



Mechanism and kinetic considerations of TOC removal from the powdered activated carbon ozonation of diclofenac aqueous solutions

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ABSTRACT

Ozonation of DCF in aqueous solution in the presence of powdered activated carbon (PAC) has been studied for mechanistic and kinetic purposes. The effects of gas flow rate, ozone gas concentration and initial TOC on the TOC elimination rate were then investigated. The use of PAC allows liquid–solid and internal diffusion mass transfer resistances being eliminated. Gas–liquid mass transfer resistance is also eliminated when ozonation is applied to DCF preozonated solutions. In the absence of mass transfer resistances a mechanism of reactions involving homogeneous and heterogeneous steps for TOC removal was proposed. From this mechanism a mathematical model constituted by mass balances of main species in water was established. Considerations about the changing nature of ozonation intermediates, as being promoters or inhibitors of ozone decomposition, is a key point to better predict the experimental concentrations of species present in this system.

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1. Introduction

The synergism between ozone and activated carbon adsorption to eliminate chemical contaminants from water by improving the removal rate of the individual processes is nowadays well accepted [1,2]. The efficiency improvement is especially important in the case of mineralization [3]. This process is often catalogued as an advanced oxidation because of the action of hydroxyl radicals that are known to be generated in the medium [4,5]. It is also well established that ozone reacts with some oxygen groups of basic nature on the carbon surface so as the activated carbon acts as a promoter rather than as a catalyst of the ozonation process [5–8]. Most of studies already published on this process are addressed to the study of the influence of variables and few considerations on kinetic aspects are developed [9,10].

Many pharmaceutical compounds identified in water present hazardous character so that processes like ozone-activated carbon oxidation can be useful to remove not only these compounds but also their oxidation intermediates. In a previous paper [11], the effectiveness of the ozone-activated carbon process compared to single ozonation to remove from water the non-steroidal anti-inflammatory drug diclofenac (DCF) was studied. Though single ozonation allowed a fast removal of the compound from water, this process was inefficient in terms of TOC removal. However, the presence of activated carbon during the ozonation, depending on the type of

activated carbon used and experimental conditions, allowed reductions of the ozone consumption from 28 to 7 mg of ozone consumed per mg TOC consumed and TOC percentage removals from 30 to 80% after 60 min reaction. The transformation of TOC in inorganic carbon, that is, mineralization reached during the single ozonation was mainly due to the action of hydroxyl radicals. The ozone-activated carbon process was controlled by the internal diffusion through the activated carbon pores and, hence, the study of the true chemical kinetics was not possible. True kinetics, that is, the determination of chemical reaction rate constants is an important issue in any heterogeneous system since this will allow the knowledge of experimental conditions for negligible mass transfer contribution that retards the process rate.

Ozonation processes are complex gas–liquid reacting systems where mass transfer and chemical reactions can control the kinetics [12]. When the process is carried out in the presence of activated carbon the kinetics becomes even more complex since additional mass transfer and chemical reaction steps develop. Thus, in addition to the gas–liquid mass transfer resistance two other mass transfer limitations have to be accounted for. These are the external liquid–solid and the internal diffusion mass transfer resistances that are highly dependent on the solid particle size. The kinetic study of any heterogeneous process such as ozone-activated carbon oxidation in water should be accomplished with no mass transfer resistances. For this reason, in this work, P110 hydraffin activated carbon that highly activates DCF and intermediate ozone reactions in water [11] has been used in powder form (PAC). In this way, the external liquid–solid and internal diffusion mass transfer resistances are eliminated [12]

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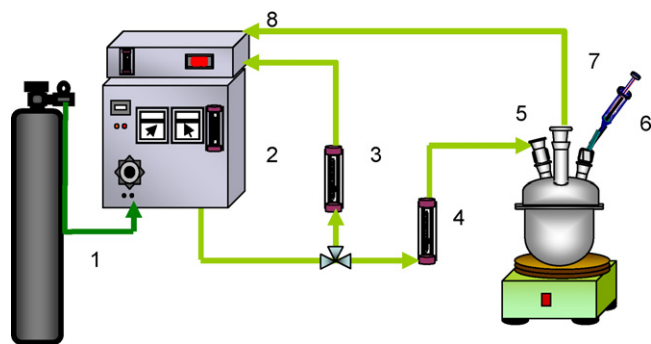
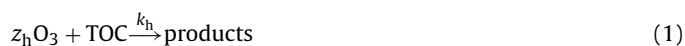


Fig. 1. Experimental set-up for ozonation experiments: (1) oxygen cylinder, (2) ozone generator, (3 and 4) gas flow meters, (5) gas reactor inlet, (6) semibatch reactor, (7) gas reactor outlet, and (8) ozone analyzer.

although the gas–liquid mass transfer resistance could still be significant.

Another problem with organic matter ozonation is the development of multiple reactions between ozone and the parent compound, DCF in this case, and ozonation intermediates. To avoid this problem and simplify the kinetics it is generally assumed the development of one single reaction between ozone and the organic matter represented by TOC:



where z_h and k_h are the stoichiometric coefficient and rate constant of this reaction, respectively. Then, reaction (1) represents the reactions between ozone and the compounds in bulk water without participation of activated carbon. It is usually called the homogeneous reaction. However, in the ozone-activated carbon process another global reaction has to be considered: the reaction on the carbon surface, usually called the heterogeneous reaction:



where z_{het} and k_{het} are the stoichiometric coefficient and rate constant of this reaction, respectively. Reaction (2) may involve, in the case of ozonation, a complex free radical mechanism plus adsorption–surface reaction–desorption steps. Although activated carbon acts as a promoter of the ozone reactions rather than as a catalyst [5,6], the kinetic equation of a gas–liquid–solid catalytic reaction can be considered as the starting rate equation for the ozone-activated carbon oxidation kinetic study.

In the present work, the ozone-activated carbon process is continued to remove the remaining organic matter resulting from the ozonation of DCF in aqueous solution. Main aims of the work were to complete the kinetic study and propose a mechanism to account for the reactions taking place both in bulk water and on the surface of the carbon.

2. Experimental

All the compounds, procedures and analytical methods are reported on the previous work [11]. In the present work, the experiments were carried out in the experimental set-up shown in Fig. 1. The reactor is basically a 300 mL cylindrical glass vessel supplied with magnetic agitation and a diffuser plate at the bottom to feed an ozone–oxygen gas mixture. The basic activated carbon used ($\text{pH}_{\text{pzc}} = 9.72$), P110 Hydrarffin, was obtained from Lurgy and applied in powder form after being crashed the original particles [11].

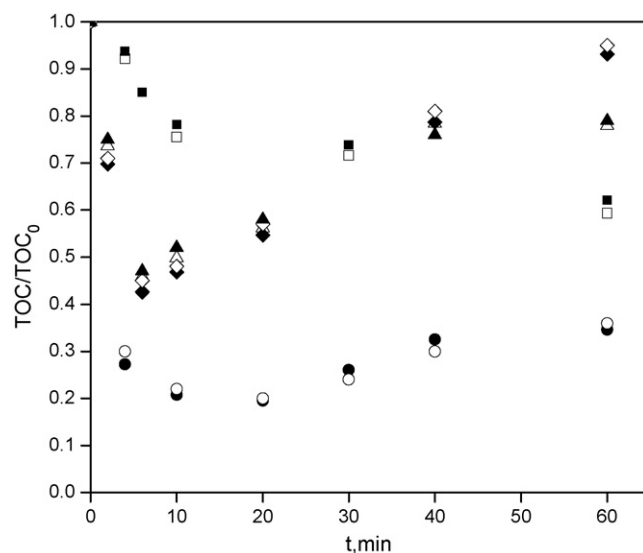


Fig. 2. Changes of total organic carbon with time during the ozonation of a diclofenac solution in the presence of PAC. Influence of gas flow rate (experiments in duplicate). Conditions: $\text{TOC}_0 = 15 \text{ mg L}^{-1}$, $T = 20^\circ \text{C}$; $\text{pH} = 7$; $w = 1 \text{ g L}^{-1}$; ozone gas concentration = 20 mg L^{-1} . Gas flow rate (L h^{-1}): (\diamond , \blacklozenge) 40; (\triangle , \blacktriangle) 25; (\circ , \bullet) 10; (\square , \blacksquare) in the absence of PAC and 25 L h^{-1} gas flow rate.

3. Results and discussion

According to the kinetics of a gas–liquid–solid catalytic reaction the ozone absorption rate in a process such as the one studied here can be represented through Eq. (3) [13]:

$$N_{\text{O}_3} = \frac{C_{\text{O}_3} g RT}{(\text{He}/k_L a) + [\text{He}/(\beta \phi(k_H, \text{TOC}, C_{\text{O}_3}) + w)/((1/k_C a_C) + (1/\eta F(k_{\text{het}}, \text{TOC}, C_{\text{O}_3})))]} \quad (3)$$

where w , a_C , η , β , He and $k_L a$ are the concentration of activated carbon, the external surface area of the activated carbon particles, the internal effectiveness factor of the heterogeneous reaction, the liquid hold-up, the Henry constant and the volumetric mass transfer coefficient, respectively, and $\phi(k_H, \text{TOC}, C_{\text{O}_3})$ and $F(k_{\text{het}}, \text{TOC}, C_{\text{O}_3})$ the intrinsic homogeneous and heterogeneous reaction rates. In the case the solid is in powder form, Eq. (3) can be simplified because k_C becomes very high [12] and the effectiveness factor reduces to unity. Then, Eq. (3) reduces to Eq. (4):

$$N_{\text{O}_3} = \frac{C_{\text{O}_3} g RT}{\text{He}[(1/k_L a) + 1/(\beta \phi(k_H, \text{TOC}, C_{\text{O}_3}) + w F(k_{\text{het}}, \text{TOC}, C_{\text{O}_3}))]} \quad (4)$$

where the two remaining fractional terms in the denominator represent the gas–liquid mass transfer and chemical (homogeneous plus heterogeneous) resistances. The kinetic study of a process like this one also requires the elimination of the gas–liquid resistance.

3.1. Effect of gas–liquid mass transfer resistance

A first series of DCF ozone–PAC experiments were carried out at different gas flow rates to establish the conditions needed to eliminate the gas–liquid resistance. Fig. 2 presents the results obtained. Thus, Fig. 2 shows the changes in TOC concentration with time observed in these experiments. In the absence of activated carbon, it is observed that TOC slowly decreases with time reaching about 40% conversion after 60 min reaction. However, in the presence of PAC, time TOC/ TOC_0 concentration profiles follow different trends depending on the reaction time. First, during an initial reaction period of about 10 min, TOC follows an expected decrease with time with reaction rates higher than that of ozonation alone. However,

at more advanced reaction times, TOC increases. It is also observed that the increase of gas flow rate (from 10 to 25 or 40 L h⁻¹) leads to a poorer elimination of TOC in the initial reaction period contrarily to what it could be expected. These, at first sight, anomalous results can only be due to some reaction of ozone on the carbon surface that releases organic compounds into bulk water. This type of reaction was not noticed when activated carbon was used in granular form in the previous paper [11] although some authors have reported this reaction to occur even with granular activated carbons [8]. As stated before, literature [8,14] reports reactions of ozone with different surface oxygen groups on the carbon surface, especially of basic nature. These reactions can be followed by desorption steps that finally lead to new compounds in water, that is, to an increase of TOC. In addition, ozone surface reactions also lead to hydrogen peroxide and, hence, to hydroxyl radicals that improve TOC elimination from water [3]. Thus, in the ozone–PAC oxidation of DCF two heterogeneous main reactions may develop: one positive because it reduces TOC and another negative that increases TOC.

3.2. Ozone reactions with PAC

In order to confirm these assumptions some ozone reactions on the PAC in the absence of DCF were carried out. The results of these reactions (not shown) confirm the appearance of organic matter (TOC) in the aqueous solutions. Measurement of 254 nm absorbance of these solutions confirms that at least a fraction of this TOC is constituted by unsaturated compounds that are known to react very fast with ozone. Also, hydrogen peroxide concentrations that increase with the increasing gas flow rate were measured undoubtedly due to the reactions of ozone and unsaturated compounds [15]. However, the most important fact regarding the study of this work was the negligible presence of TOC and hydrogen peroxide when gas flow rate applied was ≤ 10 L h⁻¹. Then, at these conditions contributions of the direct reactions of ozone with oxygen groups of the carbon surface are negligible when DCF and/or ozonation intermediates are also present in water. Thus, in the absence of DCF (with 10 L h⁻¹ gas flow rate) the ozone–PAC reaction leads to as much as 0.5 mg L⁻¹ of TOC and less than 10⁻⁶ M of hydrogen peroxide concentration in 30 min reaction while in the presence of DCF or ozonated DCF aqueous solutions (see later) TOC and hydrogen peroxide concentrations in the aqueous solutions were between 3 and 15 mg L⁻¹ and 5×10^{-5} M, respectively, in the same reaction period. Another important point to be considered when ozonation processes in water are studied is the presence of hydroxyl radicals. These free radicals are the responsible species of transforming the ozone refractory organic matter in aqueous solutions. The presence of hydroxyl radicals was also confirmed by carrying out some ozone–PAC experiments in the presence of *t*-butanol, a strong scavenger of these free radicals [16]. Finally, some other experiments of ozone and hydrogen peroxide decomposition in the presence and absence of PAC showed the importance of this material to accelerate the reaction between both oxidants that will be considered later in the kinetic modeling section.

In summary, according to the results obtained in organic-free water, ozonation of PAC leads to undesirable increases of TOC and hydrogen peroxide that, nonetheless, are negligible when gas flow rates ≤ 10 L h⁻¹ are applied. However, low gas flow rates do not favor the elimination of gas–liquid mass transfer resistance. Then, for the kinetics of TOC ozone–PAC oxidation different conditions should be investigated as shown below.

3.3. PAC adsorption kinetics of DCF intermediates

Another important aspect to consider in the DCF ozone–PAC oxidation system is the adsorption of DCF and ozonation intermediates on the PAC surface. Thus, some DCF ozonation experiments

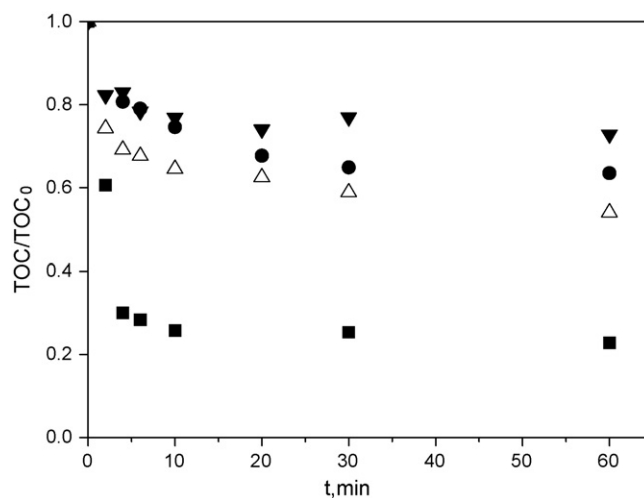


Fig. 3. PAC adsorption kinetics of remaining total organic carbon coming from the ozonation of a diclofenac solution at different ozonation times. Conditions: $T = 20^\circ\text{C}$; pH 7; $w = 1 \text{ g L}^{-1}$; (■) after 1 min ozonation; (Δ) after 4 min ozonation; (●) after 10 min ozonation; (▼) after 30 min ozonation.

were first carried out in the absence of PAC and stopped at different reaction times so as the water matrix contain intermediates of different nature. These solutions were then put into contact with PAC and TOC adsorption kinetics was followed as shown in Fig. 3. Thus, Fig. 3 presents the changes of TOC with time corresponding to PAC adsorption of DCF aqueous solutions previously treated with ozone at different reaction times. It can be seen that the lower the preozonation time the higher the adsorption rate of DCF ozonation intermediates. Thus, after 1 min ozonation about 70% TOC adsorption is noticed in hardly 5 min while after 30 min preozonation TOC adsorption removal is only about 15% for the same time. These results are due to the different nature of intermediates of DCF ozonation. Thus, at low ozonation times DCF and some unsaturated compounds remain in water which are non-polar compounds while at advanced preozonation times the intermediates present (carboxylic acids, see Ref. [11]) are more polar and, thus, show less affinity towards PAC as experimentally observed in this work. The results also show that for the first 20 min of adsorption of intermediates resulting from DCF ozonation for times higher than 10 min TOC adsorption rates do not increase. In the ozone–PAC oxidation of organic compounds conditions that favor chemical reactions instead of adsorption are more recommended since adsorption does not lead to destruction of contaminants. Then, for the kinetic study, preozonated solutions of DCF during 10 min were treated with ozone and PAC.

3.4. Ozone–PAC oxidation of DCF ozonated solutions

As stated in precedent sections one problem to study the chemical (catalytic and non-catalytic) TOC removal kinetics of DCF ozone–PAC oxidation aqueous solutions is gas–liquid mass transfer. Then, experiments with 10 min DCF preozonated solutions and ozone–PAC were carried at different gas flow rates. Fig. 4 shows the results obtained. It is now seen that the gas flow rate has no effect on TOC removal during the first 10 min of reactions. This is undoubtedly due to the slower ozone reactions in water compared to gas–liquid mass transfer. However, for higher reaction times, TOC increases when gas flow rates higher than 10 L h⁻¹ are applied which is a consequence of the direct ozone reactions with the carbon surface as shown in Section 3.2. Then, for the first 10 min gas–liquid mass transfer does not affect the process rate. Also, with 10 L h⁻¹ gas flow rate, ozone reactions with the carbon surface can

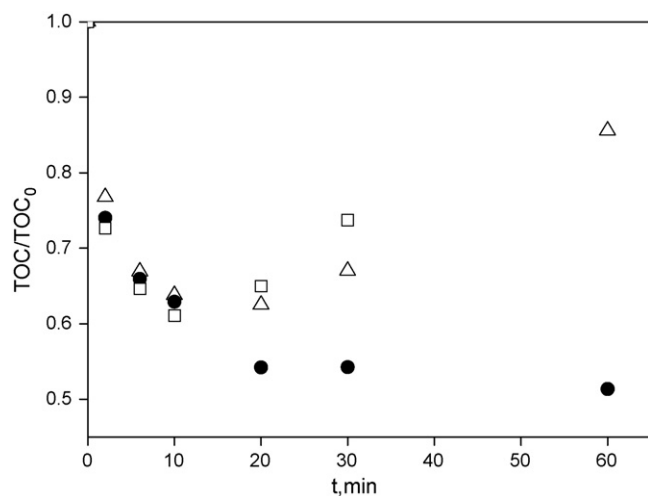


Fig. 4. PAC ozonation of intermediates (measured as TOC) resulting from 10 min ozonation of a diclofenac aqueous solution. Effect of gas flow rate. Conditions: $T=20^{\circ}\text{C}$; $\text{pH } 7$; $w = 1 \text{ g L}^{-1}$; gas flow rate (L h^{-1}): (\square) 40; (\triangle) 25; (\bullet) 10.

be considered negligible (see Section 3.2). Therefore at these conditions, Eq. (4) can be applied and simplified to Eq. (5) since the process is chemically controlled:

$$N_{\text{O}_3} = (RT/He) [\beta\phi(k_{\text{H}}, \text{TOC}, C_{\text{O}_3}) + wF(k_{\text{het}}, \text{TOC}, C_{\text{O}_3})] C_{\text{O}_3g} \quad (5)$$

In Eq. (5), however, the form of the rate terms in brackets still remains unknown. Expressions in Eq. (5) correspond to the chemical kinetics of the process and can be deduced from the proposition of a mechanism of reactions since mass transfer has already been eliminated. Some experiments with different ozone and initial TOC concentrations were then carried out since the kinetic function is dependent on these variables. Fig. 5 shows the changes of TOC with time observed when these variables were studied on 10 min pre-ozonated DCF solutions and 10 L h^{-1} gas flow rate. Thus, it is seen from Fig. 5 that both ozone and initial TOC concentrations exert positive effects on the TOC removal rates.

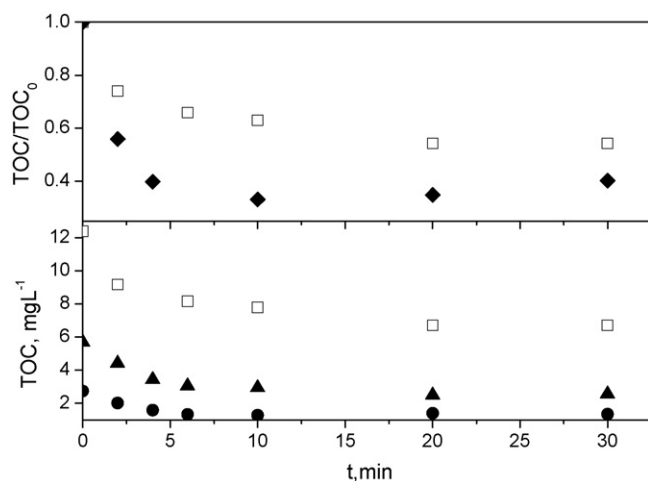
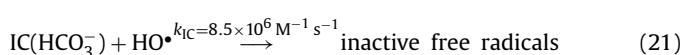
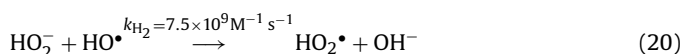
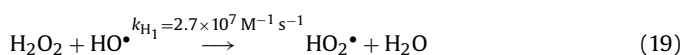
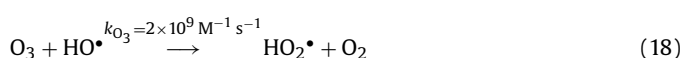
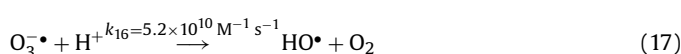
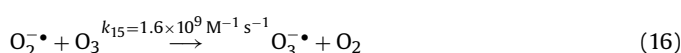
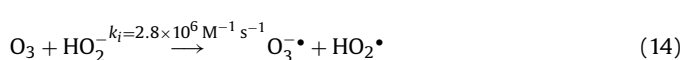
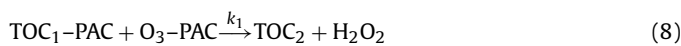


Fig. 5. PAC ozonation of intermediates (measured as TOC) resulting from 10 min ozonation of a diclofenac aqueous solution. Effect of ozone gas concentration (top) and initial TOC (bottom). Conditions: $T=20^{\circ}\text{C}$; $\text{pH } 7$; $w = 1 \text{ g L}^{-1}$; gas flow rate = 10 L h^{-1} ; gas ozone concentration = 20 mg L^{-1} ; (\square) $\text{TOC}_0 = 12 \text{ mg L}^{-1}$; (\blacktriangle) $\text{TOC}_0 = 5 \text{ mg L}^{-1}$; (\bullet) $\text{TOC}_0 = 2.5 \text{ mg L}^{-1}$; (\blacklozenge) $\text{TOC}_0 = 12 \text{ mg L}^{-1}$; gas ozone concentration = 40 mg L^{-1} .

3.5. Mechanism and kinetics

According to the experimental results, intermediates formed from the PAC ozonation of 10 min DCF ozonated solutions are saturated compounds that do not react directly with ozone (see previous paper [11]). As it is seen from Fig. 3, about 20% of this TOC can adsorb on the PAC surface during the first minute. Then, this TOC is named as TOC_1 in the mechanism proposed below. According to experimental results [3] adsorbed TOC_1 would react with adsorbed ozone to yield hydrogen peroxide and TOC_2 . Thus, surface reaction (8) (see below) justifies the increase observed in the experimental concentration of hydrogen peroxide during the first minute of reaction (see also Fig. 7 below). Notice that another way of hydrogen peroxide formation is through ozone decomposition on the PAC surface but, at the conditions applied (10 L h^{-1} of gas flow rate, see Section 3.2), concentrations of hydrogen peroxide generated in this way are more than one order of magnitude lower than those measured in the presence of DCF ozonated intermediates. Then, this contribution is not considered in the mechanism proposed. Finally, non-adsorbed TOC_2 , which is due to saturated carboxylic acids, only reacts with hydroxyl radicals to finally yield inorganic carbon. With this hypothesis and literature data [3,9,16–20] the following mechanism of reactions is proposed:



Surface reaction (11) between adsorbed ozone and hydrogen peroxide is proposed to yield hydroxyl radicals as reported in previous works [21]. Steps (12)–(21) correspond to the well known ozone decomposition mechanism in water systems [9,16–19] where an average value of $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ has been assumed for the reaction between the organic matter (TOC) and hydroxyl radicals [22]. It can be admitted that reaction (21), between IC and hydroxyl radicals, is the termination step, with IC being bicarbonate given the pH of work. In the mechanism of reactions proposed, there are bulk water and catalytic reactions that would correspond to the two terms in

brackets in kinetic Eq. (5). For the heterogenous catalytic reactions (8) and (11), kinetic expressions of the Langmuir type can first be considered [23]. Thus, for the ozone–TOC₁ and ozone–hydrogen peroxide reactions on the carbon surface the kinetic expressions can be of the form:

$$r_1 = \frac{k_1 w C_{O_3} TOC_1}{1 + K_{O_3} C_{O_3} + K_{TOC_1} TOC_1} \quad (22)$$

$$r_2 = \frac{k_2 w C_{O_3} C_{H_2O_2}}{1 + K_{O_3} C_{O_3} + K_{H_2O_2} C_{H_2O_2}} \quad (23)$$

where K_{O_3} , $K_{H_2O_2}$ and K_{TOC_1} correspond to the equilibrium constants of ozone, hydrogen peroxide and TOC₁ adsorption processes, respectively. Eqs. (22) and (23) are based on Langmuir mechanisms deduced from reactions (6)–(11). However, experiments of ozone and hydrogen peroxide decompositions on PAC and on DCF ozonated solutions (after 10 min ozonation) follow first order kinetics which suggests that, in Eqs. (22) and (23), the products between the equilibrium constants and concentrations of the denominator are much lower than 1 ($1 \gg K_i C_i$). Then, these rate equations reduce to apparent second order kinetics:

$$r_1 = k_1 w C_{O_3} TOC_1 \quad (24)$$

$$r_2 = k_2 w C_{O_3} C_{H_2O_2} \quad (25)$$

With these considerations the mass balances of main reacting species in a well-agitated semibatch reactor (as the one used in this work) can be established as follows:

For ozone in the gas phase:

$$(1 - \beta)V \frac{dC_{O_3g}}{dt} = m_{O_3e} - v_g C_{O_3g} - k_L a \left(\frac{C_{O_3g} RT}{He} - C_{O_3} \right) \beta V \quad (26)$$

For ozone in water:

$$\frac{dC_{O_3}}{dt} = k_L a \left(\frac{C_{O_3g} RT}{He} - C_{O_3} \right) - 2k_i C_{O_3} \frac{10^{pH-pK} C_{H_2O_2 T}}{1 + 10^{pH-pK}} - k_{O_3} C_{O_3} C_{HO} - w k_1 C_{O_3} TOC_1 - w k_2 C_{O_3} C_{H_2O_2} \quad (27)$$

For hydrogen peroxide in water:

$$\frac{dC_{H_2O_2 T}}{dt} = w k_1 C_{O_3} TOC_1 - w k_2 C_{O_3} C_{H_2O_2} - k_i C_{O_3} \frac{10^{pH-pK} C_{H_2O_2 T}}{1 + 10^{pH-pK}} - k_H C_{H_2O_2 T} C_{HO} \quad (28)$$

where k_H is:

$$k_H = \frac{k_{H_1} + k_{H_2} 10^{pH-pK}}{1 + 10^{pH-pK}} \quad (29)$$

For TOC₁ in water:

$$\frac{dTOC_1}{dt} = -w k_1 C_{O_3} TOC_1 - k_{HO} TOC_1 C_{HO} \quad (30)$$

For TOC₂ in water:

$$\frac{dTOC_2}{dt} = w k_1 C_{O_3} TOC_1 + k_{HO} TOC_1 C_{HO} - k_{HO} TOC_2 C_{HO} \quad (31)$$

Total TOC:

$$TOC = TOC_1 + TOC_2 \quad (32)$$

For IC in water:

$$IC = TOC_0 - TOC \quad (33)$$

where the concentration of hydroxyl radicals is:

$$C_{HO} = \frac{1}{k_{IC} IC} \left[\frac{2k_i C_{O_3} 10^{pH-pK} C_{H_2O_2 T}}{1 + 10^{pH-pK}} + w k_2 C_{O_3} C_{H_2O_2} \right] \quad (34)$$

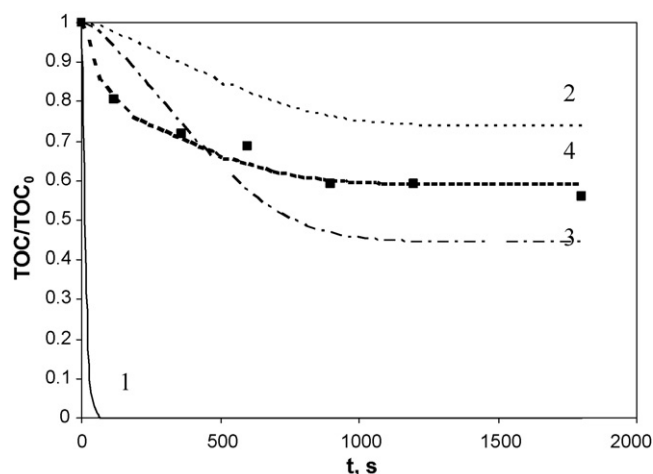
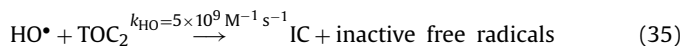


Fig. 6. Checking the kinetic model. Calculated and experimental results of the evolution of the remaining TOC with time at different conditions: $k_1 = 100 \text{ L}^{-1} \text{ g M}^{-1} \text{ s}^{-1}$. (TOC refers to that remaining from PAC ozonation of DCF ozonated solutions.) Curve 1: TOC₂ as promoter, $\omega = 0$. Curve 2: TOC₂ as scavenger, $\omega = 1$. Curve 3: TOC₂ as partially scavenger, $\omega = 0.4$. Curve 4: TOC₂ as partially scavenger depending on time, $\omega = f(t)$, ω values from 0 to 1. Solid symbols are experimental results. Experimental conditions: $T = 20^\circ \text{C}$; $\text{pH} = 7$; $w = 1 \text{ g L}^{-1}$; gas flow rate = 10 L h^{-1} ; ozone gas inlet concentration = 20 mg L^{-1} ; $\text{TOC}_0 = 12 \text{ mg L}^{-1}$.

Solution of the mathematical model formed with Eqs. (26)–(34) requires the knowledge of some rate constants (k_1 and k_2). However, only k_2 could be experimentally estimated from the results of the ozone–hydrogen peroxide reaction in the presence of PAC. This reaction has been studied in this work in the presence of *t*-butanol at pH 7. At these conditions, only reactions (11) and (14) develop. Staehelin and Hoigné [17] determined the rate constant of reaction (14) at pH 7 as $2.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ which is practically coincident to $2.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ experimentally determined in the present work. The heterogeneous rate constant k_2 was determined from the difference of the total rate constant of the ozone–hydrogen peroxide reaction in the presence of PAC and that indicated above for the homogeneous reaction. Thus, k_2 was found to be $204 \text{ L g}^{-1} \text{ M}^{-1} \text{ s}^{-1}$.

The mathematical model of Eqs. (26)–(34) was finally solved by assuming different values of k_1 to fit both experimental and calculated results. However, it was observed that k_1 only exerts an effect on the results of hydrogen peroxide concentration and that the promoting or inhibiting character of intermediate compounds (TOC₂) to decompose ozone into hydroxyl radicals is a fundamental factor to fit the calculated results of TOC. Thus, Fig. 6 presents an example of the evolution of remaining TOC (the sum of TOC₁ and TOC₂) with time at different conditions. When TOC₂ is promoter of ozone decomposition [16], as reaction (12) indicates, the calculated results underestimate the experimental ones (see curve 1). Thus, in Eq. (34) intermediates are considered promoters of ozone decomposition, that is, their reaction with hydroxyl radicals (reaction (12)) yields the hydroperoxide ion radicals that through reactions (15)–(17) regenerate the hydroxyl radical. This makes the rate of TOC removal extraordinarily high (see Fig. 6). Then, TOC₂ was considered inhibitor of ozone decomposition [16], so that in this case reaction (12) has to be substituted by reaction (35):



If reaction (35) is considered Eq. (34) for the concentration of hydroxyl radicals would become:

$$C_{HO} = \frac{1}{k_{IC} IC + k_{HO} TOC_2} \left[\frac{2k_i C_{O_3} 10^{pH-pK} C_{H_2O_2 T}}{1 + 10^{pH-pK}} + w k_2 C_{O_3} C_{H_2O_2} \right] \quad (36)$$

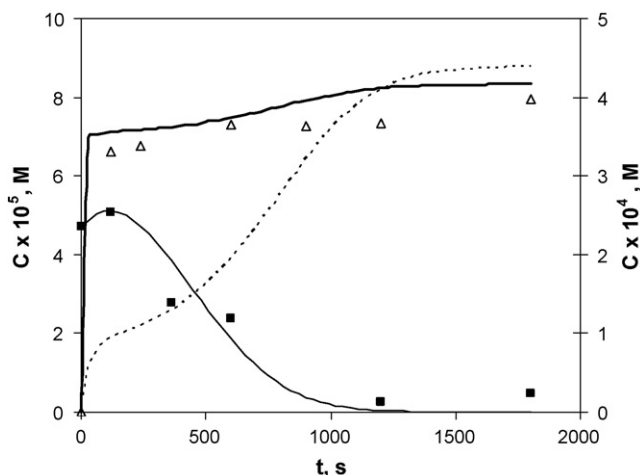


Fig. 7. Checking the kinetic model. Calculated and experimental results of the evolution of the concentrations of hydrogen peroxide, dissolved ozone and ozone gas reactor outlet with time. $k_1 = 100 \text{ L}^{-1} \text{ g M}^{-1} \text{ s}^{-1}$. (Results correspond to PAC ozonation of DCF ozonated solutions.) Experimental conditions as in Fig. 6. Solid symbols are experimental results. Curves are calculated results. Left Y axis: (■) hydrogen peroxide, dotted line for dissolved ozone concentration. Right Y axis: (△) gas ozone concentration.

Then, the mathematical model was solved by considering Eq. (36). Fig. 6 also shows the results obtained for the evolution of TOC concentration with time. It is now seen that the calculated results overestimate the experimental ones (see curve 2). These results seem to be a logical consequence of the inhibiting character of intermediates that would stop the TOC oxidation rate as calculated results confirm. An intermediate situation was then considered to solve the mathematical model. In this case, a fraction of TOC_2 , ω , was assumed to be inhibitor of ozone decomposition. Then, Eq. (36) becomes:

$$C_{\text{HO}} = \frac{1}{k_{\text{IC}} \text{IC} + \omega k_{\text{HO}} \text{TOC}_2} \left[\frac{2k_i C_{\text{O}_3} 10^{\text{pH}-\text{pK}} C_{\text{H}_2\text{O}_2} T}{1 + 10^{\text{pH}-\text{pK}}} + \omega k_2 C_{\text{O}_3} C_{\text{H}_2\text{O}_2} \right] \quad (37)$$

Now, calculated TOC time profiles are closer to the experimental ones as shown in Fig. 6 where ω was taken as 0.4 (that is, 40% of TOC_2 was considered as inhibitor, see curve 3). However, the closest fitting of experimental and calculated results was obtained by considering a changing value of ω with time. This is a logical assumption based on the changing nature of intermediates formed (TOC_2) with time during the ozonation process. Thus, at the start of reaction, intermediates are of higher molecular weight with higher probability of being promoters of ozone decomposition [16]. However, as far as the ozone reactions develop more saturated compounds are formed and their inhibiting character increases. This is why TOC oxidation rates are very high during the start of oxidation (TOC_1 can be considered promoter) and then diminish with time to become zero (see experimental results). In Fig. 6 the simulation of the process considering a changing nature (promoter to inhibitor) of intermediates (TOC_2 , $\omega = f(t)$) has also been applied (see curve 4). As it is seen, in this way, calculated and experimental results can be well fitted. Also, the concentration of main species, other than TOC, present in water can also be predicted as shown in Fig. 7 for the ozone and hydrogen peroxide concentrations. The case of hydrogen peroxide is of special interest since the concentration of this compound first increases, reaches a maximum value and then decreases as commented before. For this species, a value of $k_1 = 100 \text{ L}^{-1} \text{ g M}^{-1} \text{ s}^{-1}$ was the best to fit the experimental results with ω as a changing function of time. It should be noted that the variable values of ω applied here to prepare Figs. 6 and 7 are only approximations to

simulate what likely develops in the actual process and have no kinetic value to be used in any other PAC ozone process. The promoter and inhibitor nature of intermediates seems to be the key factor to understand the diminishing trend of TOC oxidation rates in ozonation processes.

4. Conclusions

Main conclusions reached in this work are:

1. Ozone reaction with DCF in water in the presence of powdered activated carbon allows the elimination of external liquid–solid and internal pore mass transfer resistances but it is highly dependent on gas–liquid mass transfer resistance.
2. Organic groups on the powdered activated carbon surface react with ozone to release organics into bulk water and hydrogen peroxide. This process, however, is limited with low gas flow rate conditions.
3. DCF ozonated intermediates show low affinity to PAC surface.
4. Ozonation of DCF ozonated aqueous solutions is a free gas–liquid mass transfer resistance process so as the true chemical kinetics can be studied by establishing a mechanism of reactions involving homogeneous and heterogeneous reactions.
5. Solution of the mathematical model formed with the mass balance equations of main species present in water yield close results to the experimental ones when a changing nature of ozonation intermediates (from promoters to inhibitors of ozone decomposition reactions) is considered.

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