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Oxalic acid destruction at high concentrations by combined heterogeneous photocatalysis and photo-Fenton processes

Natalia Quici, María E. Morgada, Gabriela Piperata, Paola Babay, Raquel T. Gettar, Marta I. Litter *

Unidad de Actividad Química, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Av. Gral. Paz 1499, 1650 San Martín, Prov. de Buenos Aires, Argentina

Abstract

Heterogeneous photocatalysis (HP) using UV/TiO_2, photo-Fenton (PF) reaction using UV/Fe/H_2O_2 and the combination UV/TiO_2/Fe/H_2O_2 (HP–PF) were tested as processes to degrade oxalic acid (Ox) at relatively high concentrations (0.032 M). PF reactions were generally more efficient than HP including the reaction in the absence of H_2O_2. Oppositely to previous results (e.g., with EDTA), HP–PF combinations did not result, in the case of oxalate, better techniques for degradation than systems in the absence of TiO_2. The kinetic behavior was not unique and two parameters were taken to evaluate the efficiency of each system: initial rates (R_0) and time to 95% of total mineralization (TOC_{95}). Addition of hydrogen peroxide improves the initial HP reaction rate and reduces TOC_{95}. Addition of Fe^{3+} also affects the reaction parameters but the effect of H_2O_2 seems to be higher, at least under the present conditions. When both H_2O_2 and iron were added simultaneously, the efficiency was higher. The optimal H_2O_2:Ox:Fe molar ratio was established and the results indicated that, at a fixed iron concentration, H_2O_2 increased R_0 until a limit beyond which it did not cause any effect. No intermediates were formed in the reaction, oxalate being degraded directly to CO_2. Analogies and differences with the EDTA system are presented.

Keywords: Oxalic acid; Heterogeneous photocatalysis; Advanced oxidation technologies

1. Introduction

Advanced oxidation technologies (AOTs) are innovative methods for water treatment, extremely useful in the case of substances resistant to conventional technologies [1,2]. Oxalic acid (Ox), in its different protolytic forms, is a frequent pollutant present in domestic and industrial wastewaters owing to its wide use in formulations (detergents, textile and pharmaceutical processes, metallurgy, cleaning and decontaminating mixtures for boilers and nuclear power plants, etc.) [3]. It is considered a model compound of organic substances in natural waters, and it has been found a common intermediate in the oxidation of more complex compounds. The behavior of oxalic acid and its derivatives under ionizing radiation has been extensively studied; oxalate has been used as a $HO^\bullet$ scavenger in water radiolysis experiments [4] and it constitutes the basis of a very well known chemical dosimeter in radiochemistry [5].

Several works describe degradation of oxalic acid by AOTs, generally TiO_2-heterogeneous photocatalysis (HP); only the most recent articles will be cited here, from which earlier references can be obtained. Kosanic proposed a mechanism for the TiO_2 photocatalytic degradation of oxalic acid at acid pH and very low concentrations [3]. Bangun and Adesina [6] investigated the kinetics of the photodegradation of sodium oxalate using TiO_2 in various conditions, indicating a formal Langmuir–Hinshelwood behavior, in agreement with the results of other works [3,7–10]. Guillard et al. [11] compared the photocatalytic degradation of oxalate in the presence of TiO_2 and in the presence of iron oxides, finding that the contribution of surface or dissolved FeOx complexes was more important than that of the photocatalyst. A similar conclusion had been obtained previously by our group when comparing the efficiency of TiO_2, iron oxides and mixed Ti(IV)/Fe(III) oxides [12].

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* Corresponding author. Tel.: +54 11 6772 7016; fax: +54 11 6772 7886.
E-mail address: litter@cnea.gov.ar (M.I. Litter).

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Oxalate was also used as a model compound for photo-Fenton (PF) reactions. Photolysis of Fe(III)-oxalato complexes ends in Fe(II) formation and oxalate decomposition and constitutes the most used chemical actinometer, with a high quantum yield of Fe^{2+} formation (1.0–1.2), almost independent of the wavelength in the UV–vis range (up to 440 nm) [32]. The combination UV/H_2O_2/ferrioxalate is considered an effective AOT for degradation of certain organic compounds [13–17]. The reactions have also implications in atmospheric processes in water droplets [18–20]. Recently, oxalate has been chosen as a model compound to study photo-Fenton reactions with immobilized Fe-catalysts [21].

By these reasons, elucidation of the mechanisms and factors affecting the efficiency of oxalate degradation by AOTs allows assessing not only the aptitude of these technologies for destruction of the compound, but it can also provide details on degradation mechanisms of more complex compounds where oxalate is involved as an intermediate. Studies on oxalate have been generally performed at low concentrations, with the exception of the work performed by Kosanic and Trickovic [7]. In contrast, many industrial processes use or produce oxalic acid at relatively high concentrations, which should be destroyed before discharge to water bodies. Actually, we are interested in studying the treatment of liquid wastes coming from decontamination and cleaning processes of nuclear power plants, composed mainly by a mixture of oligocarboxylic acids such as nitrilotriacetic acid (NTA), EDTA, oxalic or citric acid and their degradation derivatives at rather high concentrations. Our first studies have been performed on EDTA, and we obtained details about the degradation of the compound submitted to HP, PF, ferrioxalate and combined technologies [17,22–29]. Similar studies have been initiated with NTA [25,30] and citric acid [31].

In this work, Ox degradation at relatively high concentrations (4 g L^{-1}, 0.032 M) and pH 3.7 using HP, PF and their combination (HP–PF), is described. Concentration and pH conditions were chosen as representative of typical values found in liquid wastes coming from cleaning and decontamination processes of nuclear power plants.

2. Experimental

2.1. Chemicals

TiO_2 (Degussa P-25) was provided by Degussa AG Germany and used as received. Oxalic acid dihydrate was Riedel-De Haën. Hydrogen peroxide (Merck) was a 30% (w/w) solution. Iron was added as Fe^{3+} in TiO_2 systems, in the form of $Fe(NH_4)(SO_4)_2\cdot 12H_2O$ (Mallinckrodt), whereas in PF systems Fe^{2+} was added as the Mohr salt, $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$ (Mallinckrodt), both at the highest available purity. All other reagents were at least of reagent grade and used without further purification.

Water was doubly distilled in a quartz apparatus. $HClO_4$ and NaOH solutions were used for pH adjustments.

2.2. Degradation experiments

Irradiation experiments were performed in a recycling system (1.5 L min^{-1} flow rate) consisting of an annular reactor (415 mm-length, 35 mm-external diameter, 85 mL total volume), a peristaltic pump and a thermostatted (298 K) cylindrical reservoir. A black-light tubular UV lamp (Philips TLD/08, 15 W, $350\ nm < \lambda < 410\ nm$, 100% maximum transmission at 366 nm) was installed inside the annular reactor as the source of illumination. Actinometric measurements were performed by the ferrioxalate method [32]. A photon flow per unit volume of 8 μEinstein $s^{-1}\ L^{-1}$ was calculated.

In all cases, 350 mL of a fresh 0.032 M oxalic acid solution were adjusted to pH 3.7 with NaOH. Air (2 L min^{-1}) was constantly bubbled in the reservoir, and pH was maintained at 3.7 all throughout the experiment by periodic addition of $HClO_4$. Solutions or suspensions in the reservoir were magnetically stirred. In HP experiments, 1.0 g dm^{-3} of Degussa P-25 was suspended in the solution. The amount of TiO_2 was the same as used in our previous experiments with EDTA [28,29]. At this pH and Ox concentration, the coverage of the TiO_2 surface is complete [7,33]. The suspension was ultrasonicated for 20 min to homogenize the system, and stirred into the reservoir for 30 min in the dark to assure the adsorption equilibrium of oxalic acid onto TiO_2. However, the amount of oxalate adsorbed on the catalyst was very low, as calculated by measuring concentrations before and after the stirring in the dark. Similar results have been observed previously [7]. In the HP–PF experiments, iron was added before TiO_2. In the experiments with H_2O_2, a volume of this reagent similar to the initial quantity was periodically added. Samples were periodically withdrawn and analyzed. Samples containing TiO_2 were filtered through 0.45 μm cellulose filters. Before analysis, 1 mL of a quenching solution was added to every sample, to interrupt the reaction. The quenching solution was composed of 0.1 M Na_3PO_4, 0.1 M KI and 0.1 M Na_2SO_3. All experiments have been performed at least by duplicate and results averaged. The experimental error was never higher than 10%. Previous results of our group [12] showed that photolysis of oxalate in the absence of TiO_2 is negligible under near UV-light, and this finding, together with the lack of oxalate adsorption, indicates clearly that transformations are due only to photocatalytic effects. Blanks in the dark (no TiO_2) with the highest amount of H_2O_2 in the absence and in the presence of iron, i.e., 0.1:1:0 and 0.1:1:0.1 H_2O_2:Ox:Fe^{3+} molar ratio yielded no oxalate degradation.

Oxalate concentration was determined by capillary electrophoresis using a SpectraPHORESIS ULTRA-Thermo separation products apparatus with a UV–vis SpectraPHORESIS UV-3000 detector. The separations were performed at 303 K in a fused silica capillary tube (40.1 cm × 75 μm i.d., 36.5 cm effective length), using 20 mM, pH 8 phosphate buffer with 0.3 mM cetylpiridinium chloride as modifier of the electroosmotic flow. The runs were performed at −10 kV, with 10 μg mL^{-1} nitrate as internal standard. The mineralization degree was followed by total organic carbon (TOC) analysis, using a Shimadzu 5000 A TOC analyzer in the non-purgeable organic carbon (NPOC) mode. It was demonstrated that oxalic acid degradation matched TOC decrease (identical time profiles), indicating that no intermediates were formed in the reaction. Thus, the extent of decomposition in most of the experiments was followed only by TOC.

3. Results

Profiles of Ox concentration (or TOC decrease) versus time after UV irradiation were obtained for all conditions. As expected, due to the experimental differences and complexity of the systems, it was not possible to establish a unique kinetic regime. Thus, two parameters were taken to compare efficiencies: initial rates (R_0) and time required for 95% mineralization (TOC_{95}, in some cases extracted from the fitting of the experimental curves). TOC_{95} is considered, in this case, a reliable parameter to represent oxalate conversions at long irradiation times, due to the limit of determination of the TOC apparatus (0.5 mg L^{-1}). Table 1 presents R_0 and TOC_{95} values obtained in all experiments, together with the total amount of H_2O_2 added to the 350 mL-volume of reactioning system.

Profiles of TiO_2 photocatalytic degradation of oxalic acid versus time are shown in Fig. 1, including results in the absence of oxidants other than oxygen and with hydrogen peroxide addition. Under our conditions, photocatalytic oxidation of oxalic acid with only TiO_2 was rather slow, lasting 540 min to reach 95% of mineralization. An almost linear decay is observed, in accordance with the Langmuirian behavior previously found by other authors and the initial concentration [3,7–10]. As expected, in the final stages, the curve loses its linearity due to oxalate depletion. Addition of H_2O_2 at two different concentrations resulted in an increase on R_0 (see Table 1), in agreement with a previous report [7]; linearity of curves is preserved. An important change in TOC_{95} was also observed, to 285 and 210 min for a 0.0125:1 H_2O_2:Ox and 0.05:1 H_2O_2:Ox molar ratio, respectively. It can be concluded that H_2O_2 addition causes a profound effect on the photocatalysis, even at the low amounts added here. This contrasts with the results obtained with EDTA, where only relatively high amounts of H_2O_2 caused important changes on TOC decrease [23]. It is important to remember that the reported ratio of reagents is the initial one, and that H_2O_2 was constantly added to sustain the reaction. It was observed that the way of addition of H_2O_2 was important, because its final amount varied significantly TOC_{95}. Therefore, only experiments performed adding H_2O_2 in a similar way (i.e., adding periodically the same volume) were comparable and are reported in this work.

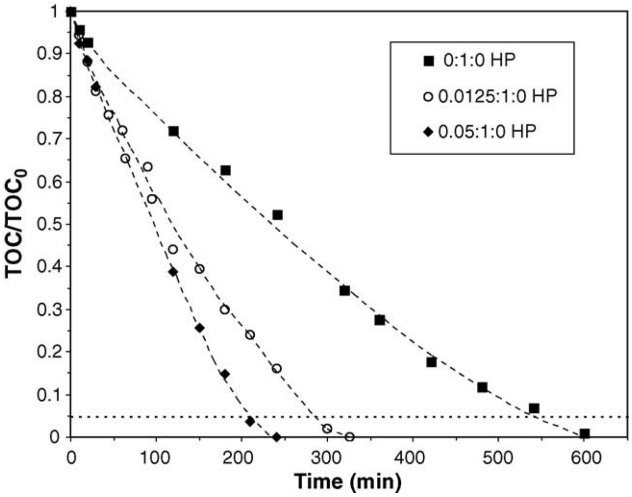

Fig. 1. Time profiles of TOC reduction for the TiO_2 photocatalytic reaction of Ox in the absence and in the presence of H_2O_2 under continuous air bubbling. Conditions: [Ox] = 0.032 M, [TiO_2] = 1 g L^{-1}, pH 3.7, T = 298 K. P_0 = 8 μEinstein s^{-1} L^{-1}. H_2O_2:Ox:Fe^{3+} molar ratio is indicated. The dotted line parallel to the x-axis represents TOC_{95}.

In Fig. 2, profiles of HP oxalic acid degradation in the presence of Fe^{3+} are presented (1:0.1 and 1:0.5 Ox:Fe^{3+} molar ratio), together with an experiment containing both oxidants, H_2O_2 and Fe^{3+} (0.05:1:0.1 H_2O_2:Ox:Fe^{3+} ratio). According to related works [35] and our own previous results with EDTA [23], higher iron concentrations are detrimental in photocatalysis and were not essayed here. Curves of Fig. 1 in the absence of oxidants and with hydrogen peroxide at the 0.05:1 H_2O_2:Ox molar ratio are shown for comparison. From the plot and from data in Table 1, it can be seen that Fe^{3+} increases the initial HP rate. Similar results were obtained by Byrne and Eggins [34], even in the absence of molecular oxygen. Also, when Fe^{3+} is added to the system, the kinetic linearity is lost and a higher kinetic order is observed. An analogous kinetic change was observed by our group in the case of EDTA

Table 1
Initial rates (R_0), time required for 95% mineralization (TOC_{95}), and total volume of added hydrogen peroxide in the experiments of oxalic acid degradation under UV light in different conditions

H_2O_2:Ox:Fe molar ratio	$R_0 \times 10^7$ (M s^{-1})	TOC_{95} (min)	Total added H_2O_2 (mL)
0:1:0 (HP)	18	540	–
0.0125:1:0 (HP)	25	285	0.4
0.05:1:0 (HP)	32	210	1.7
0:1:0.1 (HP)	30	470	–
0:1:0.5 (HP)	76	360	–
0.0125:1:0.1 (HP)	38	250	0.3
0.025:1:0.1 (HP)	50	230	0.6
0.05:1:0.1 (HP)	133	130	1.5
0.1:1:0.1 (HP)	121	260	2.5
0:1:0.1 (PF)	27	280	–
0.0125:1:0.1 (PF)	74	160	0.3
0.05:1:0.1 (PF)	101	75	1.2

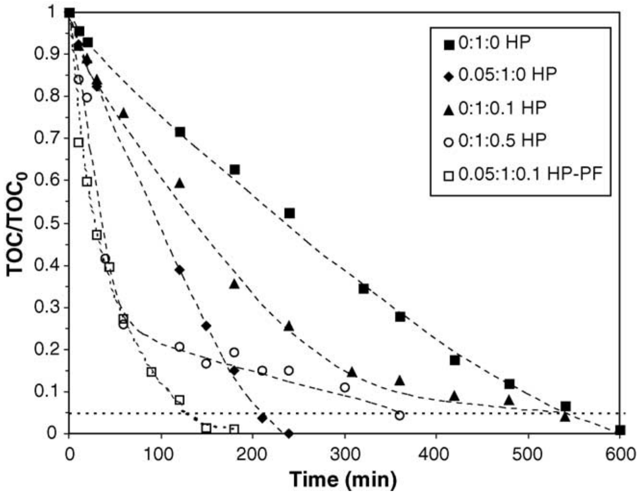

Fig. 2. Time profiles of TOC reduction for the TiO_2 photocatalytic reaction of Ox in the absence and in the presence of Fe^{3+}. Same conditions as in Fig. 1. Curves in the absence of Fe and in the presence of H_2O_2 are the same of Fig. 1. H_2O_2:Ox:Fe^{3+} molar ratio is indicated. The dotted line parallel to the *x*-axis represents TOC_{95}.

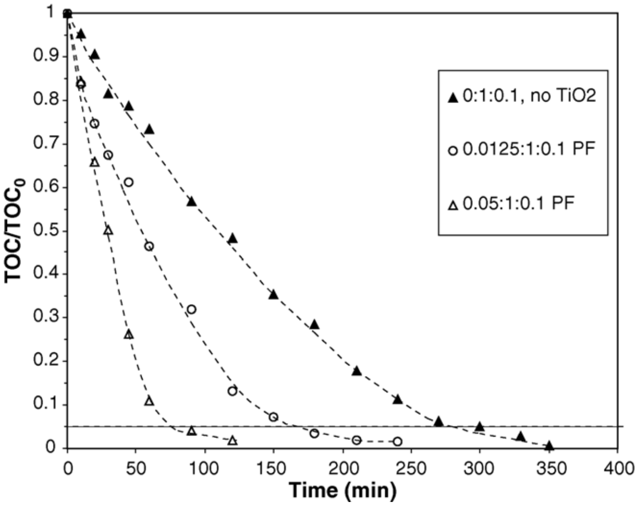

Fig. 4. Time profiles of TOC reduction for the photo-Fenton reaction of Ox (Fe^{2+}/H_2O_2). Same conditions as in Fig. 1. H_2O_2:Ox:Fe^{2+} molar ratio is indicated. The dotted line parallel to the *x*-axis represents TOC_{95}.

[22,23]. However, an important TOC_{95} reduction occurred only at the highest iron concentration. Under the conditions of this work, addition of H_2O_2 to the photocatalytic system is more efficient than iron addition to attain a high extent of TOC reduction. Simultaneous addition of both H_2O_2 and Fe^{3+} (HP–PF) gives the best results and will be analyzed in the following paragraph.

In Fig. 3, selected profiles of HP–PF systems (1:0.1 Ox:Fe^{3+} molar ratio and different initial amounts of H_2O_2) are presented. Values of R_0 and TOC_{95} are shown in Table 1 for all the experiments, from which it can be seen that H_2O_2 addition increases initial rates and reduces TOC_{95} values until the optimum 0.05:1:0.1 H_2O_2:Ox:Fe^{3+} ratio; a higher 0.1:1:0.1 H_2O_2:Ox:Fe^{3+} ratio does not give better results: although curves are very similar all through the run, the excess of H_2O_2 gives rise to a longer TOC_{95} (130 min versus 260 min).

It was very interesting to compare similar reactions in the absence of TiO_2. Fig. 4 shows the results. It is necessary to remark that in the homogeneous experiments, iron was added as Fe^{2+}, as usual in photo-Fenton systems [2]. However, an almost instantaneous oxidation of Fe^{2+} to Fe^{3+} in the highly oxidizing environment is expected [18]. It can be noticed that Ox depletion was important even in the absence of H_2O_2 and, as in the previous case, hydrogen peroxide addition increased the initial rate and decreased TOC_{95} (see Table 1). The best conditions were found again with the 0.05:1:0.1 H_2O_2:Ox:Fe ratio.

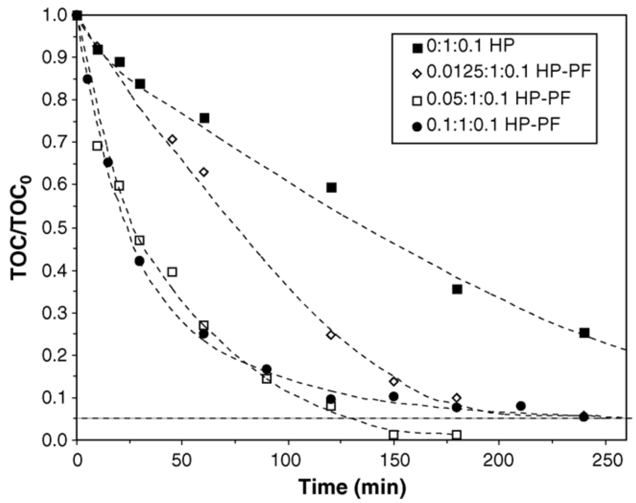

Fig. 3. Selected time profiles of TOC reduction for the TiO_2 photocatalytic reaction of Ox in the presence of Fe^{3+} and H_2O_2. Same conditions as in Fig. 1. H_2O_2:Ox:Fe^{3+} molar ratio is indicated. The dotted line parallel to the *x*-axis represents TOC_{95}.

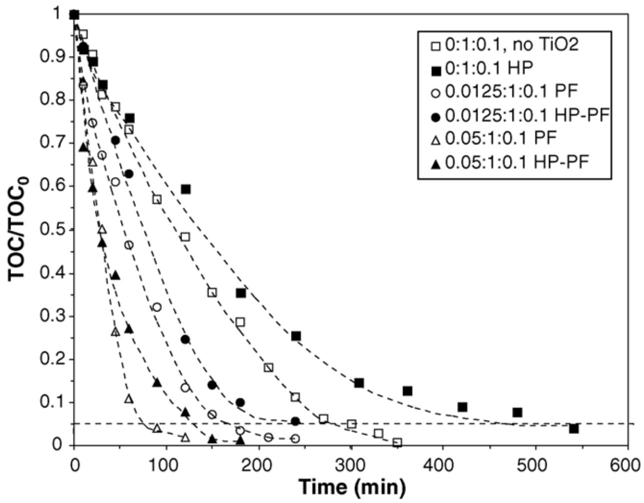

Fig. 5. Comparison of selected time profiles of TOC reduction for photo-Fenton and combined HP–PF reaction of Ox. Same conditions as in Fig. 1. H_2O_2:Ox:Fe molar ratio is indicated. The dotted line parallel to the *x*-axis represents TOC_{95}.

The comparison of results of homogeneous and heterogeneous systems with similar reagent ratios can be observed in Fig. 5. All homogeneous processes were initially faster and more efficient than the corresponding HP systems without additives, even when H_2O_2 was not added. Although a slight higher R_0 was obtained for the heterogeneous 0.05:1:0.1 H_2O_2:Ox:Fe system, TOC_{95} was shorter under homogeneous conditions. Thus, the addition of TiO_2 does not improve the performance of degradation.

4. Discussion

The very well known accepted HP mechanism [35] begins by photoproduction of electron–hole pairs after excitation of TiO_2 with light of energy higher than that of the band gap. The photoproduced electron–hole pairs migrate to the surface of the particles where they take part in redox reactions. Holes oxidize water or surface hydroxyls, whereas electrons reduce dissolved oxygen. From both reactions, strong oxidizing hydroxyl radicals are generated, which may attack in turn oxalate species. Another possibility is the direct oxidation of the organic species by holes. A simplified scheme for Ox degradation is the following:

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb} \qquad (1)$$

$$h^+_{vb} + HO^-(H_2O) \rightarrow HO^\bullet(+H^+) \qquad (2)$$

$$e^-_{cb} + O_2 \rightarrow O_2{}^{\bullet -}(HO_2{}^\bullet) \rightarrow \rightarrow H_2O_2 \rightarrow HO^\bullet \qquad (3)$$

$$h^+_{vb} + Ox \rightarrow CO_2 + H_2O \qquad (4)$$

$$HO^\bullet + Ox \rightarrow CO_2 + H_2O \qquad (5)$$

There are controversial points of view concerning the mechanism of oxalate oxidation by HP. In an early paper, Herrmann et al. proposed an attack of atomic oxygen species on the C–C bond of adsorbed $HC_2O_4{}^-$, activated by photoproduced holes [7]. Mao et al. [36] suggested a photo-Kolbe process produced by direct hole attack. Based on the experimental evidence of the low extent of oxalate adsorption on TiO_2, some authors suggested that the photocatalytic degradation occurred predominantly by $HO^\bullet$ and not by holes [3,7]. Some other authors support a process regulated by the adsorption of oxalate species on the surface [37,38]. Hug and Sulzberger [39] proposed that the reaction pathway depends on the nature of the interaction between the substrate and TiO_2, inner-sphere complexes acting as direct electron donors for holes, while physisorbed species are oxidized by $HO^\bullet$ in secondary reactions.

At the pH used in this work (3.7), oxalic acid is mainly in the $HC_2O_4{}^-$ form (77%). At this pH, the one-electron reduction potential of this species, $E^\circ_{({}^\bullet HC_2O_4/HC_2O_4^-)}$ is around 2 V versus NHE [10,12,40,41], and $HO^\bullet$ radicals coming from Eq. (2) are thermodynamically able to give rise to hydrogen abstraction. This reaction has been previously proposed to explain water radiolysis results; the monoanion was found the most reactive oxalate species [5]:

$$HC_2O_4^- + HO^\bullet \rightarrow HOOC{-}COO^\bullet + HO^- \qquad (6)$$

However, the same oxalyl radical can be obtained in HP by direct hole attack [10]:

$$HC_2O_4^- + h^+_{vb} \rightarrow HOOC{-}COO^\bullet \qquad (7)$$

The radical is decomposed to form CO_2 plus the carboxyl anion radical, ${}^\bullet CO_2{}^-$, a strong reducing agent [40]:

$$HOOC{-}COO^\bullet \rightarrow {}^\bullet CO_2^- + CO_2 + H^+ \qquad (8)$$

or, in the presence of oxygen:

$$HOOC{-}COO^\bullet + O_2 \rightarrow HO_2{}^\bullet + 2CO_2 \qquad (9)$$

$HO_2{}^\bullet$ ends in H_2O_2, which forms more $HO^\bullet$ with conduction band electrons:

$$2HO_2{}^\bullet \rightarrow H_2O_2 + O_2 \qquad (10)$$

$$H_2O_2 + e^-_{cb} \rightarrow HO^\bullet + HO^- \qquad (11)$$

Another possible route is the cleavage of the C–C bond of $HC_2O_4{}^-$ by holes or hydroxyl radicals to form directly CO_2 plus ${}^\bullet CO_2{}^-$ [40,42,43]:

$$HOOC{-}COO^- + h^+_{vb}(HO^\bullet) \rightarrow {}^\bullet CO_2^- + CO_2 + H^+(H_2O) \qquad (12)$$

Early spin trapping experiments on illuminated ZnO suspensions containing oxalate allowed to detect the ${}^\bullet CO_2{}^-$ species. Interestingly, $HO^\bullet$ could not be detected, indicating a very fast oxidation of oxalate by $HO^\bullet$ [44].

The unstable radical anion ${}^\bullet CO_2{}^-$ can be rapidly oxidized to CO_2 by dissolved molecular oxygen according to Eq. (13) or via electron injection into the conduction band, according to Eq. (14):

$${}^\bullet CO_2^- + O_2 \rightarrow CO_2 + O_2{}^{\bullet -} \qquad (13)$$

$${}^\bullet CO_2^- \rightarrow CO_2 + e^-_{cb} \qquad (14)$$

Irrespective of the operative route, only very unstable radical species are produced during the degradation, in agreement with the fact that no stable intermediates were found during the mineralization experiments, not only in the present work but also in others where oxalate was submitted to highly oxidative processes [5,7,45,46].

On the other hand, it is known that addition of H_2O_2 enhances photocatalytic reactions due to inhibition of electron-hole recombination and production of additional $HO^\bullet$ radicals through reaction with conduction band electrons or superoxide radicals, especially at high H_2O_2 concentrations [35]:

$$e^-_{cb} + H_2O_2 \rightarrow HO^\bullet + HO^- \qquad (15)$$

$$O_2{}^{\bullet -} + H_2O_2 \rightarrow O_2 + OH^- + HO^\bullet \qquad (16)$$

However, an excess of H_2O_2 can be detrimental because it is a hole scavenger and the produced hydroperoxyl radical has a less oxidizing power than $HO^\bullet$:

$$HO^\bullet + H_2O_2 \rightarrow HO_2{}^\bullet + H_2O \tag{17}$$

Turning now to reactions in the absence of TiO_2, oxalate in the presence of iron forms $Fe(C_2O_4)_3{}^{3-}$, the most important species in solution in excess of oxalate. Under irradiation, the photolytic process takes place:

$$Fe(C_2O_4)_3^{3-} + h\nu \rightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4{}^{\bullet -} \tag{18}$$

Then, a rapid decarboxylation follows, producing ${}^\bullet CO_2{}^-$ according to Eq. (8). The fate of ${}^\bullet CO_2{}^-$ depends on the competitive reactions between dissolved oxygen and ferrioxalate (Eq. (13) versus Eq. (19)):

$${}^\bullet CO_2^- + Fe(C_2O_4)_3^{3-} \rightarrow Fe^{2+} + 3C_2O_4^{2-} + CO_2 \tag{19}$$

Rates of reactions (13) and (19) are very similar [47] but, under our conditions, $[Fe(C_2O_4)_3{}^{3-}]$ is at least 3.2 mM at the beginning, a higher concentration than the saturation value of O_2 in water. Therefore, ${}^\bullet CO_2{}^-$ reacts mainly with $Fe(C_2O_4)_3{}^{3-}$, increasing Fe(II) concentration. Further reoxidation of Fe(II) is possible by several routes, giving rise to a continuous cycle. Superoxide radical (or its conjugate acid) has three reaction pathways, depending on the iron oxidation state or the H_2O_2 concentration and pH:

$$HO_2{}^\bullet(\text{or } O_2{}^{\bullet -}) + Fe^{2+} + H^+(2H^+) \rightarrow Fe^{3+} + H_2O_2 \tag{20}$$

$$HO_2{}^\bullet(\text{or } O_2{}^{\bullet -}) + Fe(C_2O_4)_3^{3-} \rightarrow Fe^{2+} + 3C_2O_4^{2-} + O_2 + H^+ \tag{21}$$

$$HO_2{}^\bullet(\text{or } O_2{}^{\bullet -}) + Fe^{3+} \rightarrow Fe^{2+} + O_2 + H^+ \tag{22}$$

$HO_2{}^\bullet$ can produce H_2O_2 and O_2 by disproportion (reaction (10)).

According to the above equations, photolysis of Fe(III)-oxalato complexes forms H_2O_2, process used to explain certain atmospheric phenomena in water cloud droplets [18–20]. Consequently, the Fenton reaction takes place: H_2O_2 decomposition catalyzed by the metal ion generates a hydroxyl radical ($HO^\bullet$) [2,48–52]:

$$Fe^{2+} + H_2O_2(h\nu) \rightarrow Fe^{3+} + OH^- + HO^\bullet \tag{23}$$

Fe^{3+} (added or generated from Fe^{2+}) gives rise to the radical chain mechanism described above, and the Fenton reaction (23) is enhanced by the participation of photogenerated Fe^{2+}. Therefore, the photochemical reduction of the Fe(III)-complex will be coupled to a Fenton reaction [13,18], with the production of oxidative species such as superoxide, hydroperoxyl and $HO^\bullet$ radicals, the process becoming more important if H_2O_2 is externally added, because reaction (21) is operative at high H_2O_2 concentrations [2,53]. Indeed, as we found here, oxalate can be excellently degraded by UV irradiation in the presence of iron alone and no other oxidants (see Fig. 4).

Concurrently, addition of Fe^{3+} to HP systems affects sensibly photocatalytic rates, acting as an electron scavenger that inhibits recombination of electron and holes and participates in many processes as those described above [35]. Byrne and Eggins [45] demonstrated that Fe^{3+} may effectively replace oxygen as electron acceptor in the photoelectrocatalytic oxidation of oxalic acid, due to the positive value of the Fe^{3+}/Fe^{2+} couple and a faster reduction by e_{cb}^-. It is important to point out that Fe(III)-oxalato complexes formed by addition of Fe(III) to the oxalate system can be also photocatalyzed, according to the following global reaction, which shows the whole species suffering simultaneously the different redox processes involved in photocatalysis:

$$Fe(C_2O_4)_3^{3-} + h\nu + TiO_2 \rightarrow Fe(II) + CO_2 \tag{24}$$

This has been used to explain the small but detectable degradation of oxalic acid under visible irradiation, which does not occur on bare titania but does take place with Fe-doped TiO_2 photocatalysts [54].

Besides the heterogeneous photocatalytic reaction, homogeneous photolysis of Fe(III)-oxalate and photo-Fenton reactions are simultaneously operative in the heterogeneous system, according to the routes shown above. This constitutes, then, a combined HP–PF technology, and we are in the presence of a very complex system in which several processes occur at the same time contributing to the overall rate. Concurrent homogeneous processes, occurring with different kinetic regimes, complicate heterogeneous reactions, both type of processes being inherently complex. This reinforces the election of initial rates (R_0) to compare the system under different experimental conditions, because this approach allows assessing the performance in the first stages, independently of processes at longer times, which could change and affect the kinetics. Furthermore, from the experimental point of view, this value permits to consider the initial amount of H_2O_2 as a reliable variable, taking into account that its concentration was constantly modified throughout the irradiation by periodic external addition.

4.1. Comparison with the EDTA system

For EDTA, it was possible to differentiate two alternative treatments: (a) homogeneous photo-Fenton process, with high hydrogen peroxide concentrations leading to a high degradation efficiency; (b) TiO_2 heterogeneous photocatalysis with Fe^{3+} with a minimal H_2O_2 addition, rendering a lower but still effective degradation. This latter method is cheaper and safer from the industrial point of view, especially to be used in controlled zones of nuclear power plants [29]. This is not the case of oxalate.

Major analogies of both EDTA and Ox systems refer to the fact that they can be efficiently degraded by HP, PF and combined processes. Degradation is notably accelerated by addition of H_2O_2 and Fe^{3+}/Fe^{2+} at different molar ratios with respect to the organic substrate. However, in the case of EDTA, although degradation of the compound itself is rather fast, mineralization is difficult, due to the formation of resistant intermediates [22,23]. TOC removal could be improved by the addition of oxidants like Fe(III) or H_2O_2. Oxalic acid, a simpler compound, does not give rise to intermediates alongside its degradation, TOC reduction paralleling the decrease of Ox concentration. One important difference between EDTA and oxalate comes from the different quantum yield of the photolysis of the respective Fe(III)-complexes, more than one order of magnitude lower for Fe-EDTA [17]. In this case, degradation promoted by HP is important, the homogeneous process contributing only to a lesser extent. In contrast, in the oxalate system, TiO_2 would act as a screen or optical filter, reducing the efficiency of FeOx photolysis. This is evident when data of Fig. 5 and Table 1 are compared for the 0:1:0.1 systems with and without TiO_2: R_0 are rather similar but TOC_{95} is very much lower in the absence of the photocatalyst. Thus, HP plays a minor role compared with that played by FeOx photolysis and homogeneous reactions. Guillard et al. [11] arrived to the same conclusion working on the photocatalytic oxalate degradation over iron oxides. This behavior contrasts to that found for EDTA, where photo-Fenton and photocatalysis yielded similar results regarding mineralization [28,29].

5. Conclusions

The studies indicate that it is possible to degrade oxalic acid under the present conditions of high concentrations either by HP or PF systems with good conversions in short irradiation times. Addition of hydrogen peroxide and iron to the HP system improves the reaction, but H_2O_2 seems to be a better oxidant. The experiments showed that PF is more efficient than HP–PF, due to the extreme importance of the homogeneous photolysis.

Further studies are underway with NTA and citrate. The final aim of this work is to treat a mixture of oligocarboxylic acids at relatively high concentrations in the presence of iron to evaluate the efficiency of AOTs for destruction of the whole content of organic matter before discharge of the wastes, especially for nuclear applications.

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