Diclofenac removal from water with ozone and activated carbon

Fernando J. Beltrán [a],*, Pablo Pocostales [a], Pedro Alvarez [a], Ana Oropesa [b]

[a] Departamento de Ingeniería Química y Química Física, Universidad de Extremadura, Avenida de Elvas S/N, 06071 Badajoz, Spain
[b] Departamento de Sanidad Animal, Universidad de Extremadura, Avenida de Elvas S/N, 06071 Badajoz, Spain

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ABSTRACT

Diclofenac (DCF) has been treated in water with ozone in the presence of various activated carbons. Activated carbon-free ozonation or single ozonation leads to a complete degradation of DCF in less than 15 min while in the presence of activated carbons higher degradation rates of TOC and DCF are noticeably achieved. Among the activated carbons used, P110 Hydraffin was found the most suitable for the catalytic ozonation of DCF. The influence of pH was also investigated. In the case of the single ozonation the increasing pH slightly increases the TOC removal rate. This effect, however, was not so clear in the presence of activated carbons where the influence of the adsorption process must be considered. Ecotoxicity experiments were performed, pointing out that single ozonation reduces the toxicity of the contaminated water but catalytic ozonation improved those results. As far as kinetics is concerned, DCF is removed with ozone in a fast kinetic regime and activated carbon merely acts as a simple adsorbent. However, for TOC removal the ozonation kinetic regime becomes slow. In the absence of the adsorbent, the apparent rate constant of the mineralization process was determined at different pH values. On the other hand, determination of the rate constant of the catalytic reaction over the activated carbon was not possible due to the effect of mass transfer resistances that controlled the process rate at the conditions investigated.

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1. Introduction

Nowadays, pollution in the aquatic environment is an important issue to consider and study. Everyday new pollutants are found and the conventional methods of water treatment seem to be insufficient in the removal of these contaminants. In the last years especially concerning is the case of pharmaceuticals and their metabolites. After human consumption most of these compounds are excreted and make their way into the sewage system, easily reaching the environment due to an incomplete degradation in the sewage treatment plant [1–3]. Although municipal water is the main source of those pollutants to the environment, other ways of contamination such as production points of this kind of compounds and incorrect disposals should also be considered [4]. The risks of aquatic life to the exposure to these compounds have been a growing concern in recent years, along with its effects on human health [5].

Diclofenac (DCF) is a non-steroidal antiflammatory drug, used as an analgesic, to reduce inflammation in arthritis, rheumatic conditions and even to ease menstrual pain. Also it can be found marketed

as Flector patch, Voltarol, Voltaren, Diclo, etc. As literature reports, DCF is one of the pharmaceuticals most detected in water sources, it can be detected in influents and effluents from water treatment plants at concentrations up to μg/L level [6,7]. Under normal conditions this pharmaceutical species is relatively stable, but as others non-steroidal antiflammatory drugs is photochemical active, this mechanism likely being the main decomposition pathway on the surface water [8].

As literature reports, biological treatments seem to be inefficient on the degradation of this compound, being necessary the study of new technologies such advance oxidation processes (AOPs) to avoid the contamination of natural waters [9]. Ozonation and AOPs are widely studied and used on the removal of non-biodegradable compounds, allowing a good elimination of the pollutants and the final mineralization of the by-products formed. Recently, some researches have been published on the capacity of AOPs to remove DCF from water [10–13]. However, among the various advanced oxidation processes proposed on the degradation of this compound the combination of ozone and activated carbons has not yet been investigated.

On this paper, ozonation of DCF in the presence of three different activated carbons has been studied as a method to remove this compound and its ozonation by-products. The aim of this study focuses on the synergistic effect of ozone and activated carbon, to establish the mechanisms that take place on the system with the determi-
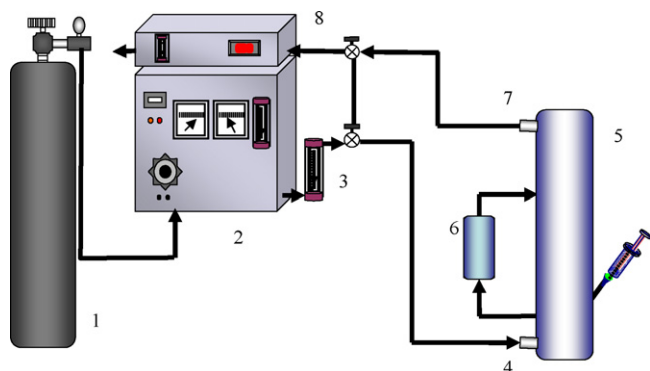
Fig. 1. Experimental set-up for ozonation experiments. 1, Oxygen cylinder; 2, ozone generator; 3, flow meter; 4, gas inlet; 5, column reactor; 6, catalyst bed; 7, gas outlet; 8, ozone analyzer.

nation of the ozonation kinetic regime and observe the toxicity of ozonated samples.

2. Materials and methods

DCF was obtained from Sigma–Aldrich and used as received. All the solutions were buffered in ultrapure water (Millipore Q Millipore system) at pH 7 with NaH_2PO_4 and Na_2HPO_4 and ionic strength at 0.05 M. The commercial activated carbons used were: P110 Hydraffin, Darco 12–20, and GMI2000 obtained from Lurgy, Aldrich and Galaquim S.L., respectively. The particle size selected for all the carbons was 1–1.25 mm. Textural characterization of activated carbons was accomplished by adsorption of nitrogen at 77 K (Quantachrome Autosorb-1 automated gas adsorption system) and by mercury porosimetry (Thermo Scientific Pascal 240 porosimeter device). Chemical surface of activated carbon samples was characterized by analyzing the concentration of surface oxygen groups and the point of zero charge, pH_{PZC}, by the Boehm and Noh and Schwarz's methods, respectively [14,15].

Fig. 1 shows the experimental set-up. A tubular glass reactor (300 mm-long and 50 mm-diameter) with a porous plate at the bottom of the reactor was used in series with a 30 mm-long, 30 mm-diameter packed bed column for all experiments. The tubular reactor was used as ozonation chamber while the activated carbon laid down on the bed reactor. The aqueous solution was continuously recirculated at a flow rate of 2 L h^{-1} from the tubular reactor through the bed reactor with a 7418-00 Easy-load Masterflex peristaltic pump. A 250 cm^3 aqueous solution was charged on the reactor with approximately 30 mg L^{-1} (10^{-4} M) of DCF and the bed was filled up with 5 g of activated carbon. Ozone was produced from oxygen in a Sander Laboratory Ozonator. The gas flow rate was 25 L h^{-1} with an ozone concentration of 20 mg L^{-1}. Samples were withdrawn with a syringe from the reactor and prior the analysis they were filtered using 0.45 μm Millipore filters.

DCF concentration was determined by high-performance liquid chromatography with a L-2455 Hitachi diode array detector. Detection was made at 277 nm. The analysis was performed with a 250 mm length, 4.60 mm i.d. 4 μm Hydro-RP 80A Phenomenex Synergi column. A mixture of methanol–water (containing 0.1% phosphoric acid) (80:20, v/v) in isocratic mode at a flow rate of 0.6 mL min^{-1} was used as mobile phase. Some by-products (carboxylic acids) were identified and monitored by HPLC using a Supercogel C610H column (Supelco) and the diode array detector. In this case, acidified water was used as mobile phase at 0.75 mL min^{-1} flow rate and detection was made at 210 nm.

Prior sample filtration, dissolved ozone concentration was measured by the method proposed by Bader and Hoigné [16]. In the gas,
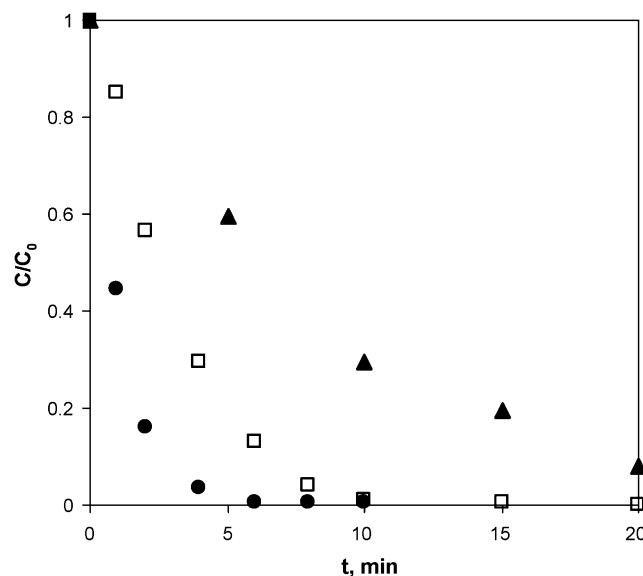

Fig. 2. Time evolution curves of dimensionless concentration of DCF. Conditions: initial concentration, 30 mg L^{-1}; $T = 20$ °C; pH 7; liquid recirculation flow rate = 2 L h^{-1}; gas flow rate, 25 L h^{-1}; (▲) adsorption P110 Hydraffin; (□) ozonation; (●) ozonation in the presence of P110 Hydraffin.

ozone concentration was followed with an Ozomat GM-6000-PRO ozone analyzer. Hydrogen peroxide concentration was determined from the formation of a complex between cobalt (II) and hydrogen peroxide [17]. Aromaticity of the solution was simply monitored by spectrophotometric determination at 254 nm and total organic carbon was measured with a Shimadzu TOC-V$_{CSH}$ analyzer.

Ecotoxicity of the initial DCF solution and ozonated solutions was determined with *Daphnia magna* immobilization essays. Acute toxicity *Daphnia* tests were conducted following the commercial test kit DAPHTOXKIT F^{TM} (Creasel BVBA; Deinze, Belgium) using the water flea *D. magna*. These tests were performed in accordance with testing conditions prescribed by OECD Guideline 202 (*Daphnia* sp. Acute Immobilization Test) [18]. Immobility was observed after 24 and 48 h with the latter being the endpoint for effect calculation. A *Daphnia* was considered to be immobile if it does not move after 15 s of gentle agitation. Immobilization of the animals leads to their death because of inherent impossibility of capturing food. A limit test was performed with the solutions in order to demonstrate that the EC$_{50}$ (EC$_{50}$ is the concentration estimated to immobilize 50% of the daphnids within a stated exposure period) is greater than the concentration sampled. When the percentage of immobilization is minor or equal 10% at the end of the test (48 h), it can be considered that solution does not show acute toxicity to *D. magna*. Potassium dichromate ($K_2Cr_2O_7$) was the reference chemical used. An EC$_{50}$ 24 h of 1.72 mg L^{-1} was obtained for the reference compound which is within the range of the 0.6–2.1 mg L^{-1} stipulated in the ISO 6341 to ensure test validity [19]. No swimming inhibition was observed in the controls exposed in each plate.

3. Results and discussion

Three different activated carbons were used to study its capacity on the catalytic ozonation of DCF and ozonation by-products. Table 1 shows the characterization of the adsorbents. Both GMI2000 and P110 Hydraffin were basic activated carbons (see pH_{pzc}) and the latter presents the highest B.E.T. surface area. These activated carbons have shown its capacity for the adsorption of other chemicals such as phenols and carboxylic acids [20].

Table 1
Characterization of activated carbons used

Activated carbon type	S_{BET} (m²/g)	ρ_p (g/cm³)	ρ (g/cm³)	Microporosity (%)	V_{me} (cm³/g)	V_{mi} (cm³/g)	Average pore radius (μm)	pH$_{pzc}$
Darco	659	0.61	1.98	48.8	0.51	0.162	1.879	6.35
GMI2000	683	0,81	1.56	78.1	0.160	0.333	1.891	9.23
P110 Hydraffin	950	0.81	2.03	78.1	0.132	0.395	1.907	9.72

ρ_p, apparent density; ρ, real density; V_{me}, mesopore volume, V_{mi}, micropore volume.

Fig. 2 presents the dimensionless change of the concentration of DCF with time, in buffered solution at pH 7, corresponding to ozonation, adsorption (P110 Hydraffin) and combination of both systems (ozone and P110 Hydraffin). As can be seen from Fig. 2 DCF can be removed from water through the three systems investigated but with different rates. Thus, at the conditions applied, about 93% DCF removal is achieved after 20 min with adsorption while single ozonation allows complete elimination of DCF in less than 15 min of reaction. In any case, the simultaneous combination of ozone and activated carbons leads to degradation rates higher than with single ozonation and single adsorption. The increase of DCF removal rate observed with the combined effect of ozone and activated carbon cannot be due to some sort of catalytic activity but to the sum of adsorption and ozonation effects. The reason is due to the very fast direct ozone reaction with DCF and first aromatic intermediates (not detected in this work but confirmed with the evolution of aromaticity, as shown later). At these conditions, ozone is consumed in the proximity of the gas liquid interface, then it is unlikely that ozone decomposes on the carbon surface in free radicals to accelerate the oxidation rate. The absence of dissolved ozone during this initial reaction period reinforces this conclusion [21]. The results obtained with the other two activated carbons are similar. The three solids seem to have, then, a similar capacity of adsorption and degradation of the studied compound. On the other hand, the fact that the compound reacts so fast with ozone makes more necessary the study of the process in terms of total organic carbon removal that represents in a better way the real capacity of the catalyst to deal with mineralization of the DCF and by-products ozonation. Thus, in Fig. 3 the changes of TOC with time corresponding to experiments of single ozonation and ozone-activated carbon

oxidation are shown. As can be observed from Fig. 3 ozone alone leads to a fast TOC removal rate during the first 20 min of reaction. Then, TOC decreases more slowly to reach a stationary value after 2 h reaction (40% TOC removal is achieved after 120 min). In the case of the combined process and regardless of the activated carbon used, TOC removal rates are higher during all reaction time investigated (between 90 and 95% TOC removal in 120 min). During the process, carboxylic acids such as maleic, malonic, pyruvic and oxalic acids are formed. Since these secondary reaction products do not react with ozone [22], show some polar character and, then, they poorly adsorb on activated carbons, TOC removal should be due to the catalytic or promoting effect of activated carbon in decomposing ozone to yield hydroxyl radicals. Notice that hydroxyl radicals do react with carboxylic acids [23]. Then, mineralization achieved can be attributed to free radicals action as also observed in previous works [24]. Also, experimentally observed in this work, most of these acids disappear with time except oxalic and pyruvic acids that accumulate in water although eventually they also start to disappear as shown in Fig. 4. As commented above, the more refractory character of these acids explains these results.

Though the three activated carbons used in this work show a similar capacity on TOC removal, in terms of ozone consumption (defined as mg of ozone consumed per mg TOC eliminated), some differences can be noticed. Thus, Fig. 5 shows the ozone consumption values for the ozonation of DCF in the presence and absence of activated carbons used. As observed from Fig. 5, ozone consumption in any ozone-activated carbon oxidation process and for any reaction time is lower than that measured in the ozonation alone system. Also, basic activated carbons allow lower ozone consumption. These results are in agreement with others previously
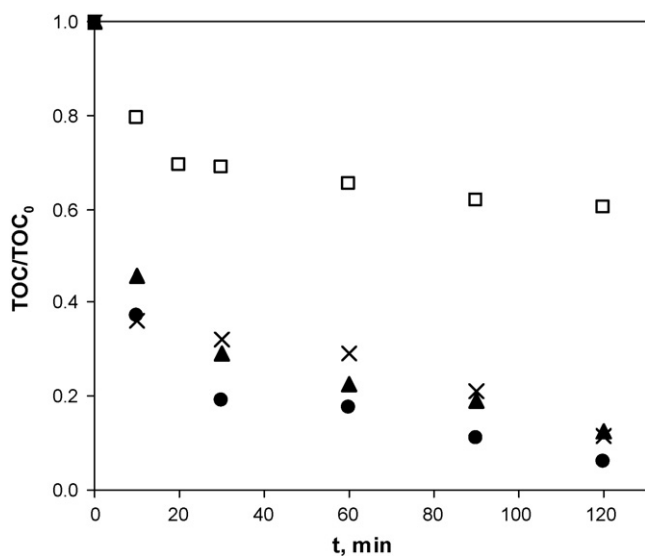

Fig. 3. Time evolution curves of normalized TOC. Conditions: initial TOC, 15 mg L; T = 20 °C; pH 7; liquid recirculation flow rate, 2 L h⁻¹; gas flow rate, 25 L h⁻¹; (□) ozonation; (●) ozonation-Darco; (▲) ozonation P110 Hydraffin; (×) ozonation-GMI2000.
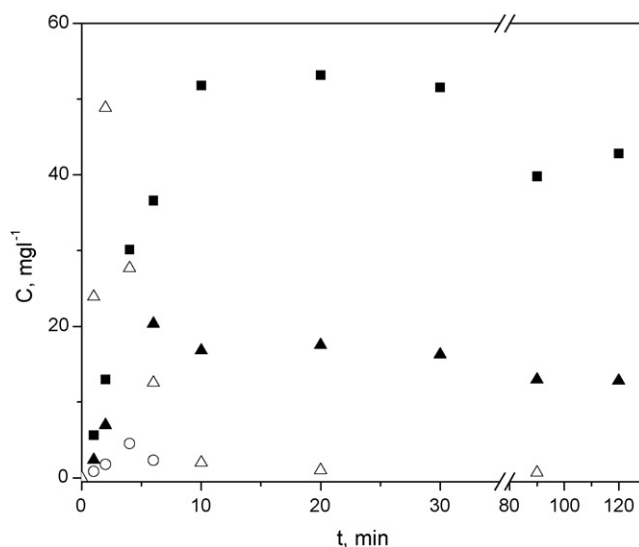

Fig. 4. Time evolution curves of the concentration of some carboxylic acid detected on the catalytic ozonation in the presence of P110 Hydraffin-activated carbon. Conditions: initial TOC, 15 mg L⁻¹; T = 20 °C; pH 7; liquid recirculation flow rate, 2 L h⁻¹; gas flow rate, 25 L h⁻¹; (■) oxalic acid; (▲) pyruvic acid; (×) acetic acid; (△) formic acid; (○) maleic acid.
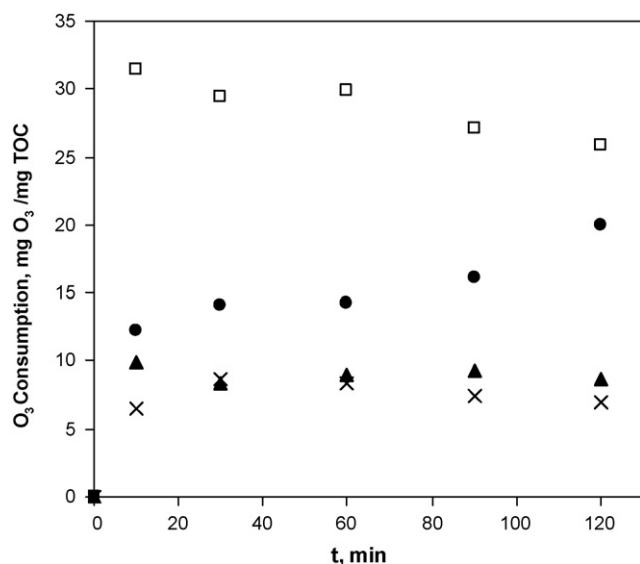
Fig. 5. Change of ozone consumption with time as mg of O_3 per mg of removed TOC. Conditions: initial TOC, 15 mg L; $T = 20\,^\circ C$; pH 7; liquid recirculation flow rate, 2 L h^{-1}; gas flow rate, 25 L h^{-1}; ($\square$) ozonation alone; ($\bullet$) ozonation-Darco; ($\blacktriangle$) ozonation-P110 Hydraffin; ($\times$) ozonation-GMI2000.

Fig. 6. Equilibrium adsorption isotherms of ozonation intermediates on the activated carbons used (n_e: g adsorbed TOC/g of activated carbon; C_e: TOC at Equilibrium in water). Conditions: initial TOC, 15 mg L; $T = 20\,^\circ C$; pH 7. Symbols: ($\square$) GMI2000; ($\blacktriangle$) Darco; ($\diamond$) P110 Hydraffin.

published on the influence of surface oxygen groups of activated carbons to improve the ozone decomposition to yield hydrogen peroxide. Thus, Alvarez et al. [25], while studying the ozone decomposition in water in the presence of different activated carbons, proposed a mechanism involving the ozone decomposition on basic surface oxygen groups such as 4-pyrone and 4H-chromene present in the activated carbon. The authors also reported that some type of surface oxygen groups such as phenolic structures could react with ozone. In all these surface reactions hydrogen peroxide is formed. Then, hydrogen peroxide reacts with the activated carbon surface or with ozone itself to yield hydroxyl radicals. In the present work, hydrogen peroxide has also been detected and its concentration measured as discussed below.

3.1. Equilibrium and kinetics of the adsorption of ozonation by-products

In addition to the importance of surface oxygen groups, the adsorption capacity of the carbons used has also been checked in this work. Thus, adsorption isotherms of the ozonation by-products (that, after an initial short period, constitute the TOC present in water) were determined. From ozonation results, after the first 10 min of ozonation, DCF has been totally eliminated and the solution contains a mixture of saturated and unsaturated carboxylic acids and other intermediates (some of them not identified). Solutions at these conditions were prepared and the equilibrium adsorption on the activated carbons used was measured as presented in Fig. 6. As can be seen from Fig. 6, up to TOC values about 9 mg L^{-1} P110 Hydraffin and Darco-activated carbons present similar adsorption capacity but over this concentration the isotherm prepared with GMI2000-activated carbon is coincident with that made with P110 Hydraffin. Then, P110 Hydraffin-activated carbon seems to be the most suitable for TOC adsorption on the whole range of concentrations investigated (up to 12 mg L^{-1} of TOC). In summary, P110 Hydraffin-activated carbon leads to the lowest ozone consumption values and presents the highest adsorption capacity for ozonation-by-products. As a consequence, herein this activated carbon was selected for the rest of experimental series.
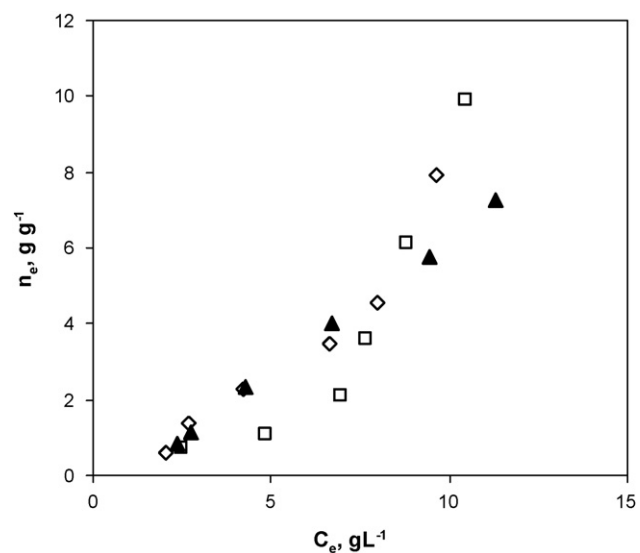
Since TOC present in water after the first 10–20 min ozonation is mainly due to saturated compounds (i.e. carboxylic acids), the kinetics of the adsorption process of intermediates was then carried out. Thus, some ozone-activated carbon DCF oxidations were carried out for a short reaction period (between 5 and 20 min) and then ozone feeding was stopped to follow the single effect of adsorption on intermediates formed (measured as TOC). As Fig. 7 shows the longer the time ozone was initially applied the lower the adsorption capacity of P110 Hydraffin-activated carbon to remove intermediates from water. The lower adsorption capacity is likely due to the increase of the polarity of intermediates with ozone time applied. According to this, if ozone and activated carbon are
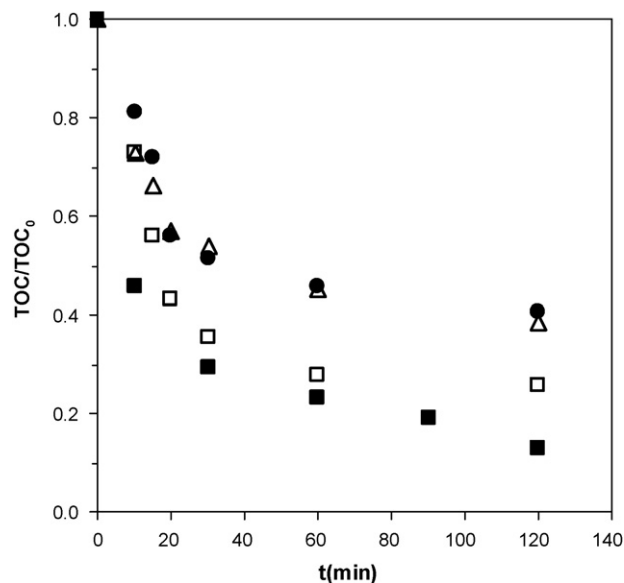

Fig. 7. Dimensionless change of TOC of the adsorption process in the presence of P110 Hydraffin-activated carbon after catalytic ozonation of the parent compound at various reaction time. Conditions: initial TOC, 15 mg L; $T = 20\,^\circ C$; pH 7; liquid recirculation flow rate, 2 L h^{-1}; gas flow rate, 25 L h^{-1}; symbols: ($\blacksquare$) catalytic ozonation; ($\square$) 5 min reaction plus adsorption; ($\triangle$) 10 min reaction plus adsorption; ($\bullet$) 20 min reaction plus adsorption.
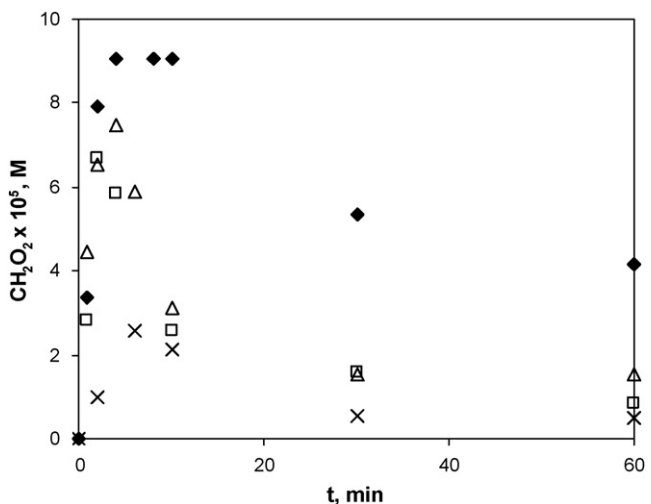
Fig. 8. Time evolution curves of hydrogen peroxide from ozonation experiments. Conditions: initial TOC, $15\,mg\,L^{-1}$; $T=20\,°C$; pH 7; liquid recirculation flow rate, $2\,L\,h^{-1}$; gas flow rate, $25\,L\,h^{-1}$ symbols: Without activated carbon: ($\square$) pH 9; ($\triangle$) pH 7; ($\blacklozenge$) pH 5. With activated carbon ($\times$) pH 7.

Fig. 9. Time evolution curves of normalized TOC during the ozonation process in the presence (void symbols) and absence (solid symbols) of activated carbon. Conditions: initial TOC, $15\,mg\,L^{-1}$; $T=20\,°C$; liquid recirculation flow rate, $2\,L\,h^{-1}$; gas flow rate, $25\,L\,h^{-1}$; symbols: ($\blacksquare$) ($\square$), pH 9; ($\blacktriangle$) ($\triangle$), pH 7; ($\blacklozenge$) ($\lozenge$), pH 5.

continuous and simultaneously applied (see Fig. 7) TOC removal should mainly be due to the catalytic or promoting action of activated carbon to decompose ozone although the activated carbon adsorption capacity for intermediates that depend on pH of water, pK of acids and pH_{pzc} also play an important role (see later pH effect).

3.2. Formation of hydrogen peroxide

In the ozone-activated carbon processes, aromatic compounds and hydrogen peroxide play a key role in TOC removal [26]. As has been experimentally observed in this work, the aromaticity of the ozonated DCF aqueous solution increases during the first 2 min of the reaction and then it decreases through the whole reaction period (not shown). Literature reports high reaction rates for the ozonation of aromatic compounds, especially those with substituting groups that activate the electrophilic substitution reactions of ozone [27]. DCF molecular structure also presents aromatic rings and some nucleophilic points that facilitate the electrophilic reactions of ozone. In these reactions hydrogen peroxide is formed [28] as experimentally observed in this work (see Fig. 8). This also confirms the fast consumption of DCF in ozone processes (see later kinetic study). As far as hydrogen peroxide concentration is concerned Fig. 8 presents the changes of its concentration with time in ozonation experiments in the presence and absence of activated carbon. Formation of hydrogen peroxide is due to two possible mechanisms of reactions: the direct reactions of ozone with DCF, aromatic and unsaturated organics intermediates formed during the first minutes of the process and the ozone decomposition on the activated carbon surface. As it is seen from Fig. 8, in all cases, hydrogen peroxide concentration first increases with time and then it decreases to follow a similar trend to that observed for TOC removal. Also, hydrogen peroxide concentration in the presence of activated carbon is lower than in its absence. The lower hydrogen peroxide formation during the ozone-activated carbon process is undoubtedly due to its reactivity with the activated carbon surface where likely reacts with adsorbed ozone to yield hydroxyl radicals [26]. Notice that the main initiation step of the mechanism of ozone processes in water to yield hydroxyl radicals is the hydrogen peroxide-ozone reaction.
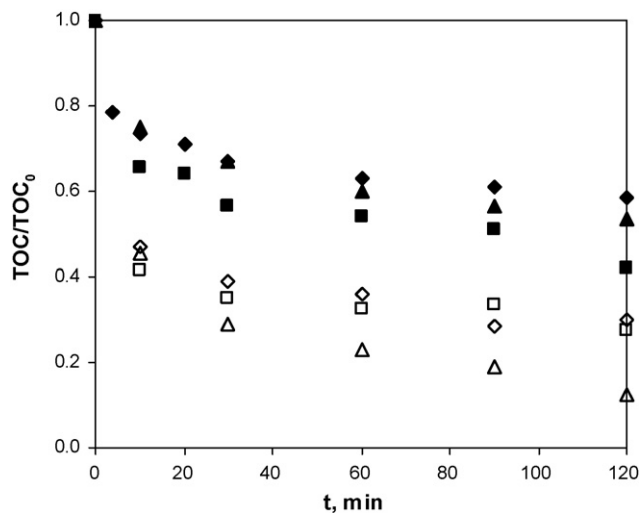
3.3. Effect of pH

Since ozone only reacts with the ionic form of hydrogen peroxide [29] the increase of pH should increase the mineralization rate of TOC. This has also been checked in this work. Thus, Fig. 9 presents the TOC/TOC_0 changes with time corresponding to experiments of DCF ozonation in the presence and absence of P110 Hydraffin-activated carbon at three pH values: 5, 7 and 9. As can be seen from Fig. 9 the effect of pH on TOC removal depends on the presence or absence of activated carbon. Thus, in the absence of activated carbon there is a clear positive effect of pH on the TOC removal rate that can be explained because of the dissociating character of hydrogen peroxide whose ionic form predominates with the increasing pH, thus favoring the formation of free radicals. In ozonation alone processes TOC removal percentages of 43, 46 and 59% are achieved after 120 min reaction at pH 5, 7 and 9, respectively. In ozone-activated carbon processes, however, TOC removal percentage is similar at pH 5 and 9 (about 75% in 120 min) and higher at pH 7 (90% in 120 min). It is observed from Fig. 9 that the highest TOC removal rates are achieved during the first 10 min of ozonation where about 55% TOC removal is achieved. In this initial period TOC adsorption, direct ozone reactions and hydrogen peroxide formation from direct ozone reactions can explain the results. After this first reaction period, the concentration of saturated intermediates increase, they show more polar character and are less reactive towards ozone. Since there is no a positive effect of pH, when activated carbon is also present, TOC removal rate cannot only be due to the action of free radicals formed from the hydrogen peroxide-ozone reaction where hydrogen peroxide comes from the ozone decomposition on the carbon surface. At these conditions other factors clearly affect the oxidation rate. These factors must be due to the interaction between the organic intermediates and the activated carbon surface. Most of the carboxylic acids formed during the process (pyruvic acid, oxalic acid, malonic acid, acetic acid, etc.) present pK_a values lower than the pH of the water, which means that the anionic species of the acids is the predominant form present in water. According to this and considering that the adsorption of these compounds is mostly due to electrostatic interactions, the adsorption process is favored with the decreasing pH. Thus, at pH 9, where the TOC removal rate is lower to that obtained at pH 7, the surface-

Time exposure to ozone	24 h (%) immobilization	48 h (%) immobilization
Blank, 0 min	85	100
Single ozonation, 10 min	75	85
Single ozonation, 120 min	0	15
Ozonation in presence of P110 Hydraffin	0	10

Initial concentration of DCF: 10^{-4} M.

activated carbon is nearly neutrally charged ($pH_{pzc} = 9.72$) and adsorption of anionic carboxylic acids diminishes. Then, possible surface reactions between these intermediates and adsorbed free radicals generated from any possible ozone-hydrogen peroxide surface reaction are less probable than at pH 7. On the contrary, adsorption of intermediates is favored at pH 5 but conditions for the ozone-hydrogen peroxide (ionic form) reaction to develop are more difficult. As a consequence pH 7 represents the best conditions for the ozone-activated carbon process to mineralize the organic content of water.

3.4. Stability and activity of Hydraffin-activated carbon

A very important point on the study of a catalyst and its role in a catalytic reaction is the stability and activity. In this work, four consecutive ozone-activated carbon experiments with the same sample of P110 Hydraffin-treating fresh DCF solutions each time were carried out. From the results obtained no apparent loss of capacity on the elimination of TOC was noticed after three cycles of use. Differences in activity start to be noticed after the fourth cycle of use. Thus, in the first three cycles of activated carbon use and after 60 min reaction about 83% TOC removal was measured while for the same conditions in the fourth cycle of use, approximately 75% TOC reduction was achieved. It is believed that this slight lost of activity is due to the lost of basic surface oxygen groups on the carbon surface as a result of their reaction with ozone. For example, in other experiments of the ozonation of P110 Hydraffin-activated carbon we noticed that after the four cycle of use the basic oxygen surface groups diminish from 650 (for non-ozonated activated carbon) to 537 (for ozonated activated carbon). On the other hand, the number of acid surface oxygen groups increase from 139 (for non-ozonated activated carbon) to 320 (for ozonated activated carbon). Also, the pH_{pzc} diminished from 9.7 (non-ozonated activated carbon) to 8.3 (ozonated activated carbon in fourth cycle of use). On the contrary, BET surface practically remained constant. Then, as a result of the ozonation the activated carbon becomes more acidic and, therefore, shows less active site for ozone transformation into hydroxyl radical as well as lower ability to adsorb ozonation by-products such as carboxylates. A more detailed discussion of the ozone-basic surface oxygen group's reactions is reported in a previous publication [25].

3.5. Ecotoxicity

Ecotoxicity analyses were made to determine the viability of the ozone-activated carbon process from an ecological point of view. The grade of ecotoxicity of a sample is measured in terms of *D. magna* immobilization. As can be seen in Table 2, the initial solution of DCF achieves total death of the crustacean after 48 h exposition. Similarly, after 10 min of single ozonation the solution also presents a high toxicity, at this point there is no DCF present in water but the intermediates formed lead to an elevated *D. magna* mortability. On the other hand, 2 h of single ozonation significantly reduces the toxicity of the contaminated water. Thus, in these samples, after 48 h exposition, only 15% of the organisms are death. At this time of reac-

tion, oxalic and pyruvic acids are the most concentrated species on the water along with other refractory compound not identified. As it can also be deduced from Table 2 the ozonation in the presence of activated carbon leads to the lowest toxicity compared to ozonation alone results.

### 3.6. Kinetics aspects of DCF ozone-activated carbon process

The kinetics of the ozone-activated carbon oxidation of DCF should be addressed by considering the fast direct reaction of ozone with DCF and the complexity of the reaction mixture, that, in addition, react more slowly with ozone. For the kinetics of these latter reactions, TOC has been selected as surrogate parameter representing the organic content of the water. Also, the process should be studied by first considering the ozonation alone system and then the combined ozone system.

3.6.1. The free activated carbon ozonation system

The ozone-DCF reaction is the first one taking place in this system. As a gas-liquid reaction mass transfer and chemical reaction must be considered to study the kinetics. The dimensionless number of Hatta (Ha) establishes the relative importance of chemical reaction and mass transfer rates and it allows classifying the ozonation kinetic regime [28]. For a second-order reaction, as most of ozone reactions in water [30], the Hatta number is defined as

$$Ha = \frac{\sqrt{k D_{O_3} C_B}}{k_L} \tag{1}$$

where k is the rate constant of the direct reaction between ozone and a compound B, D_{O_3} the diffusivity of ozone in water, C_B the concentration of B and k_L the individual liquid phase mass transfer coefficient. Literature reports values of ozone diffusivity and individual liquid side mass transfer coefficient of 1.3×10^{-9} m^2 s^{-1} [31] and 5×10^{-5} m s^{-1} [32], respectively. Also, the rate constant of the direct ozone-DCF reaction has been reported to be 10^6 M s^{-1} at pH 7 [33]. At the experimental conditions applied in this work, for an initial DCF concentration of about 10^{-4} M (C_B) the Hatta number of DCF-ozone reaction is higher than 3. In fact, Ha was higher than 3 for the first 3–6 min of ozonation, depending on the presence or absence of activated carbon. This means the DCF-ozone reaction was fast. Also, during this initial period of time dissolved ozone was not detected in water which supports the fast kinetic regime of ozonation [32]. The fast ozone-DCF reaction is undoubtedly due to the presence of nucleophilic points on the DCF molecular structure where electrophilic agents like ozone promptly react. Accordingly, the reaction of DCF and ozone first leads to some aromatics intermediates and then ring opening takes place (dipolar cycloaddition reactions [27]) where hydrogen peroxide is formed and unsaturated carboxylic acids appear. For example, in this work, maleic acid was detected and its concentration reaches a maximum of 1 mg L^{-1} after 2 min reaction. Due to ring opening and double bond addition reactions, during this initial period hydrogen peroxide concentration accumulates in water (see Fig. 8). As commented above, ozone reacts with the ionic form of hydrogen peroxide according to reaction (2) with a high reaction rate constant value ($k_1 = 2.8 \times 10^6$ M^{-1} s^{-1}) to generate hydroxyl radicals [24,29]. The fact that ozone only reacts with this ionic species makes this process be strongly conditioned by the pH and the hydrogen peroxide concentration (see also Figs. 8 and 9).

$$O_3 + HO_2^- \rightarrow O_3 \cdot + HO_2 \cdot \tag{2}$$
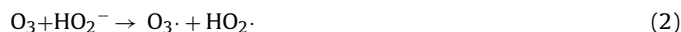
The effect of pH on the changes of hydrogen peroxide concentration during the single ozonation can be clearly seen in Fig. 8. At pH 5, due to the negligible concentration of HO_2^- species reaction (2) is
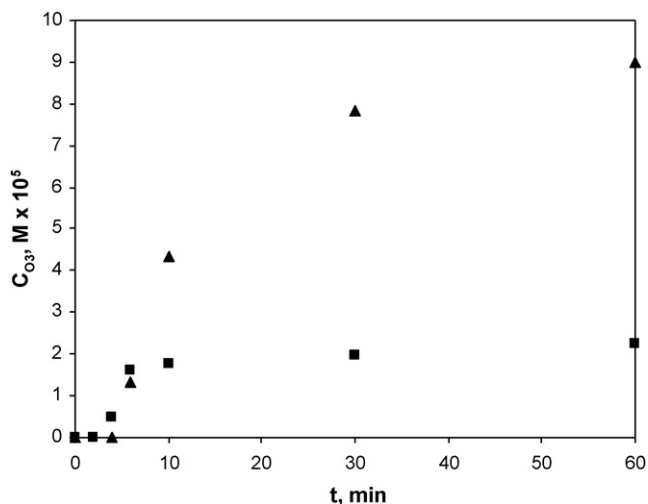
Fig. 10. Evolution of dissolved ozone concentration with time during the ozonation of DCF in the presence or absence of activated carbon. Conditions: initial TOC, 15 mg L^{-1}; $T = 20\,^\circ$C; liquid recirculation flow rate, 2 L h^{-1}; gas flow rate, 25 L h^{-1}; symbols: (▲) dissolved ozone-single ozonation; (■) dissolved ozone catalytic ozonation.

unfavored, the hydrogen peroxide concentration being higher and its decomposition rate slower than at pH 7 and 9. On the other hand, at higher pH, hydrogen peroxide reacts fast with ozone and its concentration remains low.

According to precedent comments, mineralization of organics in water during ozonation is a free radical process or advanced oxidation process. Due to the very complex matrix of the organics in water and since hydrogen peroxide and free radicals comes from the ozone reactions in water, for the kinetic study one simple reaction between ozone and the organic matter, with TOC as parameter representing its concentration, has been considered. The rate of ozonation is then given by the following equation:

$$r_{TOC} = -k_H C_{O_3} TOC \qquad (3)$$

where k_H is the apparent reaction rate constant of the homogenous reaction, C_{O_3} the dissolved ozone concentration and TOC the total organic carbon.

Because of the presence of dissolved ozone in water (just after a few minutes from the start of ozonation ozone starts to accumulates in water, see Fig. 10) the kinetic regime of TOC ozonation can be classified as slow. In the semibatch reaction system used, the TOC mass balance is then as follows [32]:

$$-z_H \frac{d\,TOC}{dt} = \frac{C_{O_3g} RT/He}{1/(k_L a) + 1/(k_H TOC)} \qquad (4)$$

where z_H is the stoichiometric ratio of the ozone-TOC reaction, $k_L a$ the volumetric mass transfer coefficient and He the Henry constant. In Eq. (4) the two fractions of the denominator correspond to the gas–liquid mass transfer ($1/k_L a$) and chemical reaction ($1/k_H TOC$) resistances. Eq. (4) can be integrated with the following limits:

$$\begin{aligned} t &= t_i \quad TOC = TOC_i \\ t &= t \quad TOC = TOC \end{aligned} \qquad (5)$$

where t_i and TOC_i is the time when dissolved ozone appears in water (then the kinetic regime is slow) and the corresponding TOC value, respectively. Integration of Eq. (4), once variables have been separated, yields Eq. (6):

$$\ln\left(\frac{TOC_i}{TOC}\right) = k_H \lambda \qquad (6)$$

where

$$\lambda = \int_{ti}^{t} \frac{C_{O_3g} RT}{z_H He} dt - \frac{TOC_i - TOC}{k_L a} \qquad (7)$$

and the stoichiometric ratio can be calculated as follows:

$$z_H = \frac{\upsilon_0 \int_{ti}^{t} (C_{O_3ge} - C_{O_3g}) dt - C_{O_3} V}{V(TOC_i - TOC)} \qquad (8)$$

where C_{O_3g} is the outlet gas ozone concentration, C_{O_3ge} the inlet ozone gas concentration, υ_0 the gas flow and V is the volume of reaction (values of z_H are coincident with those of ozone consumption shown in Fig. 5). In this procedure, $k_L a$ was experimentally obtained from ozone absorption experiments in organic free water ($k_L a = 0.184\,min^{-1}$). Eq. (6) was checked with the experimental results obtained in this work. Thus, the plot of $\ln(TOC/TOC_i)$ against λ (for different pH values) (not shown) leads to straight lines. The slopes of these lines obtained from least squares analysis give the values of the homogenous apparent rate constant of the TOC ozonation reaction at different pH conditions that were found to be 1.14 ± 0.01, 1.36 ± 0.05 and $1.51 \pm 0.10\,M^{-1}\,s^{-1}$ at pH 5, 7 and 9, respectively. The increase of k_H with pH is expected as reaction (2) suggests. In addition, the very low values of Ha obtained, from Eq. (1), confirm that the ozonation kinetic regime of mineralization is very slow [32].

3.6.2. The activated carbon ozone system

In the presence of activated carbon, the abatement of TOC can be related to various processes, the direct ozonation that has evidently shown its incapacity in terms of mineralization and the indirect reaction between hydroxyl radicals and organic matter which presents two sources of radicals: the homogeneous reaction between hydrogen peroxide-ozone and reactions on the surface of the activated carbon involving the adsorbed species of both oxidants and the adsorbed hydroxyl radicals and by-products. The concentration of dissolved ozone was lower than in the absence of activated carbon at the three pH conditions studied and, hence, lower than the interface ozone concentration (see Fig. 10). On the other hand, contrary to the case of the activated carbon free ozonation the increasing pH does not lead to an increase of TOC removal (see Fig. 9). While the homogeneous reaction rate on the bulk of water slightly increases with the increasing pH, the adsorption capacity of the catalyst seems to be negatively affected as explained above. To simplify the chemical term of the process and similarly to the homogeneous case, all reactions that take place over the surface of the solid have been represented by a unique chemical reaction whose rate equation is given below:

$$r_{TOC} = -k_{HET} C_{O_3} TOC \qquad (9)$$

where k_{HET} is the apparent heterogeneous rate constant. On the other hand, the kinetic of the global process must be studied as a gas–liquid–solid catalytic reaction plus a homogenous reaction and, *a priori*, gas–liquid mass transfer and liquid solid (external and internal) mass transfer cannot be negligible [34]. Thus, the TOC mass balance is now [34]

$$-z_T \frac{d\,TOC}{dt} = \frac{C_{O_3g} RT/He}{1/(k_L a) + [1/(k_H TOC) + w/1/(k_C a_C) + 1/(\eta k_{HET} TOC)]} \qquad (10)$$

where z_T is the stoichiometric of the whole ozonation process (about 9.5 mg ozone consumed per mg TOC consumed), w the concentration of activated carbon, k_C the liquid–solid mass transfer coefficient, a_C the external surface area of the activated carbon particles and η is the internal effectiveness factor of the heterogeneous reaction. Furthermore, it is possible to determine the relative

importance of the solid external diffusion ($1/k_C a_C$) and the surface reaction ($1/\eta k_{HET} TOC$) resistances by applying Mears criterion (C_M) to the organic matter and ozone as can be seen in Eqs. (11) and (12), respectively [35]:

$$C_M = \frac{-d\ TOC/dt}{k_C a_C w TOC} \quad (11)$$

$$C_M = \frac{-z_T d\ TOC/dt}{k_C a_C w C_{O_3}} \quad (12)$$

where k_C is taken as $4.1 \times 10^{-4}\ ms^{-1}$, obtained from empirical correlations [34] and a_C is $5.77 \times 10^{-3}\ m^2\ g^{-1}$ (for spherical particles of 1.3 mm diameter and $0.8\ g\ cm^{-3}$ apparent density, see Table 1). In the case of the organic matter C_M presents, after 20 min of reaction, values lower than 0.1 which means that the reaction process on the solid is controlled by internal mass transfer and heterogeneous chemical reaction. However, Mears criteria, in the case of the ozone, presents values around unity, which indicates that the process is controlled by the external mass transfer of the ozone to the activated carbon surface. Considering this situation, Eq. (10) can be simplified since the internal mass transfer and surface reaction resistance can be considered negligible as far as ozonation kinetics is concerned. Eq. (10), then, reduces to

$$-z_T \frac{d\ TOC}{dt} = \frac{C_{O_3 g} RT/He}{1/(k_L a) + [1/(k_H TOC + w k_C a_C)]} \quad (13)$$

The results obtained show that the term, $k_C a_C w$ ($4.8 \times 10^{-3}\ s^{-1}$) is not negligible against the value of the homogeneous chemical rate term, $k_H TOC$, which is between 1.9×10^{-3} at the start of reaction and $2.4 \times 10^{-4}\ s^{-1}$ after 120 min). However, between 70 and 60% gas–liquid mass transfer resistances ($1/k_L a$) are determined in this process depending on the reaction time.

4. Conclusions

The most important conclusions reach in this work are:

- The ozone absorption in DCF aqueous solutions follows a fast kinetic regime as Hatta numbers indicate. The absence of dissolved ozone during the early reaction turns down a possible catalytic reaction of the compound on the surface of the solid. However, after this initial period, ozone accumulates in water and the catalytic reactions become the key step for mineralization.
- Single ozonation is not able to remove compounds formed during the first minutes of the ozonation, most of them of carboxylic acid nature, since they are refractory to the ozone attack (40% TOC removal in 120 min).
- Ozonation in the presence of activated carbon clearly improves the mineralization of the contaminated water (about 95% TOC removal in 120 min).
- According to the ozone consumed during the ozonation, basic carbon P110 Hydraffin shows the lowest ozone consumption. Also, P110 Hydraffin presents a better adsorption capacity than the other carbons for the ozonation by-products.
- The longer the reaction time in the DCF-activated carbon ozonation the lower the affinity of by-products to adsorb on the activated carbon surface and the lower the direct reactivity with ozone. Therefore, TOC removal is mainly due to the catalytic or promoting action of activated carbon on the ozone decomposition to yield hydrogen peroxide and then hydroxyl radicals and, also, to the nature of intermediates being adsorbed.
- DCF is a toxic compound for *D. magna*. However, ozonation allows significant decreases of toxicity and total removal of toxicity when activated carbon is present.

- Rate constant of the homogenous mineralization process (ozone-TOC reaction) was found to be 1.14 ± 0.01, 1.36 ± 0.05 and $1.51 \pm 0.10\ M^{-1}\ s^{-1}$ at pH 5, 7 and 9, respectively.
- According to the evaluation of the different resistances present on the heterogeneous system and, at the experimental conditions here applied, gas–liquid ozone mass transfer was the main resistance of the process rate.

Due to the promising results further research is now carried out to investigate conditions of chemical regime control and to determine the rate constant of the heterogeneous reaction on the activated carbon surface.

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