cu^{2+} ions can be also used (Fenton-like reagents). The efficiency of the Fenton reagent for destruction of organic matter can be enhanced by irradiation with light in the UV range (photo-Fenton reaction); even solar light can be used [12,13,17,18].

The influence of iron salts on the decomposition of EDTA under UV light in the presence of H_2O_2 has been observed previously [19,20], at low concentrations of EDTA and with Fe^{2+}/EDTA molar ratios close to 1. In a series of studies previously undertaken by us, the performance of several AOTs for EDTA degradation at concentrations usually found in some wastewaters (e.g., those coming from decontamination and cleaning of nuclear components) was evaluated. Previous papers reported the action of UV-C/H_2O_2 [21] and solar ferrioxalate and photo-Fenton processes [22] under solar light.

The main objective of the present work was to test the influence of UV-A on EDTA degradation, using Fenton and photo-Fenton-like reactions in the presence of Fe^{2+}, Fe^{3+}, Cu^{2+} and mixtures of Fe^{2+}/Cu^{2+} and Fe^{3+}/Cu^{2+} ions. There is great environmental interest in destruction of this substance because (1) it is found in many rivers and lakes under anthropogenic stress; (2) the microbial degradation of EDTA is relatively poor and takes place only under very special conditions; (3) treatment with chlorine or other disinfectants does not result in any significant degradation of EDTA; (4) both EDTA and nitrilotriacetic acid (NTA) are found predominantly in complexed forms with Ca^{2+}, Zn^{2+}, and Cu^{2+} ([19] and references therein).

2. Experimental

2.1. Materials and methods

2.1.1. Standard solutions

Na_2EDTA (Mallinckrodt) was weighted and dissolved in deionized water to reach a 50 mmol/l concentration. H_2O_2 (Douglas p.a.) was a 30% (w/w) solution. A 50 mmol/l Fe^{2+} solution was prepared from Mohr salt, $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$ (Mallinckrodt) and a 50 mmol/l Fe^{3+} solution was prepared from $Fe(NH_4)(SO_4)_2\cdot 12H_2O$ salt (UCB-Belgium), both by dissolution in 0.5 mol/l sulfuric acid (Merck). A 50 mmol/l Cu^{2+} solution was prepared from $Cu(NO_3)_2\cdot 3H_2O$ salt (Mallinckrodt), by dissolution in 1 mol/l nitric acid (Merck). All other reagents were analytical grade and used without purification.

2.1.2. EDTA determination

EDTA concentrations were determined using Test Method A—Total Sodium Salt of EDTA (ASTM Standards) [23] with some modifications. The intensity of the red-colored zirconium–xylenol orange complex formed in a strong acid medium is reduced in the presence of free EDTA or its metallic complexes through formation of a more stable zirconium–EDTA complex, measured at 535 nm, using an UV-Vis spectrophotometer (Double Beam UV-210A, Shimadzu) and 10 mm cell. A series of standards were prepared by pipetting 0, 2.5, 5, 7.5, 10, and 12.5 ml aliquots of EDTA standard solution (0.107 mmol/l) into 25 ml volumetric flasks containing 2.5 ml of zirconium reagent solution (0.526 mmol/l) and 2.5 ml of xylenol orange. For samples, 250 μl aliquots were used, obtained at the following intervals: 0, 5, 10, 15, 20, 40, and 60 min.

2.1.3. H_2O_2 determination

H_2O_2 concentration was determined using an UV-Vis spectrophotometric determination [24], with minor modifications. Hydrogen peroxide reacts with an ammonium metavanadate solution in acid medium, forming a colored product, measured at 450 nm with a 10 mm cell. A series of standards were prepared by pipetting 0, 75, 188, 375, 563, and 750 μl aliquots of H_2O_2 standard solution (0.196 mol/l, prepared from 30% (w/w) H_2O_2 solution) into 50 ml volumetric flasks containing 20 ml of NH_4VO_3 solution (0.125 mol/l, prepared from NH_4VO_3 salt in a H_2SO_4 medium). The volume was completed with water. For samples, 1.25 ml aliquots were treated as above, sampled in the time intervals: 0, 30, 60, 90, 120, 150, 180, 210, and 240 min.

2.1.4. TOC determination

The percentage of TOC removal was measured using a Shimadzu TOC 5000-A apparatus. For samples, 1.0 ml aliquots were used, placed into 10 ml volumetric flasks containing 250 μl of "reduction agent" [18] (composed of 0.10 mol/l Na_3PO_4, 0.10 mol/l KI, and 0.10 mol/l Na_2SO_3), 3–5 drops of HCl solution (2 mol/l). The volume was completed with water. Samples were taken at the following intervals: 0, 30, 60, 90, 120, 150, 180, 210, and 240 min. This method led to a complete reduction of the residual H_2O_2 as well as to interruption of the Fenton-like reaction.

For simplicity, from this point on, Fenton-like and photo-Fenton-like reactions will be referred to in the text as Fenton and photo-Fenton.

2.2. EDTA degradation experiments

Degradation experiments of EDTA (5 mmol/l) at initial pH 3 were performed in the dark (Fenton reaction) and under UV-A irradiation in the presence of H_2O_2 and different metal ions at various conditions, as shown in Table 1. Fenton reactions were done under conditions very similar to the photo-Fenton experiments, for the sake of comparison. An annular glass reactor, 415 mm in length, 35 mm external

Table 1
Experimental conditions for 5 mmol/l EDTA degradation with Fenton and photo-Fenton reactions

Experiment	Metal	Metal concentrations (mmol/l)	EDTA:metal (molar ratio)	H_2O_2:EDTA (final molar ratio)
1	Fe^{2+}	1.25	1:0.25	80:1
2	Fe^{2+}	5.0	1:1	100:1
3	Fe^{3+}	5.0	1:1	120:1
4	Cu^{2+}	5.0	1:1	20:1
5	$Fe^{3+} + Cu^{2+}$	2.0 (iron); 2.5 (copper)	1:(0.4; 0.5)	40:1
6	$Fe^{2+} + Cu^{2+}$	2.0 (iron); 2.5 (copper)	1:(0.4; 0.5)	60:1

Initial $[H_2O_2] = 100$ mmol/l; H_2O_2:EDTA initial molar ratio of 20:1.

diameter, 85 ml total volume, provided with a 366 nm UV (Yaming Lighting) lamp, 15 W, 466 mm in length was used, in a such way that both ends of lamp were kept outside the reactor body to facilitate the electrical contacts (see [25] for details on the reactor construction). The distance between the internal reactor wall and the lamp was 4 mm. The total incident photon flow or photon generation rate obtained, determined by potassium ferrioxalate actinometry measurements [26], was 1.06×10^{-5} einstein/s, at a flow rate of 750 ml/min.

Fenton and photo-Fenton experiments were performed in a similar way, except for the fact that in the Fenton systems, H_2O_2 was added only once, to provide a H_2O_2:EDTA molar ratio of 20:1. Since it was observed in our preliminary study that a significant EDTA degradation (ca. 55% after 60–90 min) took place in the dark in the presence of H_2O_2 (H_2O_2/EDTA molar ratio > 3) alone, the order of addition of the reagents was carefully respected. A 255 ml EDTA solution, containing the corresponding volume of metal ion solution and magnetically stirred, was recycled at a 750 ml/min flow rate to the reactor for 3 min before the addition of H_2O_2. For each experiment 2.6 ml of 30% (w/w) H_2O_2 solution was initially added to give a H_2O_2:EDTA initial molar ratio of 20:1. A good mixing and aeration of the chemical system was then assured. In photo-Fenton experiments, the UV lamp was started at this stage. Samples were taken periodically from the reservoir for determination of EDTA and H_2O_2 concentrations and %TOC removal. The reaction was monitored for 4 h and the pH was controlled during the entire time, using a 1 mol/l nitric acid solution (Merck). The monitoring of both TOC and the target compound was carried out in most reactional systems were the formation of numerous by-products were detected, since under this situation, EDTA removal is not proportional to TOC decrease in the solution.

Due to the fact that the target compound (EDTA) is rapidly destroyed in the photo-Fenton systems [3,4,8,9,22,27], the monitoring of this compound was performed during the first hour of the reaction only. For the Fenton systems, EDTA concentrations were determined only at the beginning and at the end of the experiment (after 4 h).

To all photo-Fenton experiments, hydrogen peroxide addition to the reaction medium was carried out whenever residual H_2O_2 concentrations dropped nearly zero, thus avoiding H_2O_2 excess that could compete for the hydroxyl radical ($HO^{\bullet}$). So, a variable number of H_2O_2 additions was made in each experiment. For Experiment 1 three additions were made (0, 105, 165, and 225 min) and the final H_2O_2:EDTA molar ratio obtained was 80:1; Experiment 2 received four additions of H_2O_2 (0, 45, 105, 165, and 215 min) and the final molar ratio was 100:1; Experiment 3 received five additions (0, 35, 65, 95, 135, and 195 min), with a final molar ratio of 120:1; for Experiment 4 no additional H_2O_2 was used; Experiment 5 had only one addition (initially and after 105 min), to give a final molar ratio of 40:1; finally, Experiment 6 had two H_2O_2 additions (0, 75, and 165 min), and a final molar ratio was 60:1.

In our earlier studies it was observed that the reproducibility of the experimental measurements (TOC) was between 8 and 10%. From this, in this present work control experiments (blanks) were made when Fenton's reagent was employed in the absence of irradiation.

3. Results and discussion

Table 2 shows the results of TOC removal, EDTA degradation and H_2O_2 residual concentration for the different experimental conditions listed in Table 1. It was found that, in the dark (Fenton systems), TOC removal was very low at the end of 4 h for all experiments, reaching a maximum of 31.9% removal in the case of 1:1 EDTA:Fe^{2+} and 13.0% in the case of 1:1 EDTA:Fe^{3+} (Experiments 2 and 3, respectively, Table 1). For the other systems, average TOC removals did not exceed 8%. According to Lunar et al. [28], the Fenton's reaction in the absence of photons can be ineffective due to competition between the substrate and H_2O_2 for the hydroxyl radical ($HO^{\bullet}$). In addition, some by-products formed in this process, in particular oxalic acid, can be accumulate in the reaction media due to its refractory nature to Fenton's reagent [29]. Rivas et al. [29] observed this behavior when *p*-hydroxybenzoic acid, a phenolic model compound, was oxidized in aqueous solutions by $Fe^{2+}/Fe^{3+}/H_2O_2$, in the dark.

In contrast to this, all photo-Fenton systems (except for the one using only Cu^{2+}, Experiment 4) yielded a TOC removal above 80% after 4 h irradiation. TOC removal profiles as a function of time are shown in Fig. 1. In some cases (Exper-

Table 2
Extent of TOC removal, EDTA degradation and H_2O_2 residual concentration for different experiments in the dark (Fenton) and in the presence of irradiation (photo-Fenton)

TOC removal (%)			EDTA degradation (%)		Residual H_2O_2 (%)	
Experiment	Fenton[a]	Photo-Fenton[a]	Fenton[a]	Photo-Fenton[b]	Fenton[a]	Photo-Fenton[a]
1	2.6	80.1	6.1	76.3	94.7	59.3
2	31.9	88.4	92.7	93.9	0.2	7.9
3	13.0	89.7	83.1	82.4	6.1	27.7
4	1.8	31.1	6.6	64.5	99.2	53.0
5	1.7	84.0	0.5	100	99.0	0.8
6	7.7	92.0	27.0	100	90.3	8.3

UV-A irradiation (366 nm); pH 3; total incident photon flow = 1.06×10^{-5} einstein/s; [EDTA] = 5 mmol/l; initial [H_2O_2] = 100 mmol/l.

[a] After 4 h of reaction.

[b] After 1 h of reaction.

iments 1, 5, and 6), an induction period was observed. This behavior is commonly observed in oxidative reactions using H_2O_2 [22,29], and it is probably due to the formation of transient species that latter undergo further oxidation to the final CO_2 product. Some experiments were conducted in the presence of a possible hydroxyl radical scavenger (*tert*-butyl alcohol) by Rivas et al. [29], and an induction period at the beginning of the process was also experienced by them.

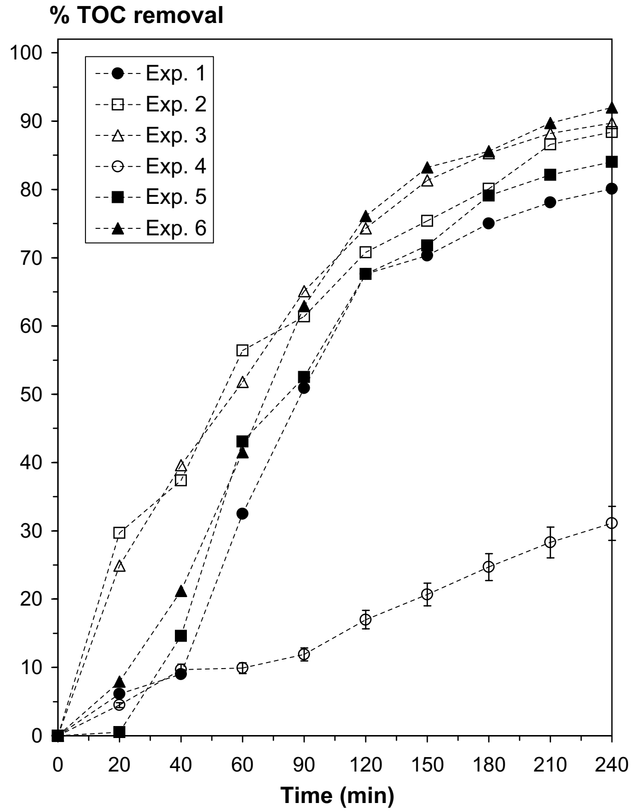

Fig. 1. Profiles of TOC removal as a function of the irradiation time (after 4 h) for the different photo-Fenton experiments. Conditions as in Table 1. Error bar represents the maximum standard deviation obtained for triplicate analysis (8%).

For most photo-Fenton systems, the final degradation extent was the same. However, the initial rate of mineralization was higher for 1:1 EDTA:Fe^{2+} and 1:1 EDTA:Fe^{3+} systems (Experiments 2 and 3, respectively), as shown in Fig. 1. These results indicate that iron species act as better catalysts than does Cu^{2+}, even though $HO^{\bullet}$ is a relatively nonselective transient oxidizing species.

Based upon the fact that TOC removal was very efficient under irradiation, a more detailed work evaluating EDTA destruction was carried out. The results are also presented in Table 2. Due to the fact that EDTA degradation was very fast in light mediated experiments (UV/H_2O_2), such as previously observed by Ku et al. [4] in which EDTA was destroyed almost completely within 1 h, while the organic intermediates were mineralized to CO_2 within 5 h, the comparative results obtained to EDTA degradation at the end of 1 h of light exposure (photo-Fenton systems) and 4 h in the dark (Fenton systems) are showed in Table 2. Again, as observed for the TOC results, EDTA degradation attained a higher extent in all photo-Fenton processes, as compared with the Fenton ones (above 75%, except for EDTA:Cu^{2+}, Experiment 4). However, dark reactions in the EDTA:Fe^{2+} and EDTA:Fe^{3+} systems (both at 1:1 ratios, Experiments 2 and 3) also achieved high EDTA degradations after 4 h, reaching values above 80%. Interestingly, this high destruction extent in the absence of irradiation is not translated to TOC removal in the same period of time, as seen in Table 2.

Although in these experiments EDTA concentration has dropped after 4 h of reaction in the dark, some organic compounds such as ethylenediaminediacetic acid (EDDA), iminodiacetic acid (IDA) and oxalic acid could be formed. These compounds were detected by several authors [3,4,8,9,27] as by-products of the decomposition of EDTA in aqueous solution when different AOTs were employed. Thus, the TOC values were not noticeably decreased in these cases, even though the EDTA concentration dropped drastically.

Time profiles observed for EDTA degradation during the first hour of irradiation in all six experiments are shown in Fig. 2. Very fast initial EDTA destruction is observed for both 1:1 EDTA:Fe^{2+} and 1:1 EDTA:Fe^{3+} (Experiments 2

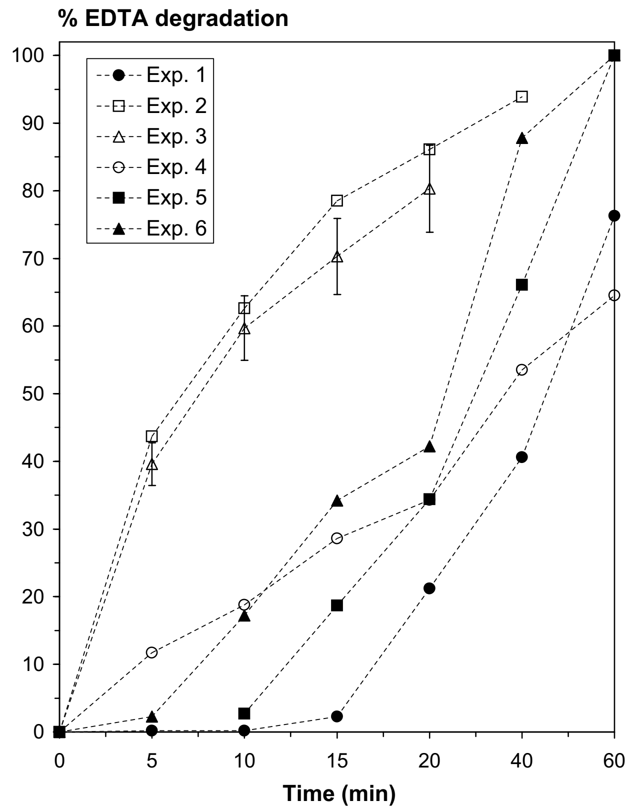

Fig. 2. Profiles of EDTA degradation as a function of the irradiation time (after 1 h) for the different photo-Fenton experiments. Conditions as in Table 1. Error bar represents the maximum standard deviation obtained for duplicate analysis (10%).

and 3) although the final conversion is quite similar for all the systems, except for the one with Cu^{2+} (Experiment 4). Another important aspect worth mentioning is that one cannot ruled out the possibility of the induction period observed in Experiments 1 and 5, and to a lesser extent in Experiment 6, be due to an analytical artifact caused by the interference of some EDTA-similar by-product in the colorimetric EDTA assay.

Hydrogen peroxide demand was also evaluated in all six systems during the course of the reactions. When EDTA is in the presence of either Fe^{2+} or Fe^{3+} in 1:1 ratios (Experiments 2 and 3, respectively), the H_2O_2 consumption is complete in the first 30 min, whereas for the mixed metal systems ($Fe^{2+} + Cu^{2+}$ and $Fe^{3+} + Cu^{2+}$), as well as for EDTA:Fe^{2+} (1:0.25), the oxidant consumption only reached ca. 100% after 60 min. The copper containing system (Experiment 4) shows a totally different behavior concerning H_2O_2 consumption, attaining only 47% depletion of the oxidant after 240 min. It is important to mention that, in the dark, the EDTA:Fe^{2+} and EDTA:Fe^{3+} systems (Experiments 2 and 3, respectively) also showed a high H_2O_2 demand, as previously reported by Sundstrom et al. [1]. However, the same behavior was not observed, in the dark, for the other systems (Experiments 1, 4, 5, and 6), where the H_2O_2 consumption did not exceed 10%.

The following subsections discuss the data obtained to provide a better comprehension of the systems used in these experiments.

3.1. EDTA degradation experiments using $Fe^{2+/3+}$ systems

Fenton reactions are based on a hydrogen peroxide solution and Fe^{2+} or Fe^{3+} salts in an acid medium. Fenton-like reactions use other metal salts also in an acid medium. Decomposition of H_2O_2 catalyzed by the metal ion generates a hydroxyl radical ($HO^\bullet$), as shown for Fe^{2+} in the following simplified equations ([11–14,17,18,28–30] and references therein):

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

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

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{–}OOH^{2+} + H^+ \qquad (2)$$

$$Fe\text{–}OOH^{2+} \rightarrow Fe^{2+} + HO_2^\bullet \qquad (3)$$

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

$$Fe^{2+} + HO_2^\bullet + H^+ \rightarrow Fe^{3+} + H_2O_2 \qquad (4)$$

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

The rate of reaction (1) is much higher than that corresponding to reaction (2). Indeed, it can be said that, in excess H_2O_2, the Fenton reaction (1) is rate-limiting only in the first seconds (or minutes) of the reaction. After this short time, the rate of oxidation is controlled by reaction (2). The rate constant for reaction (5) is smaller than that for reaction (4) in the acidic pH range [17,28,31].

The hydroxyl radicals also attack an organic molecule by several degradative mechanisms [32,33]:

$$RH + HO^\bullet \rightarrow H_2O + R^\bullet \qquad (6)$$

$$R^\bullet + Fe^{3+} \rightarrow Fe^{2+} + R^+ \qquad (7)$$

$$R^\bullet + H_2O_2 \rightarrow ROH + HO^\bullet \qquad (8)$$

The species $HO_2^\bullet$ is a weak oxidant. The identity of this species is still under discussion; however, it is accepted that, besides $HO^\bullet$ radicals, active intermediates species such as FeO^{2+} or FeO^{3+} (iron as Fe(+IV) and Fe(+V), respectively) can take part of the oxidation process, as suggested by Kremer [34] and Bossmann et al. [18].

It is known that Fenton processes generally do not lead to mineralization of EDTA, and that light must be used to promote a more extensive substrate degradation [11], in agreement with the results obtained in this work.

Under irradiation, Fe^{3+} (present as hydroxylated species) is continuously reduced to Fe^{2+}

$$FeOH^{2+} + h\nu \rightarrow Fe^{2+} + HO^\bullet \qquad (9)$$

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

EDTA and other aminocarboxylic acids such as ethylenediaminediacetic acid, nitrilotriacetic acid (NTA) and iminodiacetic acid, its intermediate degradation products, form strong chelates with Fe(III). These species absorb strongly in the UV range, and their photolysis through intramolecular LMCT (ligand to metal charge transfer) transitions occurs with good quantum yields

$$Fe(III)(RCO_2)^{2+} + h\nu \rightarrow Fe(II) + CO_2 + R^\bullet \quad (10)$$

For example, Fe(III)–EDTA absorbs at 220–400 nm ($\varepsilon_{254} = 7890$ ml/mol cm, [8]); $\phi_{Fe^{2+}}$ at 366 nm for Eq. (10) is about 0.08 [35]. Photolysis of these carboxylates gives rise to decarboxylation, forming radicals $R^\bullet$. In contrast, the Cu(II)–EDTA has been found inactive for this type of reaction [35]. In addition, it has been proposed that a nucleophilic adduct of Fe(II)–EDTA with H_2O_2 can be an additional oxidizing species [36]. These radicals react with dissolved O_2 and generate intermediates that form additional Fe(III) complexes and contribute to the cycle, even in the absence of H_2O_2

$$R^\bullet + O_2 \rightarrow ROO^\bullet \rightarrow \text{oxygenated products} \quad (11)$$

$$\text{oxygenated products} + Fe^{3+} \rightarrow HO^\bullet + Fe^{2+} \quad (12)$$

Recently, it has been reported that azo dyes can be oxidized with good yields using a Fe(III)–EDTA–H_2O_2 system, although it was not indicated if the reaction was performed in the dark or under illumination [37]. Of course, by external addition of H_2O_2, the photo-Fenton reaction (1) takes place continuously.

Fenton and photo-Fenton reactions are strongly dependent on pH, and an optimum value around 2.8 has been found. At higher pH, oxides or hydroxides precipitate, slowing down the reaction. Moreover, these precipitates must be removed at the end of the process, with additional cost [17,38]. The H_2O_2/Fe^{3+} system is more sensitive to pH than the H_2O_2/Fe^{2+} one because, at pH values lower than about 2, inhibition of prior complexation of Fe^{3+} by H_2O_2 occurs (Eq. (2)) and, when the pH is increased above 3, precipitation of Fe^{3+} to amorphous oxyhydroxides ($Fe_2O_3 \cdot nH_2O$) decreases the iron concentration in solution [17,28].

Fenton's reagent is known to be a very powerful oxidizing agent. There are, however, species that show resistance to oxidation by the dark Fenton reaction [39]. These species are small chlorinated alkanes (tetrachloroethane, trichloroethane), *n*-paraffins and short-chain carboxylic acids (maleic, oxalic, acetic, malonic) [39,40]. As EDTA degrades, Fe(III) complexes formed from degradation products, such as oxalic acid, can be formed, which are very stable in the dark, inhibiting further decomposition. Light promoted a very rapid EDTA degradation (about 80% after 20 min in Experiments 2 and 3) and indicated the important role of the photolysis of Fe(III)–EDTA complexes or their decomposition products through reaction (10) [22]. Comparison of Experiments 1 and 2 shows that the reaction is more sensitive to a higher Fe^{2+} amount, as demonstrated elsewhere for other substrates [38,41]. The influence of this type of reaction is noticeable and explains the lower results obtained in the dark and under irradiation when only copper is present. Although $HO^\bullet$ radicals can be generated in photo-Fenton-like reactions and the rate constants are similar for EDTA:Fe^{3+} and EDTA:Cu^{2+} systems [42], these results show the marked influence of the photoactivity of the iron–EDTA complex. Both EDTA degradation and TOC removal enhance under irradiation, indicating that some intermediates of EDTA degradation are photoactive when complexed with iron.

According to the mechanisms that are proposed here, H_2O_2 is produced through reaction (4) and it can be also produced via photochemical/chemical cycling of Fe(III) complexes, especially Fe(III)–oxalate (see [31,38,43] for more details). The higher reactivity of the photo-Fenton systems rests on the formation of a continuous amount of $HO^\bullet$ radicals. Direct photolysis can also contribute, but to a lower extent. Moreover, it has been observed, as described elsewhere [22], that EDTA can be almost completely destroyed in 1 h in the presence of Fe^{3+} and H_2O_2 under solar irradiation. Therefore, the use of an UV lamp seems to be unnecessary, making the process economically more attractive.

3.2. EDTA degradation experiments using Cu^{2+} and $Cu^{2+}/Fe^{2+/3+}$ systems

As indicated in previous subsection, the formation of $HO^\bullet$ from H_2O_2 is enhanced by the presence of a catalyst, such as uncomplexed iron in both the (+II) and (+III) valence states. Copper, on the other hand, often disproportionates H_2O_2 intermediates (superoxides), converting them partially back to H_2O_2. Thus, uncomplexed copper may act to reduce the oxidative capacity of H_2O_2 [1]. In this way, these factors might explain why, in our study, both TOC removal and EDTA degradation results were very low at the end of 4 h of reaction, in the absence of UV-A irradiation (Fenton reaction), as shown in Table 2. For these systems (Experiments 4–6), average TOC removals did not exceed 8%. On the other hand, a small amount of the target compound was degraded in Experiment 6 (in the dark), reaching a maximum of 27.0% EDTA degradation.

Ku et al. [4], studying the decomposition of EDTA in aqueous solution using H_2O_2 in the presence of Cu^{2+} ions, found that H_2O_2 was very stable at pH 3, when the system was in the absence of irradiation. However, the disappearance rates of H_2O_2 were markedly increased by UV irradiation in the absence or in the presence of Cu^{2+}, at the same pH. According to these authors, the decrease in the concentration of H_2O_2 was due to photolytic decomposition of H_2O_2 by UV irradiation to generate $HO^\bullet$, as well as by increasing the catalytic effect of Cu^{2+}.

Cu^{2+} ions need to be reduced to form Cu^+ species. Then, Cu^+ ions can react with H_2O_2 to generate $HO^\bullet$, following the same mechanism as shown for Fenton and photo-Fenton reactions ([15] and references therein]

$$Cu^{2+} + e^- \rightarrow Cu^+ \quad (13)$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + OH^- + HO^\bullet \quad (14)$$

The effect of the presence of Cu^{2+} on the photooxidation of EDTA by UV/H_2O_2 process was interesting. For the cases where the molar concentration of copper species is less than that of EDTA, such as used in this work (Experiments 5 and 6, Table 1), most copper ions are present in the Cu(II)–EDTA form at pH 3. This species competes favorably for UV light with H_2O_2, (for example, at pH 3 the absorbance of Cu(II)–EDTA and H_2O_2 at 254 nm were determined to be 0.72 and 0.141, respectively [4]), thus slowing down the generation of $HO^\bullet$ from the photolysis of H_2O_2. The rate of H_2O_2 consumption is expected to be smaller than in photo-Fenton reactions carried out in the presence of Fe^{2+} or Fe^{3+} ions only, increasing the efficiency of these systems. In fact, this behavior was observed in our experiments when both percentages of TOC removal and EDTA degradation obtained in Experiments 5 and 6 are compared with Experiments 2 and 3, respectively, even though the EDTA:metal molar ratios were not the same. On the other hand, when the molar concentration of copper species is equal or exceeds that of EDTA, such as used in Experiment 4, the decomposition of EDTA by UV/H_2O_2 process can be accelerated because, at the same pH, $HO^\bullet$ radicals can be more easily formed by the photolytic decomposition of H_2O_2 catalyzed by free copper ions present in solution [4]. In fact, this was observed in Experiment 4, when a maximum of 64.5% EDTA degradation was achieved. However, the same behavior was not observed in terms of TOC removal. Since the photo-Fenton systems, in the presence or absence of Cu^{2+} ions (Experiments 2, 3, 5, and 6), led to very similar degree of TOC after 4 h of irradiation, it seems clear that the systems in which Cu^{2+} ions are presented overperformed the others, provided a significantly lower H_2O_2 consumption.

In our case, total depletion of organic carbon required only a few addition of oxidant and a residence time of 4 h for both the $H_2O_2/Fe^{2+}/Cu^{2+}$ and the $H_2O_2/Fe^{3+}/Cu^{2+}$ systems. The efficiency of the UV/H_2O_2 process on the photodegradation of EDTA in the presence of Cu^{2+} (Experiment 4) was not very good, maybe due to the lower reactivity of Cu^{2+} than Fe^{2+} or Fe^{3+} as catalyst. On the other hand, when $Fe^{2+/3+}$ and Cu^{2+} were present in the same system (Experiments 5 and 6), the photo-Fenton process was much more efficient because the generation of $HO^\bullet$ is strongly increased by photoreduction of ferric ions, photolysis of Fe(III)–EDTA and possible intermediate chelates and, in small proportion, by the photolysis of H_2O_2.

Chamarro et al. [40] pointed out that there are two important factors affecting the rate of Fenton's reaction: peroxide dose and iron concentration. The peroxide dose is important in order to obtain a better degradation efficiency while the iron concentration is important for the reaction kinetics. The extent of the oxidation is determined by the amount of hydrogen peroxide present in the system and the total elimination of organic carbon requires a large amount of oxidant and/or long residence times. In this way, it is possible to choose between lower operational costs associate to lower kinetic rates or higher operational costs with higher kinetic rates, without affecting the overall process efficiency.

Finally, one should bear in mind that mechanisms associated with EDTA degradation are not simple due to the amount of intermediates that can be formed during the progress of the reaction. Related papers mention numerous possible routes [3,4,8,9,27], and many possible mechanism have not been yet completely elucidated. Ku et al. [4] studied the decomposition of EDTA in aqueous solution by UV/H_2O_2 process under various solution pH values, H_2O_2 dosages, UV light intensities, temperatures, and concentrations of Cu^{2+} in order to determine the completeness of decomposition. A simplified two-step kinetic model was found to describe the concentrations of reactants and products of EDTA degradation in which each step of the reaction was assumed to be irreversible and first order with respect to the reactant.

4. Conclusion

The employment of Fenton's reagent in the treatment of an EDTA solution (at concentrations usually found in some industrial wastewaters) was found to be very efficient when combined with UV irradiation. A rapid TOC removal took place using iron species as a catalyst, either alone or in the presence of Cu^{2+} ions. TOC removal showed to be similar for all tested systems, except for the one using Cu^{2+} ions alone, but with different H_2O_2 demands. In this way, selection of the most suitable process, that is, the one offering the best cost/efficiency relation has to be made according to the peculiarities of each case, taking into account the possible presence of native iron or copper ions in the wastewaters. The rate of EDTA degradation was highly dependent on the iron concentration and the amount of oxidant, as well as on the solution pH. Since the main emphasis of this study was centered on TOC destruction, possible by-products formed during the EDTA degradation were not monitored. The important contribution of the photolysis of Fe(III)–EDTA complexes in the EDTA destruction can make the use of high H_2O_2 concentrations unnecessary. It should be stressed that wastewaters from cleaning and decontamination of nuclear power plants contain small amounts of Fe^{2+} and Fe^{3+} coming from corrosion processes. This makes the use of photo-Fenton techniques for treatment of these wastes more suitable. It is also possible that UV light could be replaced by solar light, with a significant reduction in the costs of the process, although this will demand further investigation.

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