Chemical Engineering Journal 164 (2010) 70–76

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Kinetic modeling of powdered activated carbon ozonation of sulfamethoxazole in water

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ARTICLE INFO

Article history:
Received 27 May 2010
Received in revised form 6 August 2010
Accepted 10 August 2010

Keywords:
Sulfamethoxazole
Ozonation
Catalytic ozonation
Powdered activated carbon
Kinetic modeling
Water treatment

ABSTRACT

Ozonation of sulfamethoxazole promoted by a powder activated carbon (PAC) of neutral nature has been studied for mechanistic and kinetic purposes. The main advantage of using powder activated carbon was the removal of both liquid–solid and internal diffusion mass transfer resistances. In addition, at the operational conditions applied the influence of the gas–liquid mass transfer was eliminated. As a result, in the absence of any physical mass transfer resistances, a mechanism that involves both homogenous and heterogeneous reactions for the mineralization of the water matrix was proposed and a mathematical kinetic model was obtained from the corresponding mass balances of main species present. In order to properly solve the kinetic model a term indicative of the changing nature of the water matrix was introduced. In that way the promoting or non-promoting character of water constituents was considered in the mechanism.

1. Introduction

An increasing number of hazardous organic chemicals, which must be removed before being discharged into the environment, are frequently found on wastewater effluents. Though they are partially removed in the conventional wastewater treatment plants, the occurrence of some recalcitrant contaminants in the treated effluents gives a hint of the inefficiency of some of these technologies [1]. These persistent pollutants can critically affect to the reutilization of the water effluent due to their environmental risk. Of special growing concern are the pollutants classified as endocrine disrupting chemicals (EDCs) due to their capacity to interfere with the hormonal metabolism of the endocrine systems and to disrupt the activity of the endogenous hormones even at very low concentrations [2]. Literature reports a vast number of compounds suspected of endocrine activity: pharmaceutical compounds, synthetic hormones, pesticides, personal care products, etc. [3].

Ozonation processes have widely proven their capacity as an effective technology on the removal of persistent and recalcitrant water pollutants [4]. Ozone is a powerful oxidizing agent that can directly react with the water contaminants or decompose into free radicals which are even more powerful oxidizers. Nevertheless, if used alone, ozone often does not lead to high levels of mineralization and toxicity removal [5–9]. In order to improve these drawbacks, advanced oxidation processes (AOPs) seem to be an interesting alternative. These processes are based on the generation of hydroxyl radicals or some other radical entities whose oxidation capacity is much higher and much less selective. O_3/H_2O_2, Fenton reagent, UV/O_3 or catalytic ozonation among others, are some examples of these technologies. In recent years, heterogeneous catalytic ozonation has emerged as a powerful treatment of water pollutants, particularly suited to deal with the removal and mineralization of refractory organic compounds. Among the organic compounds, which have been successfully removed by heterogeneous catalytic ozonation in laboratory and pilot-plant studies, are some pharmaceutical compounds such as clofibric acid, nanoproxen, carbamazepine, ibuprofen or diclofenac. The catalysts used for that purpose were titanium dioxide (photocatalytic ozonation), alumina-supported manganese oxide and activated carbons [10–13].

The activity of activated carbons as catalysts in an ozonation process is frequently attributed to their capacity to decompose ozone into hydroxyl radicals or other powerful oxidizing species. Nevertheless, this mechanism seems to involve the destruction of oxygenated groups at the surface of the activated carbon, which indicates the promoting role of the activated carbon in these processes more than a conventional heterogeneous catalyst [14,15]. In general, the combination of ozone and activated carbon shows interesting synergetic effects on the degradation of organic pollutants, enlarging the life of the activated carbon and demanding lower ozone consumptions [16,17].

In a previous paper [18], various catalysts were used in the catalytic ozonation of sulfamethoxazole (SMX). The occurrence of this

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doi:10.1016/j.cej.2010.08.025

compound along with other pharmaceuticals in surface waters and secondary wastewater effluents has been lately reported [19,20]. As other sulphonamide compounds, SMX is easily degradable by ozone [21], nevertheless the by-products produced during the ozonation process are highly refractory as proven in that paper. However, among the different catalysts studied activated carbon Darco12-20 and the catalyst of copper-based perovskite greatly improved the mineralization of the water matrix (about 92% of removal after 2 h of reaction). In our previous work [18], the heterogeneous reaction rate of the SMX mineralization was obtained in the case of the copper-based perovskite since the catalyst was in powdered form and the process was controlled by the catalytic reactions at the surface of the solid. Nevertheless, in the case of granular Darco12-20 the mineralization process was controlled by the physical mass transfer resistances and the kinetics of the heterogeneous catalytic reaction at the surface of the activated carbon was not studied.

According to this, the current paper focuses on the determination of the mechanisms and kinetics of the mineralization of SMX ozonation by-products in a catalytic ozonation process using powdered Darco12-20. In this way, the external liquid–solid and internal mass transfer resistances are eliminated [22]. In addition, the importance of the nature of the superficial groups of the activated carbon on the catalytic process has also been studied.

2. Materials and methods

Compounds, procedure and analytic methods are described in detail in previous works [13,18]. The powdered activated carbon Darco12-20 (PAC) of neutral nature ($pH_{pzc} = 6.4$) was used in slurry conditions in semi-continuous mode [18]. SMX initial concentration was between 5×10^{-5} and 10^{-4} M. The reactor used was a glass vessel stirred by a magnetic system and the ozone–oxygen gas mixture was fed through a porous diffuser at the bottom of the reactor. For ozonation experiments of AC free SMX solutions, conditions were: gas flow = 25 L h^{-1}, ozone concentration in the gas: 20 mg L^{-1}, pH 7 and 25 °C.

3. Results and discussion

As proven in the previous paper, ozone rapidly reacts with SMX in a fast kinetic regime [18]. As shown there, the presence of the catalyst did not improve the removal of the parent compound since it is directly degraded by ozone. Nevertheless, a positive influence on the removal of the SMX was observed in the presence of activated carbon due to the contribution of the adsorption of the target compound. According to those previous results and in order to observe the catalytic activity of activated carbon Darco12-20, SMX aqueous solutions were previously ozonated during 10 min before adding the catalysts. After this time, the target compound was totally removed. Also, according to literature [18,23–25] the first by-products are eliminated, which is a logical consequence of their molecular structure very reactive with ozone and hydroxyl radicals. From the results shown in that paper, a 10 min ozonated solution of SMX is a refractory water matrix mostly composed by recalcitrant carboxylic acids and hydrogen peroxide. This latter was found to be in the order of 4×10^{-5} M generated from the reaction between ozone and some aromatic structures present on the target compound and first ozonation by-products.

3.1. Ozone reaction with PAC

As stated, the catalytic activity of activated carbons is frequently related to the surface oxygen groups of the activated carbon, especially those of basic nature [26,27], that can react with ozone to yield more oxidizing entities (i.e. hydroxyl radicals). According to this, along the ozonation process the catalyst is slightly modified by the action of ozone and as a result the solid cannot be entirely considered as a "true" catalyst. In our case, these reactions led to the desorption of new compounds as seen from Fig. 1. As observed during the free organic ozonation process, TOC of the solution increased due to the presence of organic matter from the ozone-PAC reaction. In addition, the aromatic character of this water matrix can also be deduced from the increasing evolution of the absorbance at 254 nm, which clearly indicates that an important fraction of this TOC is formed by unsaturated compounds that *a priori* might react rapidly with ozone.

The positive influence of the gas flow on the reaction between ozone and PAC is also shown in Fig. 1. As can be seen from this figure, the increase of gas flow rate leads to an increase of TOC removal rate. In Fig. 2 the variation of the ozone concentration in the gas at the reactor outlet and the corresponding amount of ozone absorbed with reaction time are shown for the experiments of Fig. 1. From these data one can deduced the increase of ozone absorption rate when gas flow rate increased from 10 to 25 L h^{-1}. Then, the kinetic regime was mass transfer controlled.

In addition, hydrogen peroxide was also detected during the course of the ozonation of Darco12-20. However working with a flow rate of 10 L h^{-1} the concentration analyzed was almost in the limit of the analytical method used (about 10^{-6} M). As stated, the reaction between ozone and some superficial groups of Darco12-20, for example phenolic groups, can generate hydrogen peroxide

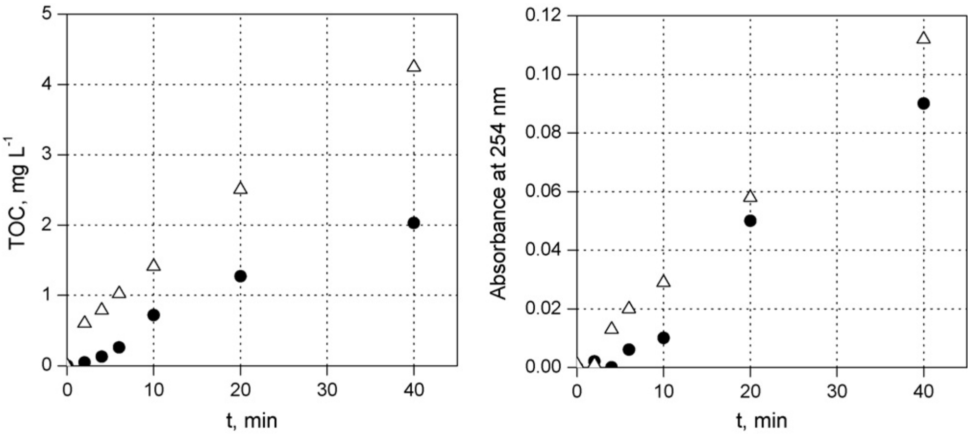

Fig. 1. Time changes of total organic carbon and absorbance at 254 nm during the ozonation of PAC-Darco12-20 in organic free water. Effect of gas flow rate. Conditions: $T = 20$ °C; pH = 7; $w = 1$ g L^{-1}; ●, gas flow rate = 10 L h^{-1}; inlet ozone gas concentration = 18.4 mg L^{-1}; △, gas flow rate = 25 L h^{-1}, inlet ozone gas concentration = 21.3 mg L^{-1}.

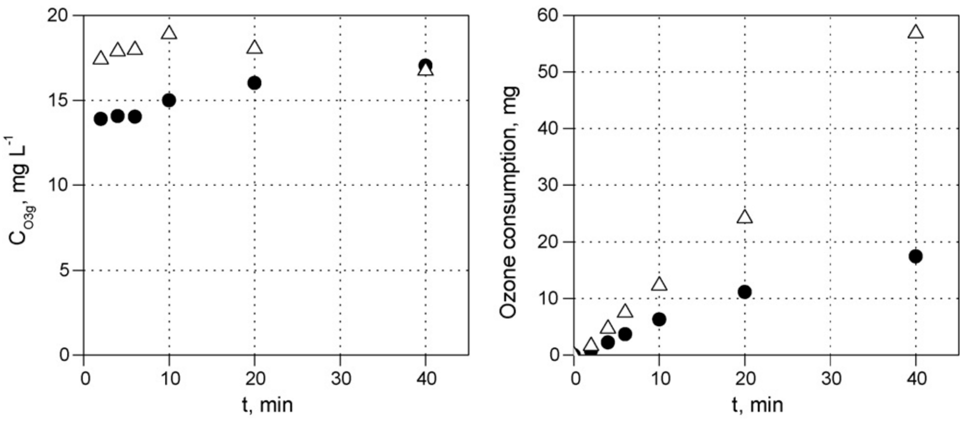

Fig. 2. Time changes of ozone concentration in the gas at the reactor outlet and ozone consumption with time for experiments of Fig. 1. Effect of gas flow rate. Conditions as in Fig. 1.

from cycloaddition of the ozone molecule to the structure of these species and breaking of aromatic ring [27].

In order to determine the effect of the ozone-PAC reaction during the ozonation process on the surface of the activated carbons, the chemical characterization of the surface oxygen groups, SOGs, of the PAC was carried out according to the method proposed by Boehm [28]. Table 1 shows SOGs concentration of virgin and 2 h ozonated activated carbon at different pH conditions. As stated, ozone reacts with some SOGs at the surface of the activated carbon rupturing some aromatic rings and structures that might generate hydrogen peroxide as a reaction by-product [26]. As can be observed in Table 1 the concentration of phenolic groups on the surface of the solid clearly decreased after the ozonation process, results also favoured with increasing pH. At basic pH the nucleophilic character of some basic SOGs increases and, then, their reaction rate with ozone as electrophilic agent becomes faster [4]. As a consequence, PAC ozonation at these pH conditions leads to a decrease of basic SOGs concentration and to the fixation of acidic SOGs such as carboxylic or lactones [29].

3.2. Ozone-PAC ozonation of sulfamethoxazole

Catalytic ozonation of preozonated sulfamethoxazole solutions was carried out in the presence of PAC. As seen from Fig. 3 this water matrix is highly refractory to single ozonation and low adsorbable onto the activated carbon (about 17 and 6% of TOC removal after 40 min of process, respectively). In one hand the water matrix is formed by refractory ozonation by-products (carboxylic acids) that barely react with ozone [30]. On the other hand the limited capacity of sulfamethoxazole by-products to be adsorbed onto activated carbon can be ascribable to two facts; (i) their higher polar character; (ii) the activated carbon Darco12-20 presents a slightly acidic PZC (about 6.4) and at the pH conditions used (pH 7) its surface would be negatively charged and the adsorption of the anionic form of these carboxylic acids would be greatly not favored attending to the electrostatic interactions.

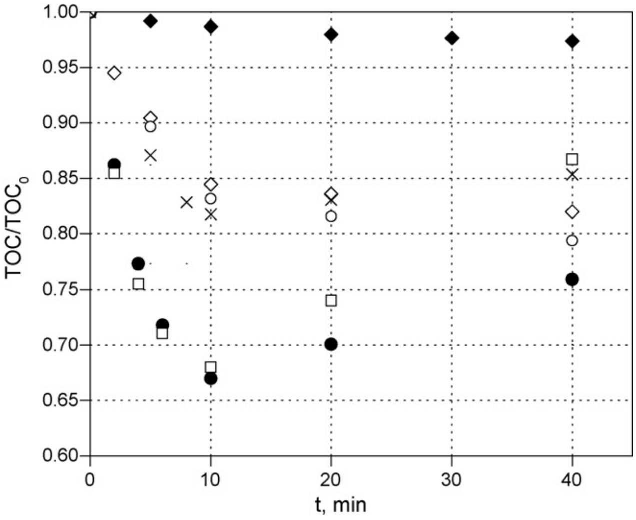

Fig. 3. Powdered activated carbon ozonation of intermediates (measured as TOC) resulting from 10 min ozonation of a 10^{-4} M sulfamethoxazole aqueous solution. Conditions: $T = 20\,°C$; pH = 7; $w = 1\,g\,L^{-1}$; inlet ozone gas concentration (average value) = 20 mg L^{-1}; □, gas flow rate = 25 L h^{-1}; ●, gas flow rate = 10 L h^{-1}; ◇, single ozonation; ◆, adsorption onto Darco12-20; ○, sum of single ozonation and single adsorption; × 1 h preozonated PAC.

As also observed in Fig. 3 the sum of both process after 10 min of reaction scarcely was able to remove 16% of the initial TOC, which clearly showed the synergetic effect of the ozone-PAC system and the contribution of the surface reactions (about 30% of TOC removed in the same period of time). On the other hand, no influence of the gas flow rate was observed in the range worked at least during the first 10 min of reaction as seen from Fig. 3. From this time, the accumulation of TOC in the bulk water is due to the increasing release of organic matter from the reaction ozone-PAC.

Table 1
Oxygenated superficial groups of Darco12-20.

	Carboxylic groups (μeq g^{-1})	Lactones (μeq g^{-1})	Phenolic groups (μeq g^{-1})	Carbonyls (μeq g^{-1})	Total acid groups (μeq g^{-1})	Total basic groups (μeq g^{-1})
Virgin	165	70	296	262	792	196
pH 4[a]	236	89	204	297	826	103
pH 7[a]	265	69	144	288	766	71
pH 9[a]	257	75	137	312	781	59

[a] Ozonated PAC.

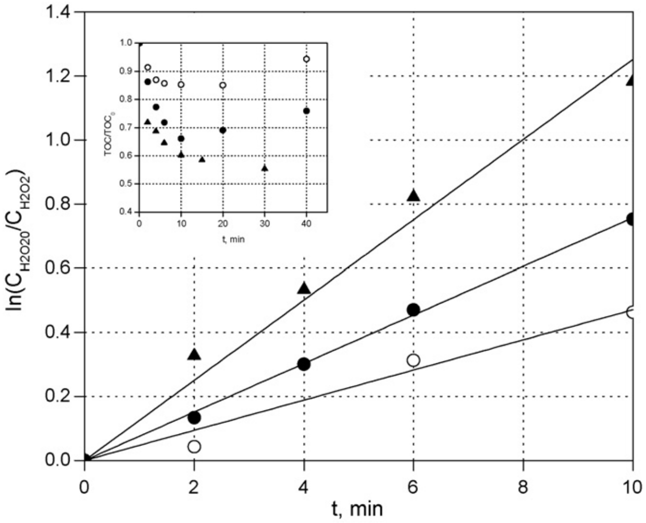

Fig. 4. Evolution of hydrogen peroxide concentration and normalized TOC (inset) during some ozonation-PAC experiments of preozonated 10^{-4} M sulfamethoxazole solutions. Effect of PAC concentration. Conditions: $T = 20\,^\circ$C; pH 7; gas flow rate = 10 L h^{-1}; inlet ozone gas concentration (average value) = 20 mg L^{-1}; ▲, $w = 2$ g L^{-1}; ●, $w = 1$ g L^{-1}; ○, $w = 0.25$ g L^{-1}.

In another experiment, a sample of PAC was preozonated during 1 h and reused in the catalytic ozonation of an ozonated sulfamethoxazole solution. As shown in Fig. 3, the results pointed out that the destruction of some SOGs during the preozonation stage clearly deactivated the catalytic activity of the activated carbon. In fact during the first 10 min of the catalytic process the results obtained were quite similar to the simple sum of adsorption and single ozonation contributions which highlights the important role of some SOGs in the catalytic mechanism. On the other hand, regardless of the ozonation pretreatment of the PAC in this experiment, the ozone-PAC reaction continued releasing organic matter in the bulk water as can be deduced from the increasing TOC from the 10 min of process. In addition, for the PAC ozonation process of 10 min preozonated SMX solution, no influence of the ozone gas flow rate was observed in the mineralization of the water matrix in the interval used as presented in Fig. 3, which suggests that mass transfer resistances have no effect on the process rate in this gas flow range at least during the first 10 min of process.

The amount of PAC-Darco12-20 was a variable studied in the catalytic ozonation of sulfamethoxazole. As seen in Fig. 4, a higher amount of activated carbon led to a faster TOC removal during the first 10 min of ozonation and before the organic matter from the reaction ozone-PAC was released into the bulk water. In addition, PAC concentration also favoured hydrogen peroxide depletion according to a pseudo first-order decay (see also Fig. 4). As stated, hydrogen peroxide can be found in the initial ozonated sulfamethoxazole solution from the reaction between ozone and the target compounds and first aromatic by-products formed. These results pointed out that a higher amount of activated carbon might favour hydrogen peroxide and ozone decomposition at the surface of the solid and consequently the mineralization of the water matrix.

3.3. Mechanism and kinetics

According to the experimental results obtained, the adsorption of the water matrix on the activated carbon was considered negligible. In addition, it is known that ozone while reacting with basic SOGs at the surface of the Darco12-20 forms hydrogen peroxide. In following steps, hydrogen peroxide can react in bulk water with ozone and hydroxyl radicals, reactions (7), (12) and (13), and be adsorbed to also react with adsorbed ozone to yield more hydroxyl radicals, reactions (3) and (4). With these premises and literature data the following mechanism of reactions is proposed [17,31–35]:

$$O_3 + PAC \overset{K_{O_3}}{\rightleftarrows} O_3 - PAC \quad (1)$$

$$O_3 + PAC \xrightarrow{k_1} TOC' + H_2O_2 + PAC^* \quad (2)$$

$$H_2O_2 + PAC \overset{K_{H_2O_2}}{\rightleftarrows} H_2O_2 - PAC \quad (3)$$

$$H_2O_2 - PAC + O_3 - PAC \xrightarrow{k_2} HO^\bullet + PAC' \quad (4)$$

$$HO^\bullet + TOC \xrightarrow{k_{OH}=5\times10^9\,M^{-1}\,s^{-1}} IC + HO_2{}^\bullet \quad (5)$$

$$H_2O_2{}^\bullet \overset{pK=11.8}{\rightleftarrows} HO_2^- + H^+ \quad (6)$$

$$O_3 + HO_2{}^- \xrightarrow{k_i=2.8\times10^6} O_3^-{}^\bullet + HO_2{}^\bullet \quad (7)$$

$$HO_2{}^\bullet \overset{pK=4.8}{\rightleftarrows} O_2^-{}^\bullet + H^+ \quad (8)$$

$$O_2{}^- + O_3 \xrightarrow{k_9=1.6\times10^9\,M^{-1}\,s^{-1}} O_3{}^{-\bullet} + O_2 \quad (9)$$

$$O_3{}^{-\bullet} + H^+ \xrightarrow{k_{10}=5.2\times10^{10}\,M^{-1}\,s^{-1}} HO^\bullet + O_2 \quad (10)$$

$$O_3 + HO^\bullet \xrightarrow{k_{O_3}=2\times10^9\,M^{-1}\,s^{-1}} HO_2{}^\bullet + O_2 \quad (11)$$

$$H_2O_2 + HO^\bullet \xrightarrow{k_{H1}=2.7\times10^7\,M^{-1}\,s^{-1}} HO_2{}^\bullet + H_2O \quad (12)$$

$$HO_2^- + HO^\bullet \xrightarrow{k_{H_2}=7.5\times10^9\,M^{-1}\,s^{-1}} HO_2{}^\bullet + OH^- \quad (13)$$

$$IC(HCO_3^-) + HO^\bullet \xrightarrow{k_{IC}=8.5\times10^6\,M^{-1}\,s^{-1}} \text{Inactive free radicals} \quad (14)$$

As stated, surface reaction (2) can also generate some organic matter but at the gas flow conditions worked (10 L h^{-1}) this contribution has been proven negligible (see Fig. 3) during the first minutes of reaction. Conversely ozone can be adsorbed at the surface of the activated carbon, reaction (1), to react with adsorbed hydrogen peroxide and generate free radicals which are the main responsible of the mineralization of the water matrix [36].

For the heterogeneous catalytic reaction (4), the kinetic expression is shown in Eq. (15) according to a Langmuir mechanism [37].

$$r_2 = \frac{k_2 w C_{O_3} C_{H_2O_2}}{(1 + K_{O_3} C_{O_3} + K_{H_2O_2} C_{H_2O_2})^2} \quad (15)$$

where K_{O_3}, $K_{H_2O_2}$ are the equilibrium constants of ozone and hydrogen peroxide adsorption, respectively, and w is the PAC concentration. Nevertheless, experiments of ozone and hydrogen peroxide carried out in the presence of Darco12-20 can be fitted by a first order kinetics, which suggests that, in Eq. (15) $1 \gg K_i C_i$ for ozone and hydrogen peroxide and then, Eq. (15) can be simplified to:

$$r_2 = k_2 w C_{O_3} C_{H_2O_2} \quad (16)$$

Taking this into account the next set of equations can be deduced from the material balances in a well agitated semi-batch reactor, as the one used in this work:

For ozone in the gas phase:

$$(1-\beta)V\frac{dC_{O_3g}}{dt} = m_{O_3e} - \upsilon_g C_{O_3g} - k_L a\left(\frac{C_{O_3g}RT}{He} - C_{O_3}\right)\beta V \quad (17)$$

where C_{O_3g} and C_{O_3} are the concentrations of ozone in the gas leaving the reactor and in water and β, V, m_{O_3g}, υ_g, $k_L a$, R and He are the liquid hold-up, reaction volume, ozone mol rate at the reactor inlet, gas flow rate, mass transfer coefficient and the universal gas perfect and Henry constants, respectively.

For ozone in water:

$$\frac{dC_{O_3}}{dt} = k_La\left(\frac{C_{O_3g}RT}{\mathrm{He}} - C_{O_3}\right)V - 2k_iC_{O_3}\frac{10^{\mathrm{pH-pK}}C_{H_2O_2T}}{1+10^{\mathrm{pH-pK}}} - k_{O_3}C_{O_3}C_{\mathrm{HO}} - wk_2C_{H_2O_2T}C_{O_3} - wk_1C_{O_3} \tag{18}$$

where $C_{H_2O_2T}$ and C_{HO} are the concentrations of total hydrogen peroxide and hydroxyl radicals, respectively.

For hydrogen peroxide in water:

$$\frac{dC_{H_2O_2T}}{dt} = -k_iC_{O_3}\frac{10^{\mathrm{pH-pK}}C_{H_2O_2T}}{1+10^{\mathrm{pH-pK}}} - k_HC_{H_2O_2T}C_{\mathrm{HO}} - wk_2C_{O_3}C_{H_2O_2T} + wk_1C_{O_3} \tag{19}$$

In Eqs. (18) and (19), the concentration of hydroxyl radicals and k_H are given as follows:

$$C_{\mathrm{HO}\cdot} = \frac{1}{(k_{\mathrm{IC}}\mathrm{IC} + \varphi k_{\mathrm{HO}}\mathrm{TOC})}\left[\frac{2kiC_{O_3}10^{\mathrm{pH-pK}}C_{\mathrm{H_2O_2T}}}{(1+10^{\mathrm{pH-pK}})} + wk_2C_{O_3}C_{H_2O_2}\right] \tag{20}$$

where φ represents the fraction of TOC that terminates the hydroxyl radical chains.

$$k_H = \frac{k_{H1} + k_{H2}10^{\mathrm{pH-pK}}}{1+10^{\mathrm{pH-pK}}} \tag{21}$$

For TOC in water:

$$\frac{d\mathrm{TOC}}{dt} = -k_{\mathrm{HO}}\mathrm{TOC}C_{\mathrm{HO}} \tag{22}$$

For inorganic carbon (IC) in water:

$$\mathrm{IC} = \mathrm{TOC}_0 - \mathrm{TOC} \tag{23}$$

In Eqs. (15)–(23) rate constants correspond to reactions (1)–(14) where their values are shown except for k_1 and k_2.

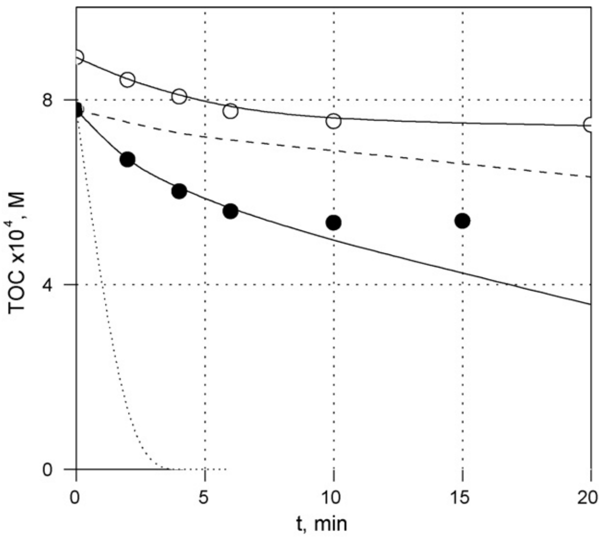

Fig. 5. Checking the kinetic model. Calculated (solid line) and experimental results (symbol) of the evolution of TOC with time with $k_1 = 210\,\mathrm{L^{-1}\,g\,M^{-1}\,s^{-1}}$, $k_2 = 0.007\,\mathrm{L^{-1}\,g\,s^{-1}}$, values of φ unless indicated: 0.25 during the first 2 min; 0.63 from 2 to 6 min; 0.95 from 6 to 10 min; and 1 from 10 min. Conditions: $T = 20\,°\mathrm{C}$; pH 7; $w = 1\,\mathrm{g\,L^{-1}}$; gas flow rate = 10 L h^{-1}; inlet ozone gas concentration (average value) = 20 mg L^{-1}; $\mathrm{TOC_0} = 12\,\mathrm{mg\,L^{-1}}$; ○, single ozonation; ●, catalytic ozonation. $\varphi = 0$ dotted line; $\varphi = 1$ dashed line.

A trial and error method was used to solve the model equation system where the rate constants k_1 and k_2 and the parameter φ are the unknown variables. The latter represents the fraction of TOC that terminates the radical chain and it varies with time during the ozonation process since it depends on the changing nature of intermediates formed during the reaction time. Thus, φ varies from 0 at the start of catalytic ozonation to as much as 1 at the end of the process. The value of 1 is assigned to intermediates that while reacting with the hydroxyl radical do not release the superoxide ion radical and, then, terminate the radical chain. These are called inhibitors of ozone decomposition [4]. On the contrary, a value of 0 is assigned for φ of intermediates that their reaction with the hydroxyl radical leads to the superoxide ion radical. This free radical propagates the radical chain through reactions (9) and (10) (see mechanism). These intermediates are called promoters of ozone decomposition [4]. The ratio of promoters to inhibitors changes with time in an ozonation process being high at the start and low at the end of ozonation, respectively. For example, aromatic compounds with hydroxyl groups or nucleophilic positions in their molecules, such as SMX, can be catalogued as promoters while oxalic acid is inhibitor [4]. The complex and unknown exact nature of intermediates makes not possible the finding of φ as an increasing function of time. Nonetheless, a rough estimation of φ can be obtained by the analysis of the single ozonation process. By application of the mechanism proposed in the absence of activated carbon, the only mechanism of mineralization is the hydroxyl radical pathway and the equation system can be solved considering different values of φ with time in order to adjust both experimental and mathematical results. Thus, the reaction time was divided in four short arbitrary time periods and a value of φ was assigned to each of them. The first period, first 2 min, corresponds to the time of highest TOC removal. The following two reaction periods were 4 min for each of them (2–6 and 6–10 min). In these two reaction periods experimental TOC was decreasing at a slower rate. Finally, a last period for reaction times higher than 10 min was considered. In this case, removal of TOC is practically stopped (see Fig. 5). Values of φ were then determined from the experiments of single ozonation by means of a trial and error procedure to minimize the function of the sum of the squares of the differences between calculated and experimental values of TOC. The Solver optimization package of Excel was used and the following φ values were finally determined:

Time (min)	0–2	2–6	6–10	>10
φ	0.25	0.63	0.95	1

This increasing value of the parameter φ with time is in accordance with the changing nature of the water matrix rising its inhibiting character along the ozonation process develops. The use of these φ values in the kinetic model for the case of single ozonation ($k_1 = 0$, $k_2 = 0$) leads to the good results shown in Fig. 5 as an example. The values of φ estimated in the single ozonation process were then used to solve the PAC ozonated kinetic model. Then, in the next step, rate constants k_1 and k_2 were also determined through a similar procedure with the same objective function to minimize but this time the results of catalytic ozonation experiments were used. The values of k_1 and k_2 that best fitted the experimental results were 220 L^{-1} g M^{-1} s^{-1} and 0.0035 L^{-1} g s^{-1}, respectively. In Figs. 5 and 6 calculated and experimental TOC values with time are presented for different catalytic ozonation experiments. In Fig. 5 calculated TOC values for one catalytic ozonation experiment for extreme values of φ are also shown. If 100% promoting character of the water matrix is assumed for all the reaction period, that is $\varphi = 0$, the mathematical solution overestimates the actual TOC removal so as within 30 s total mineralization of the water matrix was achieved (see dotted curve in Fig. 5). Clearly, this result did not fit the refractory behaviour of sulfamethoxazole ozonation byproducts. On the contrary, if $\varphi = 1$ for all the reaction period, the kinetic model underestimates the actual TOC removal rate (see dashed curve in Fig. 5). It is also evident that some intermediates are not inhibitors of ozone decomposition. Finally, when the calculated values of φ at different intervals were used the set of equations satisfactory fitted the experimental results (see solid curve in Fig. 5) during the first 10 min. A deepest examination of the equation

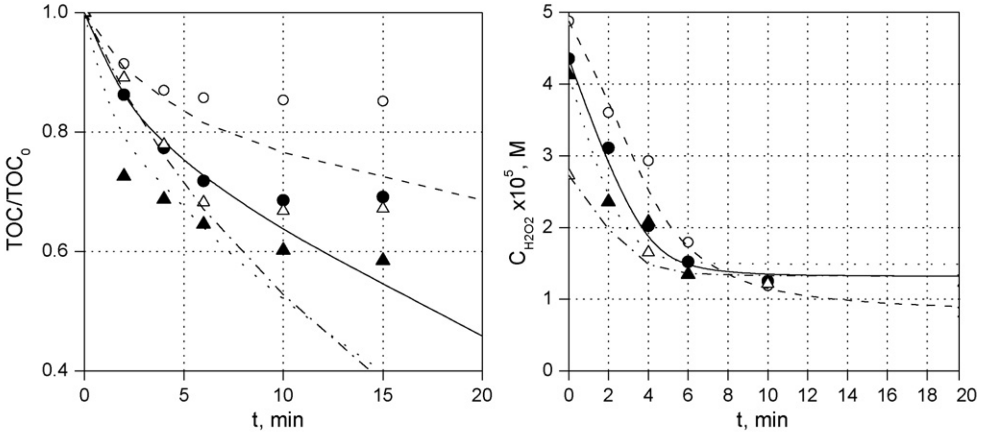

Fig. 6. Checking the kinetic model. Calculated (curves) and experimental results (symbol) of the evolution of TOC and hydrogen peroxide concentration with time. Effect of PAC concentration and initial TOC. Values of φ, k_1 and k_2 determined from the optimization procedure (see also bottom of Fig. 5). Conditions: $T = 20\,^\circ$C; pH 7; gas flow rate = 10 L h^{-1}; inlet ozone gas concentration (average value) = 20 mg L^{-1}; TOC$_0$ = 10 mg L^{-1} and $C_{\mathrm{H_2O_2 0}} = 4.3 \times 10^{-5}$ M unless indicated; catalytic ozonation: ▲, $w = 2$ g L^{-1}, dotted curves; ●, $w = 1$ g L^{-1}, solid curves; ○, $w = 0.25$ g L^{-1}, $C_{\mathrm{H_2O_2 0}} = 5 \times 10^{-5}$ M, dashed curves; △, TOC$_0$ = 5 mg L^{-1}, $w = 1$ g L^{-1}, $C_{\mathrm{H_2O_2 0}} = 2.7 \times 10^{-5}$ M, dashed-dotted curves.

system leads to the conclusion that the adjustment is only valid at the beginning of the reaction. As stated the contribution of the organic matter released by the surface reaction ozone-PAC has not been considered and probably this effect was the cause of the difference of experimental and calculates data after 10 min of reaction. In Fig. 6 calculated and experimental TOC and hydrogen peroxide concentrations with time for PAC catalytic ozonation experiments of 10 min SMX preozonated solutions carried out in the presence of different PAC concentrations and initial TOC are shown. As can be seen, TOC experimental results are in good concordance with the calculated ones but only for the first 5–10 min, that is, while no TOC release is observed. In the case of hydrogen peroxide, the model also works well even for reaction times higher than 10 min. For all these experiments the goodness of fit was determined by calculating the Theil's inequality coefficient, TIC, defined as follows [38]:

$$\mathrm{TIC} = \frac{\sqrt{\sum_i (y_{c,i} - y_{e,i})^2}}{\sqrt{\sum_i y_{c,i}^2} + \sqrt{\sum_i y_{e,i}^2}} \tag{24}$$

A value of TIC lower than 0.3 indicates a good agreement between experimental ($y_{e,i}$) and calculated, ($y_{c,i}$), results. In this work, TIC values lower than 0.011 and 0.17 were determined for TOC and hydrogen peroxide concentrations, respectively.

The kinetic model also gives the calculated concentrations of ozone in the gas at the reactor outlet and dissolved ozone with time. Some results are shown in Fig. 7. As can be observed from Fig. 7 the kinetic model, however, slightly overestimates the actual concentrations of ozone in the gas. Nonetheless, the model predicts, as expected, lower ozone concentrations for higher PAC concentration applied in consonance with reactions (1), (2) and (4) of the mechanism. Having a look at the process mechanism proposed, possible consumption of ozone in reactions with compounds release from the carbon surface (see TOC' in reaction (2)) that were not considered in the kinetic model can explain the reasons of deviations observed in Fig. 7. In any case, TIC values were also much lower than 0.3 for the calculated ozone gas concentrations.

Finally, also in Fig. 7 the calculated dissolved ozone concentrations with time for experiments at different PAC concentrations are presented. Dissolved ozone concentration could not be determined because of analytical problems (interferences of PAC with the analytical method). Thus, no comparison could be made with experimental results although it is also likely that the kinetic model slightly overestimates the actual concentration values for the reasons indicated before for the ozone gas concentration. In any case, the kinetic model, as it should be expected, also gives higher ozone concentrations with lower PAC concentrations applied.

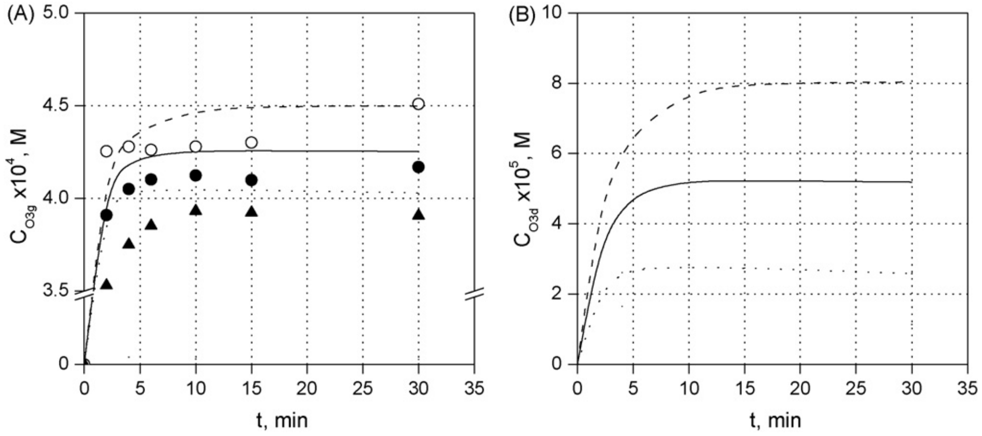

Fig. 7. Checking the kinetic model. Experiments at different PAC concentrations. (A) Calculated (curves) and experimental results (symbols) of the evolution of ozone gas concentration at the reactor outlet with time. (B) Calculated curves of the evolution of dissolved ozone concentration with time. Parameter values, conditions, meaning of symbols and curve types as in Fig. 6.

4. Conclusions

The most important conclusions achieve in this work are:

1. The used of activated carbon in powdered form (PAC) allows the removal of the external liquid–solid and the internal mass transfer resistances in the catalytic ozonation of SMX. In addition and at the conditions applied the gas–liquid mass resistance was eliminated.
2. SOGs present in the surface of the activated carbon, especially those of basic nature, are modified during the ozonation process. During this process the release into the bulk water of organics from these reactions was observed.
3. Ozonated SMX solution presents a very refractory nature and low affinity to be adsorbed onto PAC.
4. At the conditions worked ozonation of SMX ozonated aqueous solutions is a free physical mass transfer resistance process, thus, the chemical kinetics can be studied considering the different reactions that can develop in both bulk water and PAC surface.
5. The solution of the equation set of the mechanism proposed can be solved by a trial and error method that determines the unknown variables that minimize the square of the difference between the simulated and real values. Furthermore, the solution of the mathematical model considered the changing nature of the water matrix with the ozonation process by assuming the promoting or not promoting character of intermediates in the radical mechanism. The kinetic model, however, is only valid for the initial reaction times where release of TOC from the carbon surface was null or negligible.
6. From the results obtained with the highest PAC concentration applied in this work ($2\,\mathrm{g\,L^{-1}}$) a significant increase of TOC removal is observed (see Fig. 6) so that this catalytic ozonation process presents potential benefits for its application in water treatment. However, more research is needed to deal with aspects related to desactivation of PAC by ozone attack (elimination of basic SOGs) and regeneration studies of this material for reusing purposes.

Acknowledgments

Authors thank the MICINN of Spain and Feder Funds of European Commission for the economic support through projects CTQ2006-04745 and CTQ2009-13459-C05-05. Dr. Pocostales also thanks Ministry of Education of Spain for a FPU grant.

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