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Degradation of the herbicide 2,4-DP by catalyzed ozonation using the O₃/Fe²⁺/UVA system

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Abstract

Acid solutions of the herbicide 2-(2,4-dichlorophenoxy)propionic acid (2,4-DP) of pH 3.0 at 25.0 °C have been treated with ozone and ozonation catalyzed with Fe^{2+}, Cu^{2+} and/or UVA light. This herbicide is slowly degraded by ozonation alone, while its destruction is enhanced under UVA irradiation. In the presence of Fe^{2+}, the initial mineralization rate is accelerated due to the generation of oxidizing hydroxyl radical ($OH^{\bullet}$), but a large proportion of stable products are formed. These species are partially removed when Fe^{2+} and UVA light are combined, since greater amounts of $OH^{\bullet}$ are produced and Fe^{3+} complexes are photodecomposed. Addition of Cu^{2+} to this system does not significantly improve its oxidizing ability, since the Cu^{2+}/Cu^{+} pair gives a low additional $OH^{\bullet}$ concentration. The herbicide decay always follows a pseudo first-order reaction. 2,4-Dichlorophenol, chlorohydroquinone and chloro-*p*-benzoquinone are detected as aromatic intermediates by reversed-phase chromatography. The initial chlorine is always transformed into chloride ion. Ion-exclusion chromatography allows the quantification of generated carboxylic acids such as lactic, pyruvic, maleic, fumaric, oxalic and acetic. These acids are completely removed, except the two latter ones. Acetic acid remains stable in all cases. Oxalic acid is stable in the O_3 system, being partially mineralized to CO_2 by the O_3/UVA one. It also yields stable Fe^{3+}-oxalato complexes in the O_3/Fe^{2+} system, which are rapidly photodecarboxylated in the O_3/Fe^{2+}/UVA and O_3/Fe^{2+} + Cu^{2+}/UVA methods. Cu^{2+}-oxalato complexes also formed in the latter procedure are slowly mineralized with $OH^{\bullet}$. A possible reaction sequence for 2,4-DP degradation involving all intermediates detected is proposed.
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1. Introduction

Chlorophenoxy herbicides such as chlorophenoxyacetic and chlorophenoxypropionic acids are used worldwide on a large scale as plant growth regulators for agricultural and non-agricultural purposes. Among these compounds, 2-(2,4-dichlorophenoxy)propionic acid (2,4-DP or dichlorprop) is a selective pre- and post-emergence herbicide widely utilized for control of broad-leaved aquatic weeds, annual and perennial weeds in cereals, pastures, forestry and rights-of-way. Chlorophenoxy herbicides have potential toxicity towards humans and animals [1] and are consid-

ered as moderately toxic (class II or class III) by the World Health Organization. Because of their intensive use and poor biodegradability, they have been detected as major pollutants in ground and surface waters [2,3]. In the last few years, research efforts have been underway to develop powerful oxidation methods for achieving an efficient degradation of such herbicides in aqueous medium to try to avoid its dangerous accumulation in the aquatic environment.

Ozone is a chemical agent widely used for the mineralization (i.e. transformation into CO_2 and inorganic ions) of herbicides and related biorecalcitrant organic contaminants in waters [4–10]. A disadvantage of ozonation alone (O_3 system) for water treatment is the high energy cost required for its generation. Alternative procedures involving ozonation catalyzed with H_2O_2 [10–12], UV light [10,13–19],

Fe^{2+} [16–21] and TiO_2 [16,22–26] allow a quicker removal of organic pollutants, because such catalysts improve the oxidizing power of O_3 yielding a significant reduction of its economic cost. Most papers related to the ozonation of chlorophenoxyacetic acids are devoted to the degradation of 2,4-dichlorophenoxyacetic acid in aqueous medium, which can be efficiently mineralized by systems such as O_3 [4,7–10,16,19], O_3/UV [13,16,19], O_3/Fe^{2+} [16,19], O_3/H_2O_2 [12], O_3/TiO_2/UV [16] and O_3/Fe^{2+}/UV [16,19]. However, less is known about the degradative behavior of chlorophenoxypropionic acids, for which a poor destruction of 2,4-DP by the O_3 and O_3/H_2O_2 systems has only been reported [5,6,8].

When acid waters are treated with the O_3 system, molecular ozone attacks selectively its organic contaminants, especially aromatics, following second-order reactions with small rate constants [7,8,10,11]. The higher degradative ability of the different catalyzed ozonations can be related to the parallel production of other strong oxidizing agents that increase the destruction rate of organics. Thus, irradiation of the solution with UV light at $\lambda = 254$ nm induces the photolysis of ozone to H_2O_2 [10]:
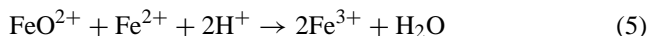
$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2 \tag{1}$$
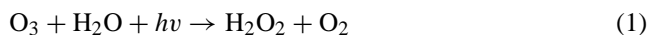
Reaction (1) also takes place when UVA light with $\lambda > 300$ nm is used (O_3/UVA system), because of the absorption of the small proportion of photons between 300 and 320 nm by ozone [18]. In alkaline medium, H_2O_2 thus formed attacks to O_3 to generate hydroxyl ($OH^\bullet$) and hydroperoxyl radicals ($HO_2^\bullet$) [10]:

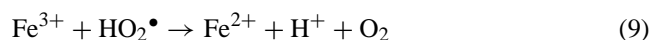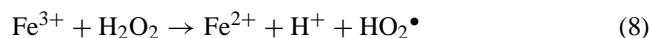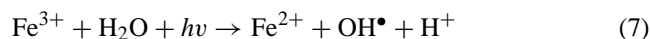$$O_3 + H_2O_2 \rightarrow OH^\bullet + HO_2^\bullet + O_2 \tag{2}$$
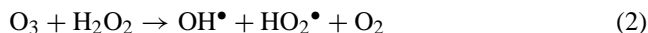
$OH^\bullet$ acts as a stronger, non-selective oxidizing agent, since it can react more quickly with organics yielding dehydrogenated or hydroxylated derivatives, until their total mineralization is reached. $HO_2^\bullet$ is a weaker oxidant than $OH^\bullet$. However, reaction (2) does not occur in the acid medium, where parallel oxidation of organics with H_2O_2 and/or their photodecomposition by light absorption favor their degradation process [18].

Addition of Fe^{2+} as catalyst (O_3/Fe^{2+} system) in the acid medium causes the formation of FeO^{2+} from ozone decomposition by reaction (3) [21]. This species can further evolve to $OH^\bullet$ by reaction (4) or can oxidize Fe^{2+} to Fe^{3+} at slower rate from reaction (5), then limiting the generation of hydroxyl radical for high Fe^{2+} concentration [16].

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \tag{3}$$

$$FeO^{2+} + H_2O \rightarrow Fe^{3+} + OH^\bullet + OH^- \tag{4}$$

$$FeO^{2+} + Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + H_2O \tag{5}$$

In previous work [16,19], we have found that acidic 2,4-D solutions can be completely mineralized at pH 3.0 by the O_3/UV system, although they are much more rapidly depolluted when ozonation is simultaneously catalyzed with Fe^{2+}

and UVA light (O_3/Fe^{2+}/UVA system). This behavior can be accounted for different parallel pathways involving: (i) photolysis of complexes of Fe^{3+} with generated carboxylic acids such as oxalic acid [27], which cannot be oxidized by $OH^\bullet$ using the O_3/Fe^{2+} system; and (ii) production of more $OH^\bullet$ either by additional oxidation of Fe^{2+} with H_2O_2 formed from reaction (1) via the classical Fenton's reaction (6) [28,29] or by photoreduction of the resulting Fe^{3+} to Fe^{2+} from reaction (7) [30]. In addition, Fe^{2+} can also be regenerated from the reduction of Fe^{3+} with H_2O_2 by reaction (8) and with $HO_2^\bullet$ by reaction (9) [28]. The existence of reactions (7)–(9) ensures the catalytic loop of the Fe^{3+}/Fe^{2+} pair, allowing the presence of sufficient Fe^{2+} concentration to propagate reactions (3), (4) and (6) leading to larger amounts of oxidizing $OH^\bullet$ for an efficient destruction of organics.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^- \tag{6}$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + OH^\bullet + H^+ \tag{7}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^\bullet \tag{8}$$

$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + H^+ + O_2 \tag{9}$$

On the other hand, other catalyzed ozonation methods involving redox pairs able of generating $OH^\bullet$ from like-Fenton's reactions have not been applied to water remediation. From literature data, it seems feasible to combine ozone with UVA light and Cu^{2+} in the presence of Fe^{2+}. In such O_3/Fe^{2+} + Cu^{2+}/UVA system, more $OH^\bullet$ could be produced by the Cu^{2+}/Cu^+ pair, since Cu^{2+} can be rapidly reduced with $HO_2^\bullet$ formed from reaction (8) to give Cu^+ via reaction (10), while Cu^+ can be further oxidized with H_2O_2 generated by reaction (1) to Cu^{2+} and $OH^\bullet$ via like-Fenton's reaction (11) [31,32]. The formation of complexes between Cu^{2+} and some products (diols, carboxylic acids, ...) could affect the degradation rate of solutions treated by such method. Recently, Gallard et al. [31] showed an enhancement of the oxidation rate of a 1 μM atrazine solution of pH 3 using H_2O_2/Fe^{3+} combined with Cu^{2+}, due to the fast production of a higher concentration of $OH^\bullet$ by the participation of reactions (10) and (11):

$$Cu^{2+} + HO_2^\bullet \rightarrow Cu^+ + H^+ + O_2 \tag{10}$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + OH^\bullet + OH^- \tag{11}$$
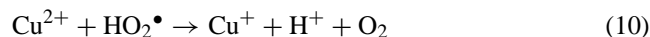
This paper reports a detailed study on the degradative behavior of 2,4-DP in the acid medium by ozone and ozonation catalyzed with Fe^{2+}, Cu^{2+} and/or UVA light. The comparative oxidizing power of the O_3, O_3/UVA, O_3/Fe^{2+} and O_3/Fe^{2+}/UVA systems has been established using a solution with an herbicide concentration equivalent to 100 mg l^{-1} of total organic carbon (TOC), at pH 3.0 and at 25.0 °C. The same solution has been degraded by the O_3/H_2O_2/UVA system to know the effect of generated H_2O_2, as well as by the O_3/Cu^{2+}/UVA and O_3/Fe^{2+} + Cu^{2+}/UVA ones to clarify the effect of the Cu^{2+}/Cu^+ pair as catalyst for ozonation. The influence of Fe^{2+} and/or Cu^{2+} concentrations on

such processes has been considered. 2,4-DP solutions up to near saturation (about 350 mg l^{-1} at 25 °C) have been treated with the O$_3$/Fe^{2+}/UVA system to test its degradation efficiency. The decay kinetics of the herbicide in each process and the evolution of its aromatic products and generated carboxylic acids have been followed by chromatographic techniques. From all intermediates detected, a general pathway for 2,4-DP degradation is proposed.

2. Experimental

2.1. Chemicals

2,4-DP, 2,4-dichlorophenol, chlorohydroquinone, chloro-*p*-benzoquinone, lactic acid, pyruvic acid, glacial acetic acid, maleic acid, fumaric acid and oxalic acid were either reagent or analytical grade purchased from Aldrich, Fluka, Sigma and Panreac. Heptahydrated ferrous sulfate and pentahydrated cupric sulfate, both used as catalyst, were analytical grade supplied by Fluka. Organic solvents and the other chemicals employed were either HPLC or analytical grade purchased from Merck, Fluka and Aldrich. All solutions were prepared with pure water obtained from a Millipore Milli-Q system, with conductivity $<6\times10^{-8}$ S cm^{-1} at 25 °C. Samples with H$_2$O$_2$ were prepared by adding the corresponding aliquot of an analytical grade hydrogen peroxide solution of 30% (w/w) from Merck. Before treatment, each herbicide solution was adjusted to pH 3.0 with 0.25 M H$_2$SO$_4$, previously prepared with analytical grade sulfuric acid supplied by Merck.

2.2. Instruments and analysis procedures

Ozone was generated with an Erwin Sander 300.5 ozonizer fed with pure O$_2$ at 1.1 bar and at a flow rate of 60 l h^{-1}. The solution pH was measured with a Crison 2000 pH-meter. Before analysis, all the samples extracted from degraded solutions were filtered with 0.45 μm PTFE filters from Whatman. The herbicide degradation was monitored by the removal of the total organic carbon of each solution, determined on a Shimadzu 5050 TOC analyzer using the standard non-purgeable organic carbon (NPOC) method. This procedure gave reproducible values for TOC removal under all experimental conditions. The decay of 2,4-DP and the evolution of their aromatic products were followed by reversed-phase chromatography, using a Waters system composed of a Waters 600 HPLC liquid chromatograph fitted with a Spherisorb ODS2 5 μm column (150 mm × 4.6 mm, i.d.) at room temperature, along with a Waters 996 photodiode array detector selected at λ = 280 nm, controlled through a Millennium-32® program. Reversed-phase chromatograms were recorded after injecting 20 μl aliquots into the HPLC chromatograph and circulating a 50:47:3 (v/v/v) methanol/phosphate buffer (pH 2.5)/pentanol mixture as mobile phase at 1.0 ml min^{-1}. Generated carboxylic acids were analyzed by ion-exclusion chromatography, using the above HPLC chromatograph fitted with a Bio-Rad Aminex HPX 87H column (300 mm × 7.8 mm, i.d.) at 35 °C and coupled with the photodiode array detector selected at λ = 210 nm. In this technique, 20 μl aliquots were also injected into the chromatograph and a 4 mM H$_2$SO$_4$ solution was used as mobile phase at 0.6 ml min^{-1}. The chloride ion concentration accumulated in treated solutions was determined by standard potentiometric titration with AgNO$_3$, with a detection limit of 5 mg l^{-1} for Cl^{-}.

2.3. Ozonation system

All experiments were carried out in an open, thermostated cylindrical Pyrex cell containing 100 ml of herbicide solution under stirring with a magnetic bar. The O$_2$ + O$_3$ mixture generated by the ozonizer was supplied to the solution through a stainless steel diffuser and its flow rate was usually regulated to 20 l h^{-1}, yielding a constant production of 1.25 g O$_3$ h^{-1}, as determined by standard iodometry. For the experiments performed with UVA light as catalyst, the solution was irradiated with a 6 W Philips fluorescent black light blue tube emitting in the wavelength range 300–420 nm, with λ_{max} = 360 nm. This tube was placed at the top of the open
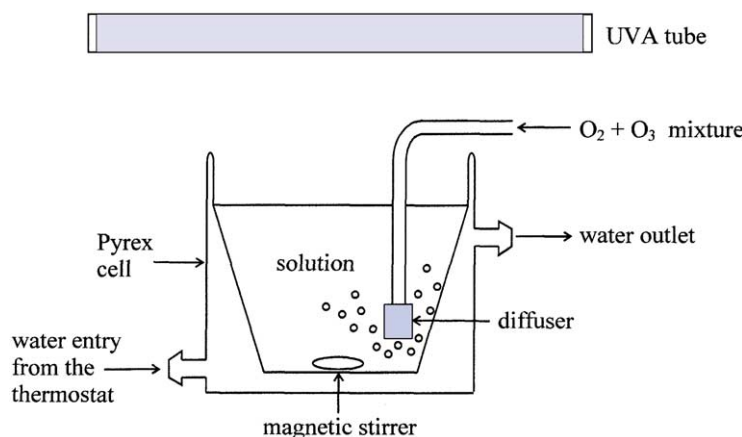

Fig. 1. Scheme of the reactor cell coupled to the UVA fluorescent tube.

cell at 4 cm over the sample, yielding a flux of incident photons by unit reactor volume of 8.3×10^{-7} Einstein l^{-1} min^{-1}, as detected with a uranyl actinometer active to photons between 250 and 500 nm. A scheme of the experimental set-up used is shown in Fig. 1.

A solution with 217 mg l^{-1} of 2,4-DP (equivalent to 100 mg l^{-1} of TOC) of initial pH 3.0 was comparatively degraded by the O_3, O_3/Fe^{2+}, O_3/UVA, $O_3/Cu^{2+}/UVA$, $O_3/H_2O_2/UVA$, $O_3/Fe^{2+}/UVA$ and $O_3/Fe^{2+} + Cu^{2+}/UVA$ systems. In such experiments, the temperature was maintained at $25.0 \pm 0.1\,^{\circ}C$, while Fe^{2+} and/or Cu^{2+} concentrations up to 2 and 1 mM, respectively, were added to the samples as catalyst before treatment. The 2,4-DP solution treated by the $O_3/H_2O_2/UVA$ method contained 16 mM H_2O_2, which corresponds to the stoichiometric concentration of this oxidant needed for the total mineralization of herbicide. The degradation efficiency of the $O_3/Fe^{2+}/UVA$ system was tested for solutions with herbicide concentration between 336 (close to saturation) and 78 mg l^{-1}. The possible influence of ozone flow rate between 0.4 and 1.5 g O_3 h^{-1} and solution temperature between 25.0 and 45.0 $^{\circ}C$ on the oxidizing power of this system was also studied.

3. Results and discussion

3.1. Comparative TOC removal

The oxidizing power of the different ozonation methods was clarified from the degradation of 100 ml of a 217 mg l^{-1} 2,4-DP solution of pH 3.0 at 25.0 $^{\circ}C$ by flowing 1.25 g O_3 h^{-1} during 2 h as maximum. For the treatments carried out with Fe^{2+} and/or Cu^{2+}, a 1 mM concentration of each catalyst was added to the above solution, while a solution with 16 mM H_2O_2 was tested for the $O_3/H_2O_2/UVA$ method. In these experiments, the pH of all solutions decreased slowly up to reach a final value between 2.7 and 2.9. Fig. 2 shows the comparative TOC abatement found under these conditions for the O_3, O_3/UVA, $O_3/H_2O_2/UVA$, $O_3/Cu^{2+}/UVA$, O_3/Fe^{2+}, $O_3/Fe^{2+}/UVA$ and $O_3/Fe^{2+} + Cu^{2+}/UVA$ systems. From these data, an initial mineralization rate of 123 mg TOC l^{-1} h^{-1} (curve (a)), 160 mg TOC l^{-1} h^{-1} (curve (c)), 180 mg TOC l^{-1} h^{-1} (curve (e)), 189 mg TOC l^{-1} h^{-1} (curve (d)), 588 mg TOC l^{-1} h^{-1} (curve (b)), 687 mg TOC l^{-1} h^{-1} (curve (f)) and 674 mg TOC l^{-1} h^{-1} (curve (g)), respectively, was determined. These results indicate an acceleration of the oxidizing ability of the O_3 system at the beginning of the process under irradiation with UVA light, as expected if a significant proportion of 2,4-DP and its oxidation products are more quickly destroyed by H_2O_2 produced from reaction (1) and/or by photolysis than by ozone. Since similar initial TOC decays are found for the O_3/UVA, $O_3/H_2O_2/UVA$ and $O_3/Cu^{2+}/UVA$ systems, one can establish that OH$^{\bullet}$ is not produced in such methods, that is, ozone does not react with H_2O_2 at pH 3.0 via reaction (2) and Cu^+ is not formed by
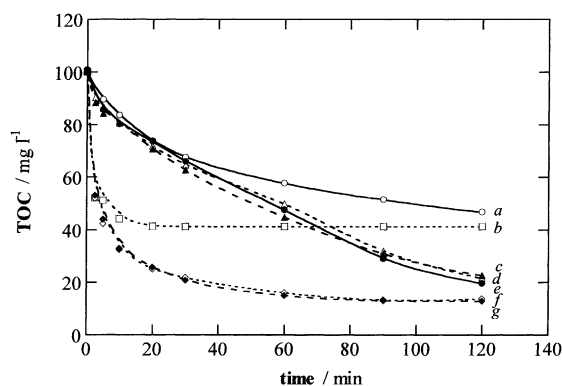

Fig. 2. TOC abatement with time for the degradation of 100 ml of a 217 mg l^{-1} 2,4-DP solution of pH 3.0 using the following conditions: (a, ○) O_3; (b, □) $O_3 + 1$ mM Fe^{2+}; (c, △) $O_3 + UVA$; (d, ▲) $O_3 + 1$ mM $Cu^{2+} + UVA$; (e, ●) $O_3 + 16$ mM $H_2O_2 + UVA$; (f, ◇) $O_3 + 1$ mM $Fe^{2+} + UVA$; (g, ◆) $O_3 + 1$ mM $Fe^{2+} + 1$ mM $Cu^{2+} + UVA$. Ozone flow rate: 1.25 g h^{-1}; temperature: 25.0 $^{\circ}C$.

reduction of Cu^{2+} from reaction (10). In contrast, the initial mineralization rate is strongly enhanced for the O_3/Fe^{2+} treatment, indicating the existence of an efficient production of the stronger oxidant OH$^{\bullet}$ from reaction (4). The positive effect of the Fe^{3+}/Fe^{2+} pair is more clear for the O_3/Fe^{2+} UVA system, which yields a much higher initial TOC decay due to the generation of large amounts of oxidizing OH$^{\bullet}$ by the simultaneous action of reactions (4), (6) and (7). The fact that the initial mineralization rate of this system is quite similar to that of $O_3/Fe^{2+} + Cu^{2+}/UVA$ evidences a poor contribution of the Cu^{2+}/Cu^+ pair to OH$^{\bullet}$ production from reaction (11).

The relative oxidizing power of the above methods changes with increasing degradation time. Curve (a) of Fig. 2 shows that ozonation alone is the slowest process, leading to a progressive depollution up to attain 54% of TOC removal at 2 h. For the O_3/UVA system (see curve (c) of Fig. 2), organics are more quickly degraded by reaction with H_2O_2 formed from reaction (1) and/or by photolysis, and the solution TOC is finally reduced by 78%. Similar mineralization rates can be observed in curves (d) and (e) of Fig. 2 for the $O_3/Cu^{2+}/UVA$ and $O_3/H_2O_2/UVA$ treatments, respectively, also yielding about 80% of TOC abatement at 2 h. This corroborates that in both cases, pollutants are mineralized by the same oxidizing agents as in the O_3/UVA one and that the degradative process is not accelerated by photodecomposition of possible complexes between Cu^{2+} and intermediates, which seems to be stable under UVA illumination. A very different behavior is found in the presence of Fe^{2+}. As can be seen in curve (b) of Fig. 2, the solution is rapidly degraded at the first oxidation stages of the O_3/Fe^{2+} system up to reach 58% of mineralization at 30 min, while at longer times, its TOC does not vary because of the formation of difficulty oxidizable products. The process becomes much more efficient using the $O_3/Fe^{2+}/UVA$ system, where 84–86% of TOC removal is achieved from 1 h (see curve (f) of Fig. 2). The $O_3/Fe^{2+} + Cu^{2+}/UVA$ system

gives a similar mineralization rate and the same final TOC reduction of 87% (see curve (g) of Fig. 2). The behavior of the two latter methods can be ascribed to the fast photodecomposition of Fe^{3+} complexes, probably formed with generated carboxylic acids [19,27], and the enhancement of the generation rate of oxidizing $OH^\bullet$ mainly by reactions (4), (6) and (7). The production of $OH^\bullet$ by reaction (11) due to the presence of the Cu^{2+}/Cu^+ pair is less significant. However, about 13% of initial TOC remain in solution at the end of both treatments, suggesting the formation of very stable species under the action of UVA light and $OH^\bullet$.

The above considerations allow us to conclude that 2,4-DP cannot be totally mineralized from catalyzed ozonation, even by the $O_3/Fe^{2+}/UVA$ and $O_3/Fe^{2+} + Cu^{2+}/UVA$ methods having the best oxidizing powers, since they only yield 87% of depollution as maximum. This is feasible by the very positive action of the Fe^{3+}/Fe^{2+} pair that generates large amounts of $OH^\bullet$ favoring a faster oxidation of organics, along with the quick photodecomposition of Fe^{3+} complexes formed. The similar catalytic effect of the Cu^{2+}/Cu^+ pair is much poorer, while Cu^{2+} complexes are not photolyzed by UVA light.

3.2. Effect of experimental parameters

Several experiments were performed to find the best operative conditions for the $O_3/Fe^{2+}/UVA$ method. To do this, the influence of ozone flow rate and temperature on the degradation of a 217 mg l^{-1} herbicide solution with 1 mM Fe^{2+} of pH 3.0 was studied. All TOC versus time plots determined for such solution at 25.0 °C by flowing ozone between 0.8 and 1.5 g O_3 h^{-1} were practically equal to that depicted in curve (f) of Fig. 2 for 1.25 g O_3 h^{-1}. For such high flow rates, the process in the small and well stirred reactor cell used does not seem limited by the mass transfer of O_3 from gas to solution phase, and similar concentrations of other oxidizing agents such as H_2O_2 and $OH^\bullet$ are always produced, thus leading to a similar decay of organics. When the flow decreased from 0.8 to 0.4 g O_3 h^{-1}, a gradual drop in initial mineralization rate was observed, which can be ascribed to an increasing control of process by O_3 mass. However, after 2 h of such treatments, 86% of mineralization was always achieved, i.e. the same value as found for 1.25 g O_3 h^{-1} in curve (f) of Fig. 2. Similar TOC abatements were also obtained by treating the above solution at 25.0, 35.0 and 45.0 °C with an ozone flow of 1.25 g O_3 h^{-1}, as expected if in such temperature range, organics react with similar relative concentrations of all oxidizing agents. The best operative conditions for mineralization by using the $O_3/Fe^{2+}/UVA$ system can then be reached with ozone flow rates between 0.8 and 1.5 g O_3 h^{-1} at 25.0 °C.

A more significant effect on the degradative behavior of the above treatment was found by varying the Fe^{2+} concentration added to the herbicide solution at ozone flow rate of 1.25 g h^{-1} and at 25.0 °C. Fig. 3 shows a strong enhancement of its mineralization rate from 0.5 to 1 mM Fe^{2+}, while
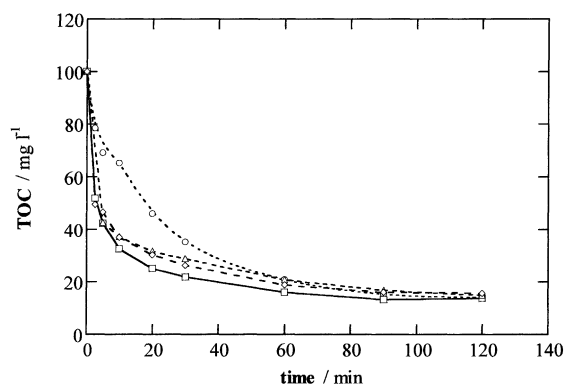
Fig. 3. Effect of Fe^{2+} catalyst on TOC removal during the treatment of 100 ml of a 217 mg l^{-1} 2,4-DP solution of pH 3.0 by the $O_3/Fe^{2+}/UVA$ system. Fe^{2+} concentration: (○) 0.5 mM; (□) 1.0 mM; (△) 1.5 mM; (◇) 2.0 mM. Ozone flow rate: 1.25 g h^{-1}; temperature: 25.0 °C.

the presence of more catalyst up to 2 mM causes a slight decrease in its TOC removal. This trend indicates that the maximum production of $OH^\bullet$ from reactions (4) and (6) is reached with an optimum Fe^{2+} concentration of 1 mM, yielding the highest efficiency for the $O_3/Fe^{2+}/UVA$ method. The slight loss of oxidizing ability at higher Fe^{2+} contents could then be related to the increase in rate of reaction (5) causing a decrease in FeO^{2+} concentration with the subsequent generation of less $OH^\bullet$ from reaction (4). Some degradations were also made for the same 2,4-DP solution with 1 mM Fe^{2+} and a Cu^{2+} concentration between 0.25 and 1 mM using the $O_3/Fe^{2+} + Cu^{2+}/UVA$ system. In all cases, a similar TOC abatement to that shown in curve (g) of Fig. 2 was found, in agreement with the poor catalytic effect of the Cu^{2+}/Cu^+ pair in this system.

To gain a better knowledge of the oxidizing ability of the $O_3/Fe^{2+}/UVA$ treatment, solutions containing a herbicide concentration between 336 and 78 mg l^{-1} with 1 mM Fe^{2+} were comparatively degraded at 25.0 °C. The fast TOC removal obtained in such trials can be seen in Fig. 4. The
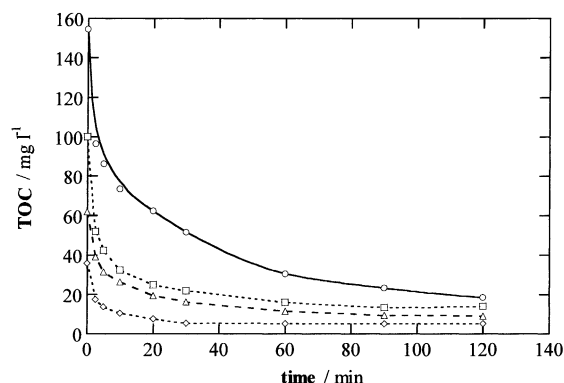
Fig. 4. TOC decay with time for the degradation of 100 ml of different 2,4-DP solutions of pH 3.0 by the $O_3/Fe^{2+}/UVA$ system. Herbicide concentration: (○) 336 mg l^{-1} (close to saturation); (□) 217 mg l^{-1}; (△) 135 mg l^{-1}; (◇) 78 mg l^{-1}. Ozone flow rate: 1.25 g h^{-1}; temperature: 25.0 °C.

initial mineralization rate is found to be of 818, 687, 368 and 267 mg TOC l^{-1} h^{-1} for 336, 217, 135 and 78 mg l^{-1} of herbicide, respectively. The quick fall of initial TOC decay with decreasing 2,4-DP concentration can be simply related to the existence of smaller amounts of degradable organics in the medium. However, all herbicide solutions attain similar final depollution, since after 1 h of treatment their TOC can only be reduced by 86–88%. These results confirm that the $O_3/Fe^{2+}/UVA$ system is unable to destroy completely 2,4-DP due to the formation of some stable oxidation products, which are produced in the same relative proportion, equivalent to about 13% of TOC, independent of the starting herbicide concentration.

3.3. 2,4-DP decay and reaction kinetics

The decay kinetics for 2.4-DP by reaction with the oxidizing species involved in each treatment (O_3, H_2O_2 and/or $OH^\bullet$) was followed by reversed-phase chromatography, where it displayed a well-defined peak with a retention time (t_r) of 10.2 min. Fig. 5 shows the evolution of the concentration of a 200 mg l^{-1} herbicide solution treated with the O_3, O_3/UVA, O_3/Fe^{2+}, $O_3/Fe^{2+}/UVA$ and O_3/Fe^{2+} $+ Cu^{2+}/UVA$ systems. As can be seen, this compound quickly disappears from the medium in less than 15 min for the three latter procedures with Fe^{2+}, while for the O_3 and O_3/UVA methods it is more slowly destroyed in 30 min, suggesting that 2,4-DP is not photolyzed under UVA irradiation. This was confirmed by checking from reversed-phase chromatography that the above 200 mg l^{-1} 2,4-DP solution remained stable after 1 h of UVA illumination. The fast and complete destruction of this herbicide by the O_3 system can then be ascribed to its direct reaction with molecular ozone, having a second-order rate constant (k_2) of 260 M^{-1} s^{-1} [8]. Its quicker removal from the different catalyzed ozonations can be explained by its parallel attack with H_2O_2 and/or $OH^\bullet$ produced in them.
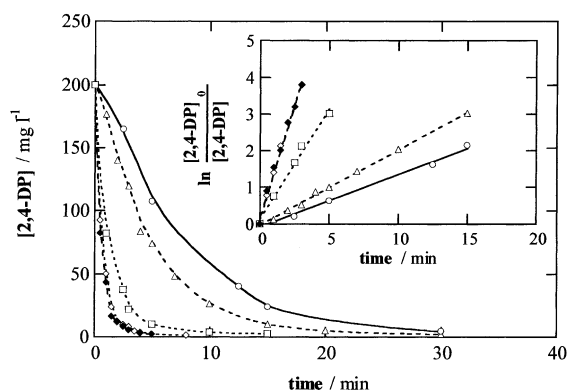

Fig. 5. 2,4-DP concentration decay for a 200 mg l^{-1} herbicide solution under the same experimental conditions as in Fig. 2. Applied system: (○) O_3; (□) O_3/Fe^{2+}; (△) O_3/UVA; (◇) $O_3/Fe^{2+}/UVA$; (◆) O_3/Fe^{2+} $+ Cu^{2+}/UVA$. The panel inset gives the corresponding kinetic analysis considering a pseudo first-order reaction for 2,4-DP.

When 2,4-DP concentration decays reported in Fig. 5 were fitted to kinetic equations related to different reaction orders, good linear plots, with regression coefficients >0.995, were only found using a pseudo first-order reaction. This kinetic analysis is depicted in the inset of Fig. 5, yielding a pseudo first-order rate constant (k_1) of 2.4×10^{-3}, 3.4×10^{-3}, 1.0×10^{-2}, 2.0×10^{-2} and 2.1×10^{-2} s^{-1} for the O_3, O_3/UVA, O_3/Fe^{2+}, $O_3/Fe^{2+}/UVA$ and O_3/Fe^{2+} $+ Cu^{2+}/UVA$ systems, respectively. The slightly higher k_1 value for the O_3/UVA system than for the O_3 one can be related to the parallel oxidation with H_2O_2 formed by reaction (1), while the great increase in k_1 for the O_3/Fe^{2+} one is due to the production of $OH^\bullet$ by reaction (4). The additional $OH^\bullet$ enhancement from reactions (6) and (7) can then justify the much higher k_1 value for the $O_3/Fe^{2+}/UVA$ treatment, thus confirming the positive synergetic effect of both catalysts, Fe^{2+} and UVA light. The fact that similar k_1 values are obtained for this system and the O_3/Fe^{2+} $+ Cu^{2+}/UVA$ one, corroborates again the poor generation of $OH^\bullet$ via reaction (11).

3.4. Identification of intermediates

Stable aromatic intermediates formed during the different degradations of the 200 mg l^{-1} 2,4-DP solution were identified by reversed-phase chromatography. All chromatograms displayed two well-defined peaks corresponding to chloro-*p*-benzoquinone at $t_r = 2.69$ min and 2,4-dichlorophenol at $t_r = 9.70$ min, along with a very small peak related to chlorohydroquinone at $t_r = 2.13$ min. These peaks were unequivocally identified from comparison of their retention times and UV-Vis spectra, determined on the photodiode array detector, with those of pure compounds. Similar oxidation products have also been detected for the degradation of 2,4-D by ozone and ozonation catalyzed with Fe^{2+} and/or UVA light [19], since for both herbicides 2,4-dichlorophenol is produced as the primary aromatic compound.

Ion-exclusion chromatograms of the same treated solutions exhibited peaks associated with generated carboxylic acids such as oxalic at $t_r = 6.58$ min, maleic at $t_r = 7.79$ min, pyruvic at $t_r = 9.08$ min, lactic at $t_r = 12.5$ min, acetic at $t_r = 15.1$ min and fumaric at $t_r = 15.6$ min. These retention times agree with those found for their pure compounds using the Aminex HPX 87H column with 4 mM H_2SO_4 as mobile phase at 0.6 ml min^{-1} and at 35 °C. Maleic and fumaric acids come from the breaking of aromatic rings of intermediates and are independently converted into oxalic acid [19]. Note that lactic acid is expected to be generated when 2,4-DP is oxidized to 2,4-dichlorophenol. To know its degradative connection with the other generated acids, a 250 mg l^{-1} solution of lactic acid (equivalent to 100 mg TOC l^{-1}) of pH 3.0 was treated with the $O_3/Fe^{2+}/UVA$ system. The evolution of the different carboxylic acids detected in the resulting solutions by ion-exclusion chromatography is presented in Fig. 6. As can be seen, lactic acid is completely removed in about 5 min, producing pyruvic, oxalic and acetic acid. The
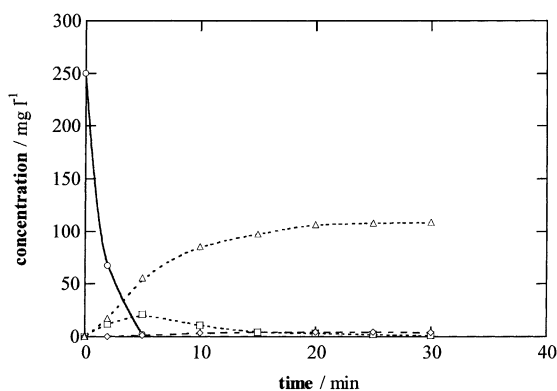
Fig. 6. Evolution of detected carboxylic acids during the degradation of a 100 ml solution with $250\,mg\,l^{-1}$ of lactic acid of pH 3.0 by the $O_3/Fe^{2+}/UVA$ system. Compound: (○) lactic acid; (□) pyruvic acid; (△) acetic acid; (◇) oxalic acid. Fe^{2+} concentration 1 mM. Ozone flow rate: $1.25\,g\,h^{-1}$; temperature: $25.0\,°C$.

two former acids also disappear in approximately 30 min, while the latter one is not decomposed, reaching a steady concentration of $108\,mg\,l^{-1}$, equivalent to $43\,mg\,TOC\,l^{-1}$. Similar studies for solutions with $100\,mg\,TOC\,l^{-1}$ of pyruvic, oxalic and acetic acids showed that: (i) pyruvic acid is totally destroyed, giving oxalic and acetic acids; (ii) oxalic acid is completely decomposed to CO_2 and (iii) acetic acid remains stable in solution, without being oxidized under the action of UVA light and $OH^•$. These findings allow us the conclusion that lactic acid formed in the primary reaction of 2,4-DP is oxidized to pyruvic acid, which is further transformed into oxalic and acetic acids.

3.5. Evolution of oxidation products

Fig. 7(a) shows a rapid formation and destruction of the primary product 2,4-dichlorophenol, which is completely removed after 14, 8, 3 and 2.5 min of the O_3/UVA, O_3/Fe^{2+}, $O_3/Fe^{2+}/UVA$ and $O_3/Fe^{2+} + Cu^{2+}/UVA$ methods, respectively. For each system, this compound disappears in less time than the initial herbicide (see Fig. 5), indicating that it reacts more rapidly with O_3, H_2O_2 and/or $OH^•$. However, 2,4-dichlorophenol is practically undetected during ozonation alone, whereas it shows a maximum concentration of about $5-8\,mg\,l^{-1}$ at 0.5–1 min of the $O_3/Fe^{2+}/UVA$ and $O_3/Fe^{2+} + Cu^{2+}/UVA$ treatments. This suggests that direct reaction of 2,4-DP with O_3, H_2O_2 and/or $OH^•$ can also give other undetected products, being favored the formation of 2,4-dichlorophenol with increasing $OH^•$ generation. As can be seen in Fig. 7(b), chloro-p-benzoquinone is accumulated in larger extent as more 2,4-dichlorophenol is present in the medium, disappearing in less than 8 min in all cases. In contrast, chlorohydroquinone is so quickly transformed into chloro-p-benzoquinone that it was only detected in small traces in the corresponding reversed-phase chromatograms. Results of Fig. 7(a and b) allow discarding direct photolysis of aromatic intermediates due to the little influence of UVA illumination on their evolution.

(a)

(b)
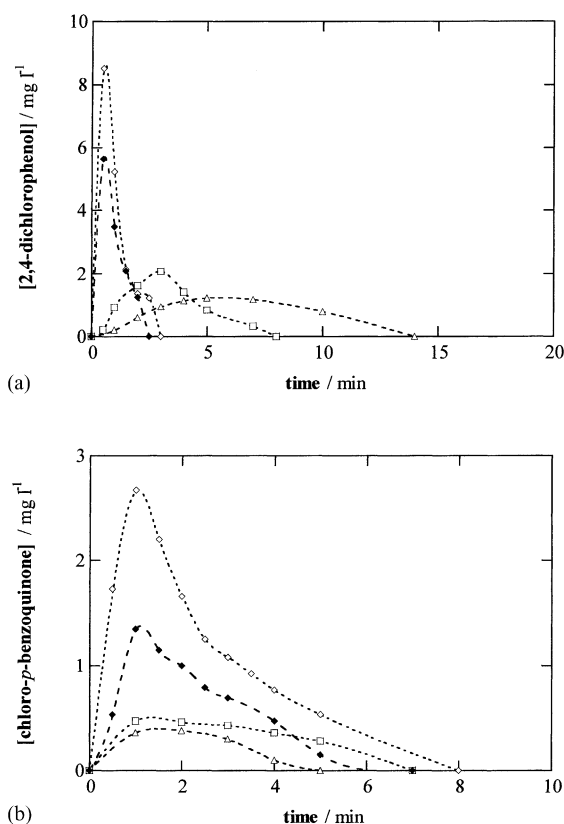
Fig. 7. Time-course of the concentration of aromatic intermediates: (a) 2,4-dichlorophenol; (b) chloro-p-benzoquinone, produced during the treatments shown in Fig. 5. Applied system: (□) O_3/Fe^{2+}; (△) O_3/UVA; (◇) $O_3/Fe^{2+}/UVA$; (◆) $O_3/Fe^{2+} + Cu^{2+}/UVA$.

The time-course of lactic acid concentration during the different degradations of a $200\,mg\,l^{-1}$ herbicide solution is depicted in Fig. 8(a). For ozonation alone, this compound is accumulated during the first 30 min while it is released from the initial herbicide (see Fig. 5), further being removed at about 90 min. Fig. 8(a) also shows that the destruction rate of lactic acid increases in the systems tested following the order $O_3 < O_3/UVA < O_3/Fe^{2+} < O_3/Fe^{2+}/UVA \leq O_3/Fe^{2+} + Cu^{2+}/UVA$. Similar trends can be observed in Fig. 8(b) and (c) for pyruvic and maleic acids, respectively. Note that both products, as well as fumaric acid accumulated in less extent, are totally removed in 2 h, even for ozonation alone. All the above generated carboxylic acids are then slowly destroyed by direct attack with ozone, gradually increasing their degradation rate as more $OH^•$ is generated in the medium by the catalyzed ozonation processes. In all cases, their removal from the $O_3/Fe^{2+} + Cu^{2+}/UVA$ system is slightly faster than from the $O_3/Fe^{2+}/UVA$ one, confirming the lower production of $OH^•$ by reaction (11) than by reactions (4), (6) and (7).

A very different behavior is found for oxalic and acetic acids, as can be seen in Fig. 8(d) and (e), respectively. Thus, oxalic acid is removed by the $O_3/Fe^{2+}/UVA$ and $O_3/Fe^{2+} + Cu^{2+}/UVA$ systems, partially destroyed by the O_3/UVA method up to reach $21\,mg\,l^{-1}$ at 2 h and accumulated in
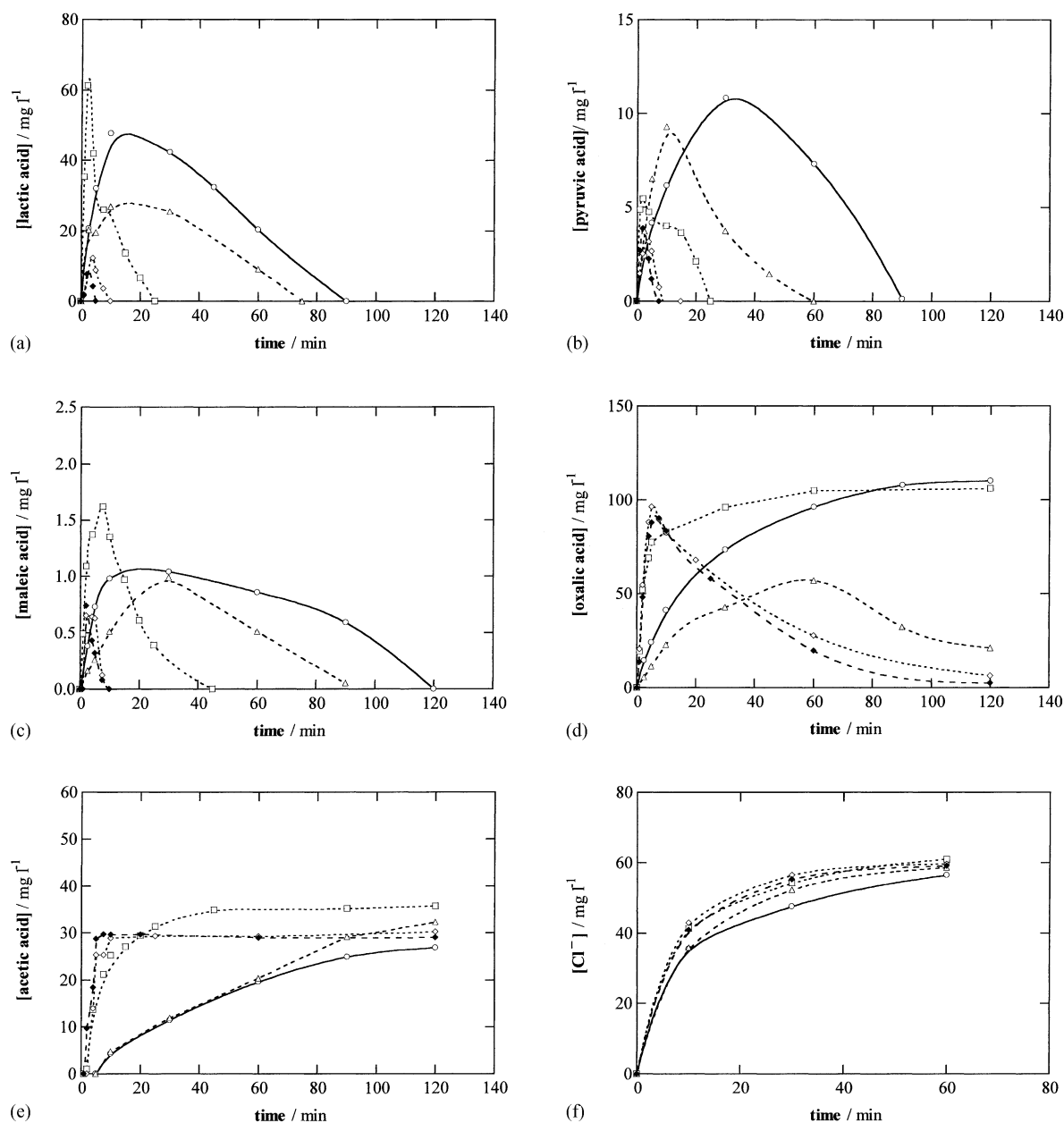
Fig. 8. Evolution of: (a) lactic acid; (b) pyruvic acid; (c) maleic acid; (d) oxalic acid; (e) acetic acid; (f) chloride ion, formed during the treatments reported in Fig. 5. Applied system: ($\bigcirc$) O_3; ($\square$) O_3/Fe^{2+}; ($\triangle$) O_3/UVA; ($\diamondsuit$) $O_3/Fe^{2+}/UVA$; ($\blacklozenge$) $O_3/Fe^{2+} + Cu^{2+}/UVA$.

the O_3 and O_3/Fe^{2+} treatments up to a steady concentration of 110 and 106 mg l^{-1}, respectively. These results agree with the formation of stable complexes of this acid with Fe^{3+}, which are photodecarboxylated under the action of UVA light [27]. In the O_3/Fe^{2+}, $O_3/Fe^{2+}/UVA$ and $O_3/Fe^{2+} + Cu^{2+}/UVA$ treatments of herbicide solutions, Fe^{3+} is generated from reactions (4), (5) and/or (6), and hence, a large proportion of Fe^{3+}-oxalate complexes is expected in the corresponding degraded solutions. The formation of such stable complexes can explain part of the poor depollution of 2,4-DP by the O_3/Fe^{2+} method, while their efficient destruction by UVA light can account for the very fast degradation rate of the $O_3/Fe^{2+}/UVA$ and $O_3/Fe^{2+} + Cu^{2+}/UVA$ sys-

tems (see Fig. 2). Fig. 8(d) also evidences a slightly faster decay of oxalic acid in the latter system, as expected if Cu^{2+}-oxalato complexes produced competitively in it are more rapidly destroyed than Fe^{3+}-oxalato ones, thus favoring its faster mineralization. These results indicate that Cu^{2+}-oxalato complexes can be slowly oxidized with OH$^\bullet$, without undergoing photolysis under UVA illumination. On the other hand, acetic acid attains a steady concentration of 35, 30 and 29 mg l^{-1} in the O_3/Fe^{2+}, $O_3/Fe^{2+}/UVA$ and $O_3/Fe^{2+} + Cu^{2+}/UVA$ treatments, respectively, being accumulated up to 27 and 32 mg l^{-1} in the corresponding O_3 and O_3/UVA systems (see Fig. 8(e)). From results of Fig. 6 for the conversion of lactic acid into acetic acid, it can be

inferred that in the oxidation of a $200\,mg\,l^{-1}$ 2,4-DP solution, $77\,mg\,l^{-1}$ of lactic acid can be produced to give $33\,mg\,l^{-1}$ of acetic acid, a value quite similar to that obtained during the degradation of the same herbicide solution by all systems. This indicates that the pathway of lactic acid to oxalic and acetic acids is practically independent of the experimental conditions tested.

The fact that 2,4-DP cannot be completely mineralized by the $O_3/Fe^{2+}/UVA$ and $O_3/Fe^{2+} + Cu^{2+}/UVA$ methods, can then be accounted for by the presence of only stable acetic acid in the final treated solutions, since all oxalic acid has been destroyed (see Fig. 8(d)). This can be confirmed from results of Fig. 8(e) that allow determining a remaining TOC of 13% related to acetic acid after degradation of the $200\,mg\,l^{-1}$ herbicide solution by both methods, i.e. the same value as found at the end of such treatments of solutions containing between 336 and $78\,mg\,l^{-1}$ of 2,4-DP (see Fig. 4). An analogous analysis for the other methods from Fig. 8(d) and (e) yields a remaining TOC of 43, 45 and 20% related to both accumulated oxalic and acetic acids for the O_3, O_3/Fe^{2+} and O_3/UVA systems, values very close to 46, 42 and 22% obtained after 2 h of the corresponding treatments of a $217\,mg\,l^{-1}$ herbicide solution (see Fig. 2). These results indicate that their final solutions are mainly composed of a mixture of oxalic and acetic acids.

The Cl^- concentration in the above-degraded solutions was also determined to know the overall rate of dechlo-rination reactions involved in the destruction of 2,4-DP. The evolution of this ion is presented in Fig. 8(f). As can be seen, more than 91% of initial chlorine ($60\,mg\,l^{-1}$) is released to the solution in the form of Cl^- after 30 min of the O_3/Fe^{2+}, $O_3/Fe^{2+}/UVA$ and $O_3/Fe^{2+} + Cu^{2+}/UVA$ treatments, whereas for the O_3 and O_3/UVA methods, a slower Cl^- accumulation takes place, reaching a concentration of 56 and $58\,mg\,l^{-1}$ at 60 min, respectively. This behavior confirms the existence of other undetected chloroderivatives of 2,4-DP, which are more slowly destroyed than 2,4-dichlorophenol (see Fig. 7(a)) and chloro-p-benzoquinone (see Fig. 7(b)), leading to the formation of stable chloride ion in all procedures tested. The dechlorination rate of such species is enhanced as higher $OH^\bullet$ concentration is produced in the medium.

3.6. Reaction sequence for 2, 4-DP degradation

A general pathway for the degradation of 2,4-DP at pH 3.0 by ozone and ozonation catalyzed with Fe^{2+}, Cu^{2+} and/or UVA light is proposed in Fig. 9. This reaction sequence involves all intermediates detected leading to oxalic and acetic acids as ultimate generated carboxylic acids. The main oxidizing agents are O_3 for ozonation alone and O_3, H_2O_2 and $OH^\bullet$ for catalyzed ozonations.

The process is initiated by the breaking of the C(1)–O bond of 2,4-DP by the direct attack of O_3, H_2O_2 and/or $OH^\bullet$ giving 2,4-dichlorophenol and lactic acid as primary

Fig. 9. General reaction sequence proposed for 2,4-DP degradation by O_3 and ozonation catalyzed with Fe^{2+}, Cu^{2+} and/or UVA light at pH 3.0.

oxidation products. This reaction is faster in the $O_3/Fe^{2+}/$ UVA and $O_3/Fe^{2+} + Cu^{2+}/UVA$ systems, where more amounts of $OH^\bullet$ can react with the initial reactant. Further hydroxylation of 2,4-dichlorophenol on C(4)-position yields chlorohydroquinone with loss of a chlorine atom, a strong oxidizing agent that is reduced to chloride ion. Chlorohydroquinone is subsequently oxidized to chloro-*p*-benzoquinone. This compound can then be degraded in consecutive steps to produce chloride ion and a mixture of maleic and fumaric acids, which are converted into oxalic acid. Parallel dehydrogenation of the initially generated lactic acid gives pyruvic acid. Further oxidation of this acid also yields oxalic acid, along with acetic acid that remains stable in solution in all treatments. The transformation of all carboxylic acids into oxalic and acetic acids is accelerated as more $OH^\bullet$ is generated in the medium by catalyzed ozonations. Oxalic acid is not mineralized by ozonation alone, but it can be slowly converted into CO_2 by the action of UVA light and H_2O_2 produced from reaction (1) in the O_3/UVA system. This acid forms stable Fe^{3+}-oxalato complexes in the O_3/Fe^{2+} system, which can be quickly photodecarboxylated with loss of Fe^{2+} under UVA irradiation in the $O_3/Fe^{2+}/UVA$ system, as proposed by Zuo and Hoigné [27]. When Cu^{2+} and Fe^{3+} are present in the medium using the $O_3/Fe^{2+} + Cu^{2+}/UVA$ system, Cu^{2+}-oxalato complexes are also competitively formed. These complexes are slowly mineralized with $OH^\bullet$, but not photodecomposed by UVA light.

4. Conclusions

Acidic 2,4-DP solutions cannot be completely mineralized by ozone and catalyzed ozonations because of the formation of stable products. Ozonation alone yields a slow degradation, which is accelerated in the O_3/UVA system by the generation of H_2O_2 from reaction (1) and photodecomposition of intermediates. Addition of catalytic Fe^{2+} causes an enhancement of the initial mineralization rate since $OH^\bullet$ is also produced by reaction (4), although degradation is inhibited by the formation of difficulty oxidizable products. This process is much faster in the $O_3/Fe^{2+}/UVA$ system due to the additional action of $OH^\bullet$ formed from reactions (6) and (7) and photodecomposition of Fe^{3+} complexes, but about 13% of remaining TOC is obtained. For this treatment, optimum operative conditions are achieved using 1 mM Fe^{2+} and ozone flow rates between 0.8 and 1.5 g O_3 h^{-1} at 25.0 °C. The initial mineralization rate of the $O_3/Fe^{2+}/UVA$ system is quicker with raising herbicide concentration. The presence of the Cu^{2+}/Cu^+ pair in the $O_3/Fe^{2+} + Cu^{2+}/UVA$ system does not improve significantly the oxidizing ability of the above method, since reaction (11) yields small amounts of $OH^\bullet$. In all cases, the 2,4-DP decay follows a pseudo first-order reaction with increasing rate constant as higher $OH^\bullet$ concentration is generated. 2,4-dichlorophenol, chlorohydroquinone and chloro-*p*-benzoquinone are detected as aromatic intermediates. The initial chlorine is released to the medium as chloride ion. Generated carboxylic acids such as lactic, pyruvic, maleic and fumaric are completely destroyed in all cases, at higher rate as more $OH^\bullet$ is produced. Oxalic acid is stable in the O_3 system, slowly being converted into CO_2 by the O_3/UVA one. For the O_3/Fe^{2+} system, it gives stable Fe^{3+}-oxalato complexes, which are quickly photodecarboxylated in the $O_3/Fe^{2+}/UVA$ and $O_3/Fe^{2+} + Cu^{2+}/UVA$ ones. In the laffer method, Cu^{2+}-oxalato complexes are also formed, slowly being mineralized with $OH^\bullet$. Acetic acid coming from lactic acid oxidation is stable under all conditions and hence, it is the only remaining species of the $O_3/Fe^{2+}/UVA$ and $O_3/Fe^{2+} + Cu^{2+}/UVA$ treatments.

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