Degradation of carbofuran by using ozone, UV radiation and advanced oxidation processes

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Abstract

The degradation of carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate), a frequently used carbamate derivative pesticide that is considered a priority pollutant, is carried out in batch reactors by means of single oxidants: ozone, UV radiation and Fenton's reagent; and by the advanced oxidation processes (AOPs) constituted by combinations of ozone plus UV radiation, UV radiation plus H_2O_2, and UV radiation plus Fenton's reagent (photo-Fenton system). For all these reactions, the apparent pseudo-first-order rate constants are evaluated in order to compare the efficiency of each process. In addition and by means of a competition kinetic model, the rate constants for the reaction of carbofuran with ozone and with hydroxyl radicals are also determined. The improvement in the decomposition levels of carbofuran reached by the combined processes in relation to the single oxidants, due to the generation of the very reactive hydroxyl radicals, is also established in every process. For the oxidant concentrations applied, the most effective process in removing carbofuran was the photo-Fenton system. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Carbofuran pesticide; Ozone; UV radiation; Hydroxyl radicals; Advanced oxidation processes; Rate constants

1. Introduction

Cultivation of plants for economical purposes requires a constant struggle against losses from pests promoted by weeds, insects, diseases, etc. The most frequent agents used for this objective are pesticides in their different forms: insecticides, herbicides, fungicides, etc. all of them have contributed in a great extent to agricultural productivity. However, pesticide pollution of surface waters and wastewaters has increased sharply, and presently, it constitutes a major pollutant problem due to an extensive use of these substances [1].

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Thus, in addition to their toxic character by themselves, the hazardous potential is increased by the possibility of generating organohalogen compounds through their reactions with chloro derivatives, the most common chemicals used for oxidation and disinfection of surface waters and wastewaters. Besides that some contaminants are especially refractory to conventional oxidation treatments, and chlorination-based methods are unable to remove them from waters [2]. In addition, biological treatment techniques, which are well established and cheap, are susceptible to toxic compounds such as pesticides that inactive the waste degrading microorganisms. In these cases, a partial elimination of the toxic waste by oxidation technologies to produce intermediates that are more readily biodegradable has been proposed [3].

Therefore, in recent times the removal of organic harmful pollutants present in water supplies is investigated by means of a variety of chemical procedures. Among them, the oxidation by several agents different to chlorine, such as ozone [4], UV radiation [5], Fenton's reagent [6,7], etc. has been extensively used with success. However, more demanding requirements imposed by law regulations to the treatment plants in the last years, or a particularly resistant character of some compounds to those oxidants, have forced to the development of new alternatives, like stronger oxidant agents or advanced oxidation processes (AOPs). These AOPs, which are constituted by the combination of several oxidants, are characterized by the generation of very reactive and oxidizing free radicals in aqueous solutions, such as the hydroxyl radicals, which achieve a great destruction power. Several of them are currently employed for the elimination of pesticides, as the combinations O_3/H_2O_2 [8], O_3/UV [9], photo-Fenton system [10] and electrochemical oxidation processes [11].

Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) is a broad spectrum systemic acaricide, insecticide and nematicide included in the general group of the carbamate derivative pesticides [12]. It is widely used in agricultural cultivations and presents a high persistance in water due to its chemical stability; consequently, it is increasingly detected in surface and wastewaters. As carbofuran exhibits a special refractory character to biodegradation methods, a research program focused on its oxidation by some single chemical oxidants like ozone and UV radiation and by different AOPs, was designed. The objectives were to provide data about the removal obtained and to report values of the rate constants for the global degradation reactions. The enhancement reached in the oxidation rate by the presence of the free hydroxyl radicals in the AOPs, when compared to the single oxidation processes, is also established. Moreover, the partial contribution of the $OH^\bullet$ radical pathway to the global degradation reactions is calculated for the different AOPs studied.

2. Experimental

The reactor used in all the experiments consisted of a 500 ml cylindrical glass contactor provided with the necessary elements for the development of the different processes: ozonation, photochemical decomposition, Fenton's reagent oxidation, and the several combinations of these oxidants: ozone plus UV radiation, UV radiation plus hydrogen peroxide and photo-Fenton system. Thus, for the ozonation experiments, the ozone was produced from oxygen taken from a commercial cylinder which was introduced into an ozone

generator (Yemar, model HPA). In the photochemical experiments, the radiation source was a Hanau TQ150 high pressure mercury vapor lamp, which emitted a polychromatic radiation. It was located in the reactor in axial position and a quartz sleeve kept the lamp. Also, an external jacket surrounded the reactor, and a water stream was pumped from a thermostatic bath in order to maintain the temperature at the selected value for each experiment.

For every experiment conducted, the reactor was filled with 350 ml of an aqueous solution of carbofuran (initial concentration of 4.52×10^{-4} M in all cases) buffered at the selected pH by adding *ortho*-phosphoric acid and sodium hydroxide. The required amounts of ferrous sulfate and hydrogen peroxide were added to the reactor in the Fenton's reagent oxidation experiments and in the photo-Fenton experiments, and only the required amounts of hydrogen peroxide in the UV/H_2O_2 experiments. In the ozonation and combined O_3/UV radiation experiments, the ozone–oxygen mixture was fed to the reactor through a porous plate gas sparger located at the bottom of the reactor. When UV radiation was present, either alone or combined, the radiation lamp was connected at the beginning of the reaction.

Analytical grade carbofuran was used, and its concentration in the samples retired from the reactor at regular reaction times were analyzed by HPLC using a Waters Chromatograph equipped with a 996 Photodiode Array Detector and a Nova-Pak C18 Column. The mobile phase was composed by a mixture methanol–water–acetic acid (45–53–2 in volume) and with a flow rate of 1 ml/min. In addition, in the ozonation experiments the ozone concentration was measured in the gas stream iodometrically by bubbling the gas in a potassium iodide solution. The concentration of H_2O_2 was determined by the colorimetric method proposed by Bader et al. [13].

3. Results and discussion

3.1. Decomposition of carbofuran by ozone and ozone plus UV radiation

Previous ozonation experiments were conducted in the way already described in a former work [14] in order to determine the stoichiometric ratio for the reaction between carbofuran and ozone. The value obtained in these experiments was $z = 3 \pm 0.1$ mol of ozone consumed per mol of carbofuran reacted.

In the carbofuran decomposition by ozone, several experiments which are summarized in Table 1, were carried out by varying the temperature (10, 20 and 40°C; experiments

Table 1
Oxidation of carbofuran by ozone and ozone + UV: experimental conditions and pseudo-first-order rate constants

Experiments	T (°C)	pH	p_{O_3i} (kPa)	$k_O \times 10^4$ (s^{-1})
O-1	10	2	0.083	5.1
O-2	20	2	0.086	7.3
O-3	40	2	0.089	8.0
O-4	20	2	0.265	19.5
O-5	20	9	0.083	6.8
O-6[a]	20	2	0.087	22.8[b]

[a] Combined ozone + UV radiation.
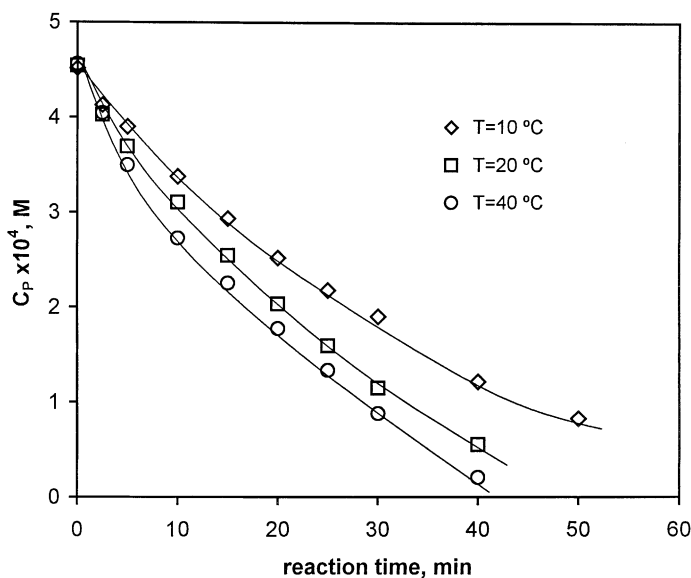[b] Value of k_{OUV} for the combined O_3/UV process.

Fig. 1. Carbofuran decomposition curves in conventional ozonation experiments performed by varying the temperature. Experimental conditions are given in Table 1.

O-1 to O-3), the ozone partial pressure in the inlet gas stream (0.265 and 0.086 kPa; experiments O-4 and O-2) and the pH (2 and 9; experiments O-2 and O-5). As it is seen in Fig. 1, the temperature exerts a positive influence on the degradation process and thus, the concentration of carbofuran is smaller at higher temperature for a given reaction time. This effect is due to an increase in the rate constant of the chemical reaction. A similar positive effect is observed for the variation of the ozone partial pressure (see Fig. 2): in this case, the disappearance rate of the pesticide rises with the increase in the ozone absorption rate, which is higher at elevated ozone partial pressure.

Regarding to the effect of the pH, initially it can be expected an increase in the ozonation rate when the pH increases. As it is known, ozone reacts with organic compounds in water through a direct pathway by molecular ozone, and through a radical pathway by means of hydroxyl radicals [15]. In addition to other ways of production of these radicals that will be considered later, one significant generation source for the radicals is the self-decomposition reaction of ozone, which is accelerated by the action of hydroxyl ions [16]. Therefore, at higher pHs the formation of hydroxyl radicals and subsequently the radical pathway would be more important. However, in this case, as Fig. 2 also shows, the experimental points corresponding to the reactions performed at pH 2 and 9 (experiments O-2 and O-5) lie around the same line. Thus, it is concluded that the contribution of the radical pathway to the elimination of carbofuran by single ozonation is almost negligible.

The global decomposition of organic compounds by ozone can be represented by the following simple reaction:

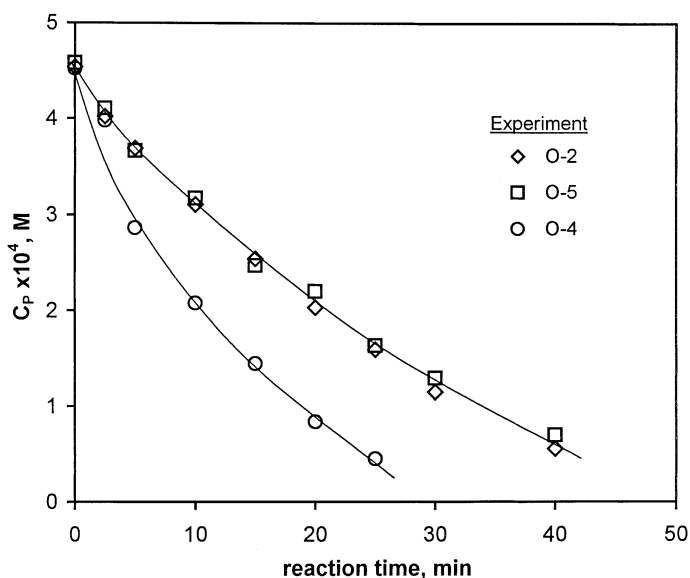$$P + O_3 \overset{k_O}{\rightarrow} P_{oxid} \tag{1}$$

Fig. 2. Carbofuran decomposition curves in conventional ozonation experiments performed by varying the ozone partial pressure and the pH. Experimental conditions are given in Table 1.

The carbofuran concentration curves versus reaction time in these ozonation experiments (see Figs. 1 and 2) suggest that in a first approach, the global ozonation reaction (1) can be described by pseudo-first-order kinetics with respect to carbofuran concentration. According to this assumption, it is proposed the following rate equation:

$$-\frac{dC_P}{dt} = k_O C_P \tag{2}$$

where k_O represents the apparent pseudo-first-order rate constant for the ozonation process. This equation, after integration with the boundary conditions $C_P = C_{P_0}$ for $t = 0$, and $C_P = C_P$ for $t = t$, leads to

$$\ln\frac{C_{P_0}}{C_P} = k_O t \tag{3}$$

Thus, a plot of $\ln(C_{P_0}/C_P)$ versus t in every experiment must lead to straight lines which slopes are k_O. Fig. 3 shows, as an example, this plot for experiments where the temperature was varied: at can be seen, points lie satisfactorily around straight lines. Similar plots are obtained for the remaining experiments. After least-square regression analysis, the values of k_O shown in Table 1 are deduced. Also, the correlation coefficients greater than 0.98 in all cases confirm the goodness of the assumed kinetics for the global ozonation reaction.

The values obtained for k_O in experiments O-2 and O-5 carried out at 20°C, but at different pH are quite similar, which indicates that the rate constants are not affected by the pH in this system as was previously observed. However, in experiments O-1 to O-3, where the pH and ozone partial pressure are the same but the temperature is modified, increasing values are
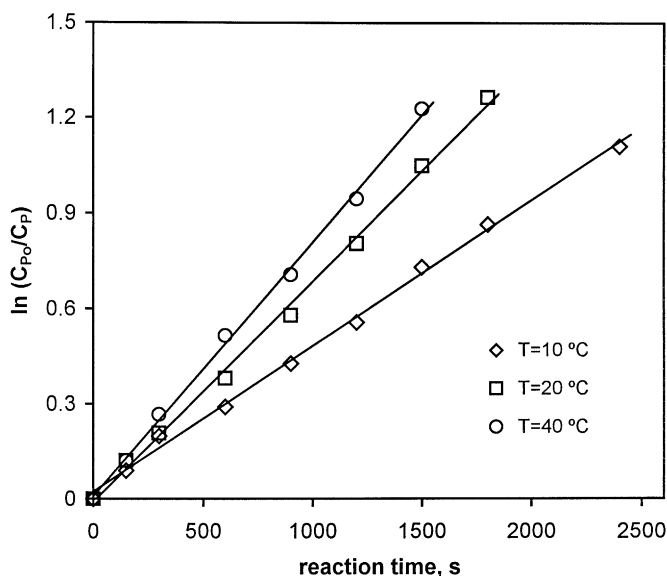
Fig. 3. Determination of the pseudo-first-order rate constants for the ozonation of carbofuran in experiments where the temperature is varied. Experimental conditions are given in Table 1.

obtained for k_O. Therefore, these apparent rate constants can be correlated by an Arrhenius expression, and a regression analysis leads to

$$k_O = 4.04 \times 10^{-2} \exp\left(\frac{-1213.1}{T}\right) \ (s^{-1}) \tag{4}$$

Once these apparent pseudo-first-order rate constants for the ozonation process have been determined, the true rate constant for the reaction of carbofuran with ozone is pursued in a second stage. This evaluation can be performed by means of a competition kinetic model, which has been previously used by several authors [17,18]. This model consists of the simultaneous ozonation of a mixture of two organic compounds: one of them is the reference compound R, whose ozonation rate constant is previously known; the second compound constitutes the target compound i, whose rate constant is unknown. This competitive method is well described in a former publication [14], and the final equation obtained is

$$\ln\frac{C_{Pi_0}}{C_{Pi}} = \frac{z_R k_{O_3 i}}{z_i k_{O_3 R}} \ln\frac{C_{PR_0}}{C_{PR}} \tag{5}$$

where C_{Pi_0} and C_{Pi} represent respectively the initial and at any reaction time concentrations of the target compound; C_{PR_0} and C_{PR} are the corresponding concentrations of the reference compound; $k_{O_3 i}$ and $k_{O_3 R}$ are the rate constants for the consumption of ozone by the target and the reference compound, respectively; and z_R and z_i represent the stoichiometric ratios for the direct reaction between ozone and the reference and target compound, respectively. According to Eq. (5), a plot of $\ln(C_{Pi_0}/C_{Pi})$ against $\ln(C_{PR_0}/C_{PR})$ must yield a straight line whose slope is the ratio of rate constants; and as $k_{O_3 R}$ and the stoichiometric ratios z_R and z_i are known, $k_{O_3 i}$ can then be determined.
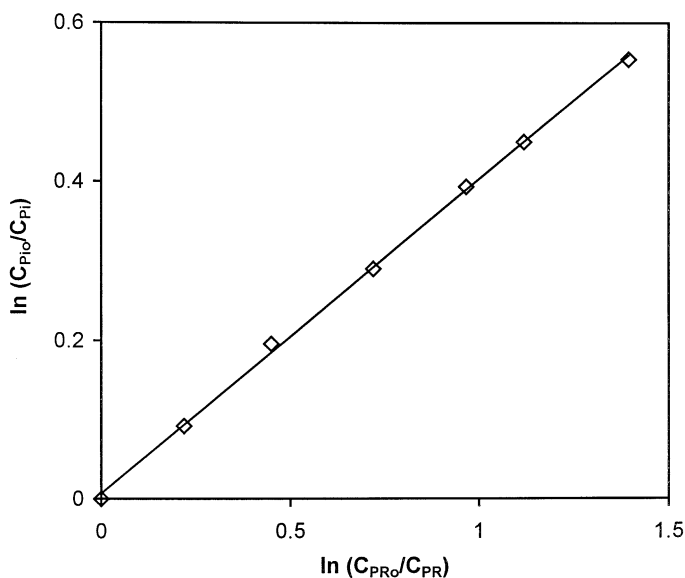
Fig. 4. Determination of the rate constant for the reaction between ozone and carbofuran by competitive kinetics with 2,4-dichlorophenol.

Following this procedure, an ozonation experiment of a mixture of 2,4-dichlorophenol and carbofuran (4.52×10^{-4} M initial concentration for each one) was performed at 20°C and pH $= 2$. This chlorophenol was selected as reference compound, whose rate constant for the oxidation by ozone was determined in a previous work [14], its value at pH $= 2$ being $k_{O_3R} = 1866$ l/mol s, and its stoichiometric ratio z_R being 2 mol of ozone per mol of 2,4-dichlorophenol. In accordance to Eq. (5), Fig. 4 shows the mentioned plot. After least-square regression analysis, a slope of 0.396 was obtained ($r^2 = 0.99$). With the values of k_{O_3R} and z_R above mentioned, and the stoichiometric ratio experimentally determined in this study for carbofuran $z_i = 3$, a value of 1108 l/mol s is deduced for k_{O_3i}, rate constant proposed at 20°C for the consumption of ozone by carbofuran.

Once the rate constant k_{O_3i} is evaluated, the true rate constant for the degradation of carbofuran by ozone, k_M, can be calculated by taking into account the stoichiometric factor z_i, in the form $k_M = k_{O_3i}/z_i$ [17,18]. Thus, the value obtained at 20°C for k_M is 369.3 l/mol s, similar to that of 387 l/mol s proposed by Hu et al. [19]. This relatively high rate constant for the degradation of carbofuran by ozone corroborates the fact that the contribution of the radical pathway is not significant when conventional ozonation is applied.

In a following step, a degradation experiment of carbofuran by the combined process O_3/UV radiation was conducted at 20°C and pH $= 2$ (experiment O-6). Similarly to the single ozonation process, the apparent pseudo-first-order rate constant (k_{OUV} in this case) is evaluated by means of Eq. (3), and the value obtained is also reported in Table 1. When compared this result to that of the single ozonation experiment carried out under the same operating conditions (experiment O-2 of Table 1), it is observed that this combined process accelerates the decomposition rate of carbofuran as can be expected.

This enhancement in the degradation rate can be explained by considering the reactions that occur in this AOP. As Peyton et al. pointed out [20], ozone absorbs UV radiation and produces hydrogen peroxide:

$$O_3 + h\nu \rightarrow H_2O_2 \tag{6}$$

and then, there is a photolysis of hydrogen peroxide to generate hydroxyl radicals in the form:

$$H_2O_2 + h\nu \rightarrow 2OH^\bullet \tag{7}$$
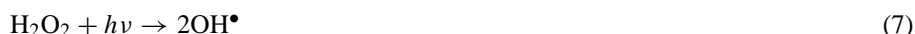
In addition, hydrogen peroxide accelerates the ozone decomposition into $OH^\bullet$ radicals [16]. Therefore, $OH^\bullet$ radicals constitute an important active species in the photolytic ozonation process and attack the organic compound P according to the following reaction:

$$P + OH^\bullet \overset{k_r}{\rightarrow} P_{oxid} \tag{8}$$

The contribution of the radical pathway in the AOP O_3/UV explains the increase of the apparent pseudo-first-order rate constant by a factor of 3 when compared to conventional ozonation (Table 1, experiments O-2 and O-6).

3.2. Decomposition of carbofuran by UV radiation and UV radiation plus hydrogen peroxide

The photooxidation of carbofuran by the polychromatic UV radiation described in Section 2 was conducted at $20°C$ and $pH = 3$, with an initial concentration of carbofuran of 4.52×10^{-4} M (experiment UV-1 in Table 2). Fig. 5 shows the decrease in the pesticide concentration as a function of irradiation time: again, the shape of the line looks like a pseudo-first-order reaction with respect to carbofuran degradation. Therefore, an approach to its kinetic study can be performed by assuming that the photochemical decomposition follows a pseudo-first-order kinetics, and can be represented by the simple expression:

$$P + h\nu \overset{k_p}{\rightarrow} P_{oxid} \tag{9}$$

where k_p is the pseudo-first-order rate constant. This approach has been frequently used by several authors in similar studies [21,22]. In order to evaluate the rate constant k_p, and

Table 2
Pseudo-first-order rate constants for the decomposition of carbofuran by UV radiation, UV/H_2O_2, Fenton's reagent and photo-Fenton system

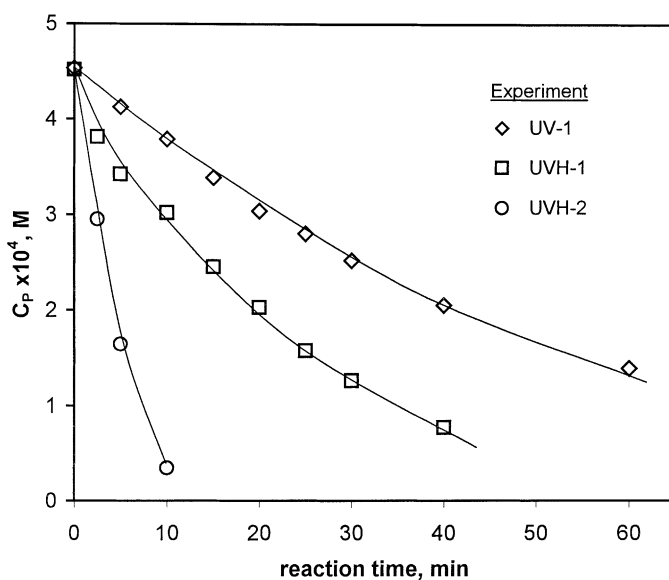| Experiments	$[H_2O_2]_0 \times 10^4$ (M)	$[Fe^{2+}]_0 \times 10^4$ (M)	$k_p \times 10^4$ (s^{-1})	$k_t \times 10^4$ (s^{-1})	$k_F \times 10^4$ (s^{-1})	$k_r \times 10^4$ (s^{-1})
UV-1	–	–	3.3	–	–	–
UVH-1	5	–	–	7.1	–	3.8
UVH-2	50	–	–	43.5	–	40.2
F-1	5	0.5	–	–	2.2	–
F-2	50	5	–	–	7.1	–
UVF-1	5	0.5	–	20.5	–	17.2
UVF-2	50	5	–	>200	–	>200

Fig. 5. Carbofuran decomposition curves by UV radiation alone and combined with hydrogen peroxide. Experimental conditions are given in Table 2.

similarly to Eq. (3), the following expression is proposed:

$$\ln\frac{C_{P_0}}{C_P} = k_p t \tag{10}$$

Thus, the terms $\ln(C_{P_0}/C_P)$ are plotted versus reaction time, and after linear regression analysis, the pseudo-first-order rate constant k_p is determined and showed in Table 2. When compared to the values of the rate constants obtained for the ozonation experiments at similar operating conditions (7.3×10^{-4} and $43.5 \times 10^{-4}\,\mathrm{s}^{-1}$ for experiments O-2 and O-4, respectively), a lower value is obtained for this photochemical process ($3.3 \times 10^{-4}\,\mathrm{s}^{-1}$), which indicates that ozone is more effective than the radiation source used for the decomposition of carbofuran, even for the lower inlet ozone partial pressure.

Later, two photodegradation experiments of carbofuran were conducted with the additional presence of hydrogen peroxide (experiments UVH-1 and UVH-2 in Table 2 and Fig. 5), with H_2O_2 initial concentration of 5×10^{-4} and $5 \times 10^{-3}\,\mathrm{M}$, respectively. As Fig. 5 shows, two effects can be clearly seen: firstly, the positive influence of the combination UV + H_2O_2 in comparison to the single photodegradation; and secondly, the positive influence of the H_2O_2 initial concentration on the process, with increasing disappearance rate when this variable is increased. This trend is confirmed with the evaluation of the pseudo-first-order rate constants k_t for this process, which are depicted in Table 2: they present higher values than that obtained in the single photodecomposition process: 7.1×10^{-4} and $43.5 \times 10^{-4}\,\mathrm{s}^{-1}$ versus $3.3 \times 10^{-4}\,\mathrm{s}^{-1}$.

These findings demonstrate the additional contribution to the single photoreaction of the hydroxyl radicals generated by the presence of hydrogen peroxide; and this

supplementary contribution can be determined by considering the mechanism of the combined process. Thus, in addition to the direct photoreaction (Eq. (9)), it must be taken into account the following reactions: the direct photolysis of hydrogen peroxide with the formation of hydroxyl radicals, given by Eq. (7), and the radical reaction between carbofuran and the hydroxyl radicals generated which is given by Eq. (8). It could be also expected a direct decomposition reaction between the organic compound and H_2O_2 alone. However, previous experiments carried out with hydrogen peroxide as single oxidant showed that no degradation of carbofuran was obtained, and therefore, that reaction can be neglected.

According to this mechanism, the reaction rate for the global photodecomposition r_T can be proposed as the addition of the direct r_P (reaction 9) and radical r_R (reaction 8) reaction rates in the form:

$$-r_T = \left[-\frac{dC_P}{dt} \right] = -(r_P + r_R) = (k_p + k_r)C_P = k_t C_P \tag{11}$$

In accordance with Eq. (11), the rate constants for the radical reaction k_r are easily deduced by subtracting the previously determined k_p from k_t, and Table 2 also depicts the values obtained for k_r. When compared these values to that of k_p, it is observed that the direct photolysis provides a smaller contribution to the total reaction than the radical reaction. This contribution of the radical pathway is specially important in experiment UVH-2 with a higher initial concentration of H_2O_2.

In order to confirm this proposed mechanism and evaluate the contribution of the different degradation pathways, Fig. 6 presents the theoretically calculated percentages of
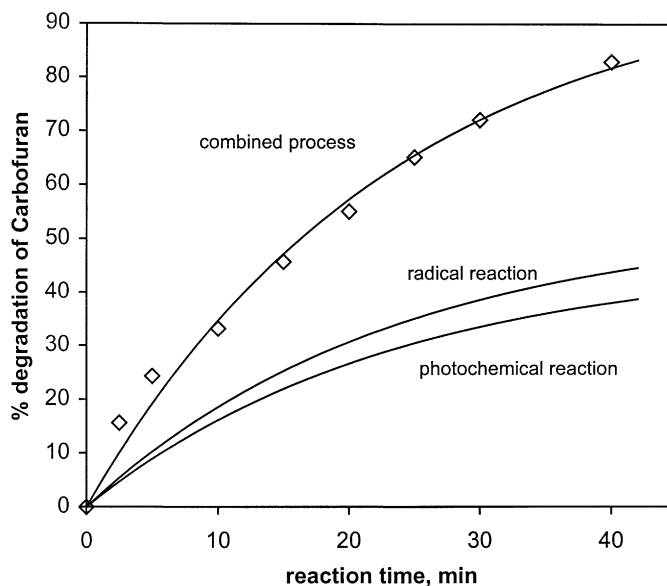

Fig. 6. Contribution of the radical and photochemical pathways to the degradation of carbofuran in the AOP UV/H_2O_2 (experiment UVH-1). Lines represent model calculations performed by ACUCHEM and symbols represent experimental data.

degradation of carbofuran with the reaction time for the single radical and photochemical reactions, and for the combined UV/H_2O_2 process (experiment UVH-1). These theoretical curves were calculated by means of computer simulations by using the program ACUCHEM [23]. This program can solve systems of non-linear differential equations and gives a time-dependant behavior of the species under question. For these calculations, the evaluated rate constants k_p and k_r have been used, and the global degradation is determined as the addition of both contributions. The experimental percentages of carbofuran degradation obtained in experiment UVH-1 are also included in Fig. 6. As can be seen, the excellent agreement between model calculations and experimental data supports the proposed mechanism. In addition, it can be observed a higher contribution of the radical reaction (53%) compared to the direct photolysis (47%) as was previously commented. Moreover, the calculated contribution of the direct photolysis in experiment UVH-2 is only 8% of the total degradation of carbofuran. Therefore, in presence of high concentration of hydrogen peroxide the contribution of the direct photochemical reaction is almost negligible and the radiation energy emitted by the lamp is mainly absorbed by hydrogen peroxide to generate $OH^\bullet$ radicals.

3.3. Decomposition of carbofuran by Fenton's reagent and photo-Fenton system

In a next step, the decomposition of carbofuran was explored by means of the very reactive and oxidizing hydroxyl radicals, which are generated by the Fenton's reagent, a mixture of hydrogen peroxide and ferrous ions, according to the reaction:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^\bullet \tag{12}$$

The hydroxyl radicals formed attack carbofuran similarly to Eq. (8)

$$P + OH^\bullet \xrightarrow{k_F} P_{oxid} \tag{13}$$

where k_F represents the pseudo-first-order rate constant for the Fenton's reaction.

Two experiments of carbofuran removal by Fenton's reaction were performed at pH = 3 by varying the initial concentrations of Fe^{2+} and H_2O_2 according to the values summarized in Table 2 (experiments F-1 and F-2). Fig. 7 shows the degradation curves of carbofuran: as can be observed, the disappearance rate is low in experiment F-1 due to its lower initial concentration of hydrogen peroxide and ferrous ions, while experiment F-2 presents a more significant oxidation rate. After regression analysis, the rate constant k_F is obtained and depicted in Table 2: these values confirm the trends observed in Fig. 7.

Once these global pseudo-first-order rate constants k_F are evaluated, the specific rate constant k_{OH} for the reaction between carbofuran and the hydroxyl radicals is investigated. For this purpose, a competition kinetic model similar to that described in Section 3.1 is again used. An experiment of simultaneous degradation of carbofuran and 2,4-dichlorophenol by the Fenton's reagent was carried out. The second one is again the reference compound, which reaction rate constant with hydroxyl radicals has been previously reported [24]: 5.14×10^9 l/mol s.

The requirements for using this method, fast reactions in aqueous solutions that follow overall second order kinetics, and more specifically, first-order with respect to each reactants,
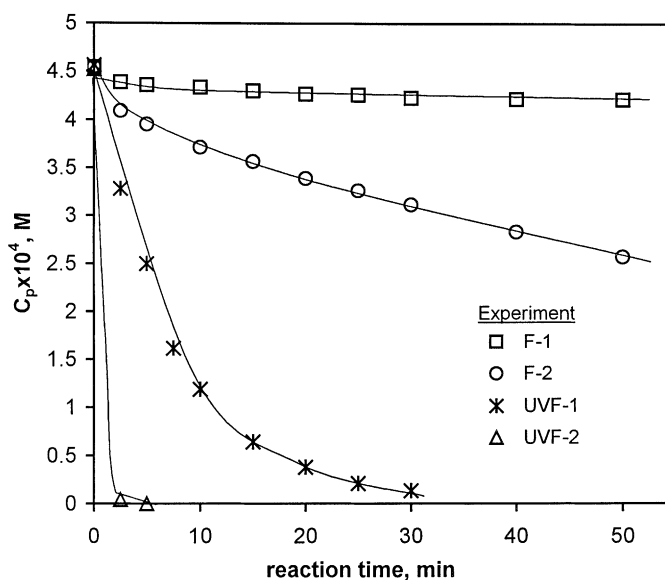
Fig. 7. Carbofuran decomposition curves by Fenton's reagent alone and combined with UV radiation (photo-Fenton system). Experimental conditions are given in Table 2.

are fulfilled in the Fenton's reagent reaction of most of the organic substances like carbofuran and chlorophenols [24]. According to these considerations, the oxidation rate by hydroxyl radicals of the target compound in the mixture (carbofuran) can be expressed as

$$-\frac{d[C_{Pi}]}{dt} = k_{OHi}[OH^\bullet][C_{Pi}] \tag{14}$$

while this rate equation for the reference compound R in that mixture (2,4-dichlorophenol) is

$$-\frac{d[C_{PR}]}{dt} = k_{OHR}[OH^\bullet][C_{PR}] \tag{15}$$

where k_{OHi} and k_{OHR} are the rate constants for the reaction between $OH^\bullet$ radicals and the target and the reference compound, respectively. By dividing both equations, and integrating between $t = 0$ and $t = t$, we can get

$$\ln\frac{[C_{Pi}]_0}{[C_{Pi}]} = \frac{k_{OHi}}{k_{OHR}}\ln\frac{[C_{PR}]_0}{[C_{PR}]} \tag{16}$$

According to Eq. (16), a plot of $\ln([C_{Pi}]_0/[C_{Pi}])$ against $\ln([C_{PR}]_0/[C_{PR}])$ must yield to a straight line which slope is the ratio of rate constants; as k_{OHR} is known, k_{OHi} can then be determined. Following this procedure, a value of 4.0×10^9 l/mol s was obtained for the rate constant for the reaction of carbofuran with $OH^\bullet$ radicals.

Finally, two carbofuran decomposition experiments were carried out by the simultaneous action of UV radiation plus the Fenton's reagent (photo-Fenton system, experiments UVF-1

and UVF-2 depicted in Table 2). Fig. 7 also shows the carbofuran degradation curves with reaction time: it is observed extremely high disappearance rate of the pesticide with the highest initial concentration of H_2O_2 and Fe^{2+} (experiment UVF-2). Table 2 reports the pseudo-first-order rate constants k_t obtained. These values of k_t are much higher than those obtained for the former oxidation systems (k_p for single photodecomposition, k_t for the combination UV/H_2O_2 and k_F for the Fenton's reagent). These findings confirm the significant contribution of the radical pathway due to the additional generation of hydroxyl radicals in the photo-Fenton system.

In order to determine this additional radical contribution, it must be taken into account the whole mechanism with the different single reactions accounting for the global process. Thus, in addition to reactions (9) and (12), corresponding to the direct photodecomposition and the generation of hydroxyl radicals by the Fenton's reagent, respectively, it must be considered another hydroxyl radicals generation reaction due to the photolysis of H_2O_2 which is represented by Eq. (7). Moreover, the Fenton's reaction can be made catalytic in presence of UV radiation. In effect, the Fe^{3+} generated in the Fenton's reaction can be photoreduced in the near UV region according to Eq. (17) that besides the formation of Fe^{2+}, constitutes an additional source of $OH^\bullet$ radicals.

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH^\bullet \tag{17}$$

According to the mechanism described by Eqs. (7), (8), (9), (12) and (17), the determination of the hydroxyl radicals contribution to the global reaction can be performed again by using Eq. (11). In this case, and according to the previous considerations, the rate r_R (and subsequently the rate constant k_r) is expected to be higher than in the former system UV/H_2O_2 for experiments performed with similar initial concentration of hydrogen peroxide. Table 2 depicts the k_r values obtained: it is clearly seen the confirmation of the previous supposition (compare experiments UVH-1 to UVF-1; and UVH-2 to UVF-2). In addition, the value of the pseudo-first-order rate constant obtained for the photo-Fenton system is higher than the sum of the rate constants calculated for the photochemical, UV/H_2O_2 and Fenton's reagent processes ($k_p + k_t + k_F$ in Table 2). Therefore, there is a synergic effect of the different reactions generating $OH^\bullet$ radicals which enhances the efficiency of the photo-Fenton system. Even the photolysis of Fe(III)-organic intermediate quelates and $[FeOOH]^{2+}$ has been reported to contribute to this enhancement [25].

Similarly to the former UV/H_2O_2 system, the theoretical degradation curves for carbofuran have been calculated by using the computer program ACUCHEM and the contribution of the photochemical and radical reactions has been established. In the photo-Fenton system the contribution of the direct photochemical reaction is not significant, with values of 16 and 2% in experiments UVF-1 and UVF-2, respectively. Therefore, the energy emitted by the lamp is mainly absorbed by hydrogen peroxide and Fe(III).

4. Conclusions

In the ozonation of carbofuran, the temperature and ozone partial pressure present a positive effect on the removal rate of the pesticide, while similar degradations are obtained for experiments at pH 2 and 9 which indicates a negligible contribution of the reaction

with hydroxyl radicals generated by the ozone self-decomposition at pH 9. The apparent pseudo-first-order rate constants for the ozonation reaction are evaluated and lay in the range 5.1×10^{-4} to $19.5 \times 10^{-4}\,\text{s}^{-1}$. The true rate constant for the reaction between ozone and carbofuran at 20°C was deduced from a competition kinetic model, its value being 1108 l/mol s. The combination of ozone plus UV radiation enhances the degradation rate due to the contribution of the hydroxyl radicals, which are now generated in this process by the photolysis of ozone. The pseudo-first-order rate constant derived for this combined reaction was $22.8 \times 10^{-4}\,\text{s}^{-1}$, three times higher than that obtained when conventional ozonation was applied under similar experimental conditions.

The photodecomposition of carbofuran by the polychromatic UV radiation used presents a lower efficiency than the ozonation process, with a pseudo-first-order rate constant of $3.3 \times 10^{-4}\,\text{s}^{-1}$. On the other hand, the combination of this UV radiation with hydrogen peroxide increases the degradation levels, with rate constants of 7.1×10^{-4} and $43.5 \times 10^{-4}\,\text{s}^{-1}$ for initial hydrogen peroxide concentrations of 5×10^{-4} and $5 \times 10^{-3}\,\text{M}$, respectively. A general reaction mechanism is proposed for this combined process. The corresponding pseudo-first-order rate constant k_r for the radical reaction obtained from its data were 3.8×10^{-4} and $40.2 \times 10^{-4}\,\text{s}^{-1}$.

The carbofuran oxidation by the Fenton's reagent alone reveals a destruction power lower than the preceding single oxidants, ozone and UV radiation, with pseudo-first-order rate constants in the range 2.2×10^{-4} to $7.1 \times 10^{-4}\,\text{s}^{-1}$. In this process, an increase in the initial concentrations of hydrogen peroxide and ferrous ions provides an enhancement in the degradation rates. The simultaneous oxidation by the Fenton's reagent of the mixture carbofuran/2,4-dichlorophenol and the use of a competition kinetic method enabled the determination of the specific rate constant k_{OH} for the reaction between carbofuran and the hydroxyl radicals, its value being 4.0×10^9 l/mol s. When the Fenton's reagent is accompanied by UV radiation (photo-Fenton system), an increase in the apparent pseudo-first-order rate constants is obtained in comparison to the former UV/H_2O_2 system, due to a higher production of hydroxyl radicals. The evaluation of the apparent rate constants for the radical reaction from the proposed reaction mechanism leads to values of 17.2×10^{-4} and $>200 \times 10^{-4}\,\text{s}^{-1}$ for the initial concentrations of oxidants used in this work.

A synergic effect is observed in the photo-Fenton system due to the generation of OH$^\bullet$ radicals in several reactions and to the catalytic character of the Fenton's reaction in presence of UV radiation. Thus, for the oxidant concentrations applied in this research, the efficiency of the photo-Fenton system is even higher than that of the conventional ozonation and the AOP O_3/UV. Therefore, the photo-Fenton process has potential for the degradation of refractory organic pollutants. However, more studies prior industrial applications are needed in order to determine the optimal conditions of oxidation (pH, doses of reactants and UV, reactor configuration, etc.) and to estimate the treatment costs.

Acknowledgements

References

[1] S. Chiron, A. Fernandez-Alba, A. Rodriguez, E. Garcia-Calvo, Pesticide chemical oxidation: state-of-the-art, Water Res. 34 (2000) 366–377.

[2] R.G. Rice, Ozone treatment of hazardous materials, AIChE Symp. Ser. 77 (1981) 79–107.

[3] J.P. Scott, D.F. Ollis, Environ. Progr. 14 (1995) 88–103.

[4] S.J. Masten, S.H. Davies, The use of ozonation to degrade organic contaminants in wastewaters, Environ. Sci. Technol. 28 (1994) 180A–185A.

[5] D.F. Ollis, E. Pelizzetti, N. Serpone, Photocatalyzed destruction of water contaminants, Environ. Sci. Technol. 25 (1991) 1523–1529.

[6] C. Walling, Fenton's reagent revisited, Acc. Chem. Res. 8 (1975) 125–131.

[7] J. Gallard, J. De Laat, Kinetics of oxidation of chlorobenzenes and phenyl-ureas by Fe(II)/H_2O_2 and Fe(III)/H_2O_2: evidence of reduction and oxidation reactions of intermediates by Fe(II) or Fe(III), Chemosphere, 2001, in press.

[8] R.T. Meijers, E.J. Oderwald-Muller, P.A.N.M. Nuhn, J.C. Kruitof, Degradation of pesticides by ozonation and advanced oxidation, Ozone Sci. Eng. 17 (1995) 673–686.

[9] W.S. Kuo, Destruction of toxic organics in water by an injection-type downflow UV/O_3 oxidation reactor, Ozone Sci. Eng. 21 (1999) 539–550.

[10] R. Doong, W. Chang, Photoassisted iron compound catalytic degradation of organophosphorous pesticides with hydrogen peroxide, Chemosphere 13 (1998) 2563–2572.

[11] E. Brillas, J.C. Calpe, J. Casado, Mineralization of 2,4-D by advanced electrochemical oxidation processes, Water Res. 34 (2000) 2253–2262.

[12] C.R. Worthing, The Pesticide Manual: A World Compendium, Published by the British Crop Protection Council, 8th Edition, 1988.

[13] H. Bader, V. Sturzenegger, J. Hoigne, Photometric method for the determination of low concentrations of hydrogen peroxide by the peroxidase catalyzed oxidation of *N,N*-diethyl-*p*-phenylenediamine, Water Res. 22 (1988) 1109–1115.

[14] F.J. Benitez, J. Beltran-Heredia, J.L. Acero, F.J. Rubio, Rate constants for the reactions of ozone with chlorophenols in aqueous solutions, J. Hazard. Mater. 79 (2000) 269–283.

[15] J. Hoigne, Chemistry of aqueous ozone and transformation of pollutants by ozonation and advanced oxidation processes, in: J. Hrubec (Ed.) The Handbook of Environmental Chemistry, Vol. 5. Part C. Quality and Treatment of Drinking Water II, Springer, Berlin, Germany, 1998.

[16] J. Staehelin, J. Hoigne, Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide, Environ. Sci. Technol. 16 (1982) 676–681.

[17] J. Hoigne, H. Bader, Rate constants of reactions of ozone with organic and inorganic compounds in water. Part I. Non dissociating organic compounds, Water Res. 17 (1983) 173–184.

[18] F. Xiong, N.J.D. Graham, Rate constants for herbicide degradation by ozone, Ozone Sci. Eng. 14 (1992) 283–301.

[19] J.Y. Hu, T. Morita, Y. Magara, T. Aizawa, Evaluation of reactivity of pesticides with ozone in water using the energies of frontier molecular orbitals, Water Res. 34 (2000) 2215–2222.

[20] G.R. Peyton, F.Y. Huang, J.L. Burleson, W.H. Glaze, Destruction of pollutants in water with ozone in combination with ultraviolet radiation. Part I. General principles and oxidation of tetrachloroethylene, Environ. Sci. Technol. 16 (1982) 449–453.

[21] D.W. Sundstron, B.A. Weir, H.E. Klei, Destruction of aromatic pollutants by UV light catalyzed oxidation with hydrogen peroxide, Environ. Progr. 8 (1989) 6–11.

[22] Y.S. Shen, Y. Ku, K.C. Lee, The effect of light absorbance on the decomposition of chlorophenols by ultraviolet radiation and UV/H_2O_2 processes, Water Res. 29 (1995) 907–914.

[23] W. Braun, J.T. Herron, D.K. Kahanar, ACUCHEM: a computer program for modeling complex reaction systems, Int. J. Chem. Kinet. 20 (1988) 51–62.

[24] F.J. Benitez, J. Beltran-Heredia, J.L. Acero, F.J. Rubio, Oxidation of several chloro-phenolic derivatives by UV irradiation and hydroxyl radicals, J. Chem. Technol. Biotechnol. 76 (2001) 312–320.

[25] J.J. Pignatello, D. Liu, P. Huston, Evidence of an additional oxidant in the photoassisted Fenton reaction, Environ. Sci. Technol. 33 (1999) 1832–1839.