

Ozonation of clofibric acid catalyzed by titanium dioxide

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ABSTRACT

The removal of clofibric acid from aqueous solution has been investigated in catalytic and non-catalytic semicontinuous ozonation runs. Kinetic data were analyzed using second order expressions for the reaction between organics and ozone or hydroxyl radicals. Catalytic runs used a commercial titanium dioxide catalyst consisting of fumed colloidal particles. The kinetic constant of the non-catalytic ozonation of clofibric acid at pH 3 was $8.16 \times 10^{-3} \pm 3.4 \times 10^{-4} \text{ L mmol}^{-1} \text{ s}^{-1}$. The extent of mineralization during non-catalytic runs ranged from 50% at pH 7 to 20% at pH 3 in a reaction that essentially took place during the first 10–20 min. The catalyst increased the total extent of mineralization, its effect being more important during the first part of the reaction. The pseudo-homogeneous catalytic rate constant was $2.17 \times 10^{-2} \text{ L mmol}^{-1} \text{ s}^{-1}$ at pH 3 and $6.80 \times 10^{-1} \text{ L mmol}^{-1} \text{ s}^{-1}$ at pH 5, with up to a threefold increase with respect to non-catalytic constants using catalyst load of 1 g/L. A set of stopped-flow experiments were designed to elucidate the role of catalyst, whose effect was probably due to the adsorption of organics on catalytic sites rather than to the promotion of ozone decomposition.

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1. Introduction

Pharmaceuticals and personal care products (PPCPs) constitute a group of emerging pollutants whose presence in water and wastewater has been well documented [1–4]. It has been recognized that the major source of these pollutants is discharged from wastewater treatment plants (WWTPs) with some other minor contributions such as manure disposal and release from the industrial production of pharmaceuticals [5]. The result of constant discharges of these chemicals in the environment may lead to public health problems even though the concentration is low, ranging from micro- to nanograms per liter [6]. In most cases, this represents concentrations far from acute toxicity levels but they are still a cause for concern due to risks associated with genotoxicity, induced pathogen resistance and endocrine disruption [7,8]. Moreover, many of these substances escape conventional wastewater treatment plants and are already becoming ubiquitous in the environment [9].

This work studies the titanium dioxide catalyzed ozonation of clofibric acid: ethyl 2-(4-chlorophenoxy)-2-methylpropanoate. It is a human metabolite of the active substance clofibrate: ethyl 2-(4-chlorophenoxy)-2-methylpropanoate, a drug used as lipid regulator whose estimated persistence in the environment is over 20 years and which has been detected in lakes even after it fell out of use [10]. Being a polar compound, it also belongs to a class of sub-

stances that are not significantly adsorbed in soil and, therefore, can easily spread in surface and groundwater. The presence of this compound in the effluent of WWTP has been repeatedly reported since Ternes [11] measured up to 1.6 µg/L of clofibric acid in the effluent of a German treatment plant. More recently Tauxe-Wuersch et al. [12] also found relatively high concentrations of several hundred nanograms per liter of clofibric acid in Swiss Municipal WWTP and Weigel et al. [13] measured concentrations slightly over 1 ng/L in different samples taken in the North Sea. As for continental surface waters, Boyd et al. [2] reported the detection of clofibric acid in Detroit River water at 103 ng/L at the inlet of a drinking treatment plant. Zuccato et al. [14] reported values of some nanograms per liter in drinking water and Heberer and Stan [15,16] detected clofibric acid in several drinking water samples from the Berlin area at concentrations of up to 270 ng/L that were associated with practices of bank filtration and artificial groundwater enrichment. Recent findings of clofibric acid in environmental water samples in China stress the fact that its occurrence is part of a global phenomenon [17].

Advanced oxidation processes (AOP) are based on the generation of hydroxyl radicals and other oxidant species in concentrations high enough to allow the oxidation of organic compounds whose chemical stability makes them difficult to degrade otherwise [18]. AOP comprise a family of technologies that differ in the approach used to generate hydroxyl radicals. Photocatalytic methods, Fenton-based systems and the direct use of the oxidants ozone and hydrogen peroxide are complemented by the less developed hydrodynamic and acoustic cavitation, radiolysis and several electrical and electrochemical methods [19,20]. Moreover, the difficulty of

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Nomenclature

$C_A C_B$	concentration of organic carbon in compounds A and B (mol/L)
C_{ACE}	concentration of acetate (mol/L)
C_i	concentration of a given organic compound (mol/L)
$C_{HO\cdot}$	concentration of hydroxyl radicals (mol/L)
C_{O_3}	concentration of dissolved ozone (mol/L)
C_o	initial concentration (mol/L)
C_s	bulk concentration of solids in the liquid phase ($\text{kg}_{\text{solids}}/\text{L}$)
D_{O_3}	diffusivity of ozone in water ($\text{m}^2 \text{s}^{-1}$)
k_a	adsorption kinetic constant ($\text{L kg}_{\text{solids}}^{-1} \text{s}^{-1}$)
k_{-a}	desorption kinetic constant ($\text{mol kg}_{\text{solids}}^{-1} \text{s}^{-1}$)
k_c	intrinsic catalytic kinetic constant ($\text{L}^2 \text{kg}^{-1} \text{mmol}^{-1} \text{s}^{-1}$)
k_d	pseudo-homogeneous kinetic constant of ozone decomposition (s^{-1})
K_a	adsorption equilibrium constant (L mol^{-1})
$k_{HO\cdot} k_{O_3}$	second order kinetic constant of homogeneous ozone reactions ($\text{L mol}^{-1} \text{s}^{-1}$)
k_R	homogeneous kinetic constant defined in Eq. (4) ($\text{L mol}^{-1} \text{s}^{-1}$)
k_{RC}	pseudo-homogeneous kinetic constant defined in Eq. (8) ($\text{L mol}^{-1} \text{s}^{-1}$)
k_L	liquid-phase mass individual mass transfer coefficient (m s^{-1})
k_A, k_{ACE}	kinetic constants defined in Eq. (12) ($\text{L mol}^{-1} \text{s}^{-1}$)
R_{ct}	ratio of $C_{HO\cdot}$ to C_{O_3} at any time, dimensionless
z	stoichiometric coefficient

application of certain methods and the relatively low efficiency of others, suggested to combine them in an attempt to treat recalcitrant pollutants in real effluents. Photo-Fenton, sonophotocatalysis, the use of oxidants combined with ultraviolet radiation ($\text{H}_2\text{O}_2/\text{UV}$ and O_3/UV) or ultrasounds have also been considered [21]. Solid catalysts can be used to promote ozonation so that they are suitable for acidic conditions with limited ozone exposure, conditions at which the rate of formation of hydroxyl radicals would be too low. The interest in such working conditions is not only to reduce the cost of ozone generation, but also to limit bromate formation [22]. On the other hand, catalytic ozonation has been proposed to remove carboxylic acids and other refractory oxidation intermediates produced during the ozonation of complex organic molecules [23]. Except for the case of activated carbon, whose role seems to be to promote the decomposition of ozone with the subsequent increase in the production of radicals, the mechanism of catalytic ozonation is still uncertain. In metal oxides, the catalytic reaction is expected to involve the adsorption of organic molecules or ions on surface sites with subsequent oxidation by Eley-Rideal or Langmuir-Hinshelwood interaction with oxidant species. In any case, it should be born in mind that the adsorption of neutral compounds on oxides in aqueous solutions has to overcome the competitive adsorption of water molecules. Adsorption is relatively favoured for ionizable compounds if the surface is charged, this being the reason why metal oxides behave as anion exchangers if the pH of the solution is below the point of zero charge (PZC) of the solid [24].

The aim of this work was to study the catalytic ozonation of clofibric acid in reactions performed in a semicontinuous regime using a commercial titanium dioxide Degussa P25. TiO_2 P25 is a nanosized material commonly used in photocatalysis whose particles tend to agglomerate in solution as a consequence of Van der Waals attractive forces. In acidic conditions the surface hydrolyzes

thus originating repulsive forces between particles that determine the effective size of the aggregates [25]. The role of TiO_2 P25 in promoting ozonation reactions has been already documented [26]. Both the oxidation of clofibric acid and the mineralization of the dissolved organic matter have been studied and fitted to kinetic models as a function of the concentration of dissolved ozone. The interaction of clofibric acid and its ozonation products with the catalyst surface has been specially taken into account in order to separate chemical oxidation from a disappearance due to a physical adsorption.

2. Experimental

Clofibric acid was supplied by Sigma–Aldrich (97% purity). Solutions were prepared with high purity water obtained from a Milipore Mili-Q system with a resistivity of at least $18 \text{ M}\Omega \text{ cm}$ at 25°C . pH adjustments were made with analytical grade sodium hydroxide or hydrochloric acid from Merck. The solid used as heterogeneous catalyst was titanium dioxide Degussa P25, a mixture 80/20 of anatase/rutile. The catalyst is a nanometric powder consisting of primary particles of about 20 nm that form aggregates of several hundred nanometers that can be removed by filtration using $0.45 \mu\text{m}$ Teflon filters. The point of zero charge (PZC) of the catalyst was determined by potentiometric titration as described by Halter [27]. The value obtained, $\text{pH}_{\text{PZC}} 6.6$, has been already reported [26] and agrees with similar data published elsewhere [28]. The BET specific surface was $52 \pm 2 \text{ m}^2/\text{g}$ determined by nitrogen adsorption at 77 K.

Ozonation runs were performed in a 1 L glass jacketed reactor connected to a Huber Polystat cc2 thermostatic regulator and agitated by means of a magnetic rod at about 700 rpm. The temperature of the liquid inside the reactor was monitored throughout the experiment by means of a Pt100 RTD sensor whose readings were transferred to an automated data processing system. The mixture of ozone and oxygen was produced by a corona discharge ozonator (Ozomatic, SWO100) fed by an AirSep AS-12 PSA oxygen generation unit. pH was measured by means of an electrode connected to a Eutech α ph-pH100 feed-back control device. The final control element was a LC10AS Shimadzu pump that delivered a solution of hydrochloric acid allowing pH to be controlled within ± 0.1 throughout the experiment. The concentration of ozone dissolved in the liquid was determined by means of an amperometric analyser Rosemount 499A OZ calibrated against the Indigo Colorimetric Method (SM 4500- O_3 B). A computer stored the signals from the concentration of dissolved ozone, pH and temperature after being captured by means of an Agilent 34970 Data Acquisition Unit. The concentration of ozone in gas phase was determined using a non-dispersive UV Photometer Anseros Ozomat GM6000 Pro. TOC was determined by means of a Shimadzu TOC-VCSH analyzer; carboxylic acids were measured using a Dionex DX120 chromatograph and the analyses of clofibric acid were performed by HPLC using a C18 250 mm column. The mobile phase for the later was a mixture of water containing 4 mL/L of phosphoric acid and 50 mL/L of methanol and acetonitrile (40:60) with an isocratic flow of 1.0 mL/min at room temperature. Detection was carried out at 230 nm. Additional details are given elsewhere [26].

Ozone decomposition experiments were performed in semicontinuous mode using a fixed volume of Mili-Q water containing different amounts of catalyst. The gaseous mixture containing ozone was bubbled into the liquid by means of a porous glass disk with a gas flow of $0.20 \text{ Nm}^3/\text{h}$. At a given time, the gas flow was stopped and the evolution of the concentration of dissolved ozone was recorded until its total depletion. In some runs, the flow of ozone was stopped one or more times during the experiment with the purpose of performing experiments in which the exposure to

ozone was not correlated with reaction time. In catalytic runs, this procedure also allowed a certain period of contact with the catalyst in the absence of ozone, used to get more insight on the possible adsorption of reaction intermediates.

The ozonation experiments were conducted in a semicontinuous mode using a fixed volume of water containing clofibric acid 25–100 mg/L (116–466 mM). High concentrations compared to that usually found in wastewater were used in order to provide a high organic load per unit mass of catalyst and to favour the accuracy in analytical determinations. Catalytic runs were performed at a bulk catalyst concentration in the 0.25–1.25 g/L range. During every run, certain samples were withdrawn for analysis at prescribed intervals. Dissolved ozone was removed by bubbling nitrogen immediately after sampling. In catalytic runs, the catalyst was previously removed by filtration by means of Teflon 0.45 μm Millipore filters. The experiments were carried out at pH in the range 3–7 and 25 °C. The decomposition of ozone acidified the reaction mixture in all cases and pH was automatically controlled by pumping a diluted sodium hydroxide as indicated before. The volumetric mass transfer coefficient had a relatively large value ($k_L a = 0.0123 \pm 0.0017 \text{ s}^{-1}$) and accounted for the rapid increase of dissolved ozone observed at the beginning of each run. The ozone profile depended on the rate of ozone consuming reactions and usually exhibited a shoulder during the first minute of reaction after which it reached a plateau value almost constant throughout the run.

3. Results and discussion

3.1. Ozonation of clofibric acid

The kinetics of a heterogeneous gas–liquid semicontinuous process is governed by the relative rates of absorption and chemical reaction. A characterization of kinetic regimes is given by Hatta number, that represents the maximum rate of chemical reaction relative to the maximum rate of mass transfer. For a second order reaction the Hatta number follows the expression:

$$Ha = \frac{\sqrt{z k_R C_{A,0} D_{O_3}}}{k_L} \quad (1)$$

where D_{O_3} is the diffusivity of ozone in water ($1.77 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$), k_R is the homogeneous second order rate constant for the depletion of the organic compound, A , whose maximum concentration in the bulk is $C_{A,0}$. The value of the mass transfer coefficient, $k_L = 5.5 \times 10^{-5} \text{ m s}^{-1}$, was evaluated according to Calderbank and Moo-Young [29]. The stoichiometric coefficient for the reaction between ozone and clofibric acid has been given elsewhere [30]. For the most unfavourable conditions tested in this work, $Ha < 0.18$, ensuring that the kinetic regime was slow. This finding is consistent with the fact that ozone was detected in solution at any time during runs and allowed the use of the concentrations of ozone and clofibric acid to develop a kinetic model for the reaction taking place in the liquid phase [31]. The homogeneous rate of ozonation of an organic compound is the result of its second order parallel reaction with dissolved ozone and with hydroxyl radicals. A mass balance to a given oxidizable compound in solution yields:

$$-\frac{dc_i}{dt} = k_{HO\cdot} c_{HO\cdot} c_i + k_{O_3} c_{O_3} c_i \quad (2)$$

Elovitz and von Gunten [32] proposed a kinetic model for the ozone-mediated removal of pollutants by using data from integral ozone exposure. According to it, the ozonation process is characterized by a parameter R_{ct} defined as the relationship between the integral exposures to ozone and hydroxyl radical and, derived from

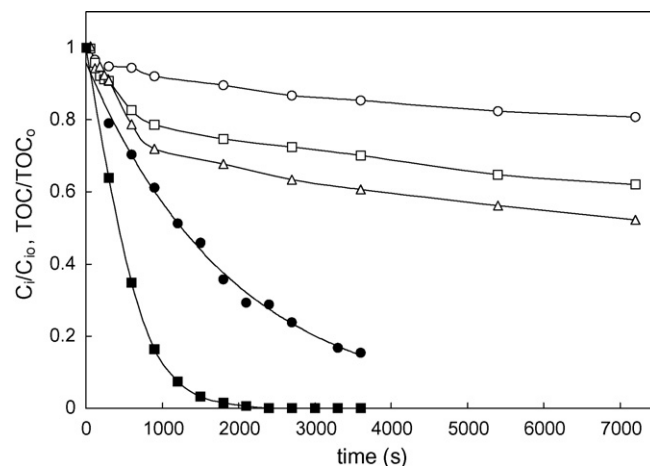


Fig. 1. Relative concentration of clofibric acid at pH 3 (●) and pH 5 (■) and TOC during the non-catalytic ozonation of 50 mg/L of clofibric acid in water at pH 3 (○), pH 5 (□) and pH 7 (△).

it, the ratio between the concentrations themselves:

$$R_{ct} = \frac{C_{HO\cdot}}{C_{O_3}} \quad (3)$$

R_{ct} represents the efficiency of the system in generating hydroxyl radicals from dissolved ozone and allows the estimation of the concentration of hydroxyl radical in water, although it is not necessarily constant throughout an ozonation run [6]. It behaves as an operational parameter that characterizes the oxidation process either in whole or in part [33]. Previous results show that R_{ct} may be considered constant during the part of the ozonation run associated to the depletion of a given type of chemical compounds [6]. By using this concept, the integration of Eq. (2) yields the logarithmic concentration decay ratio as a function of the integral ozone exposure.

$$\ln \frac{c_{i0}}{c_i} = (k_{HO\cdot} R_{ct} + k_{O_3}) \int c_{O_3} dt = k_R \int c_{O_3} dt \quad (4)$$

The kinetic parameter k_R represents the overall kinetics and may be accurately determined from the information available on the ozone profile, whose concentration was precisely recorded throughout the run with a sampling period of 5 s. Fig. 1 shows the decay of clofibric acid with time in non-catalytic runs performed at pH 3 and 5. The second order kinetic parameter k_R obtained from experimental data after evaluating the integral ozone exposure by a numerical method, yielded a value of $8.16 \times 10^{-3} \pm 3.4 \times 10^{-4} \text{ L mmol}^{-1} \text{ s}^{-1}$ at pH 3 and $1.77 \times 10^{-1} \pm 1.5 \times 10^{-2} \text{ L mmol}^{-1} \text{ s}^{-1}$ at pH 5, where the boundaries represent the respective 95% confidence intervals (Table 1). At pH 7 the kinetic regime was not slow so that the model outlined before could not be applied. Also shown in Fig. 1 are the TOC profiles for non-catalytic ozonations performed at pH in the 3–7 range, which exhibit a two-stage pattern already observed before in catalytic and non-catalytic ozonation of other organics [27]. Both TOC decay and the disappearance of clofibric acid are faster at higher pH values as expected from the higher rate of hydroxyl radical production with increasing pH [34].

Clofibric acid, whose pK_a is 3.2 [35], dissociates in aqueous solution even under acidic conditions. The results showed that the adsorption of clofibrate was favoured in conditions at which the surface behaves as an anion exchanger [24]. Fig. 2 shows the results for the adsorption of clofibric acid at pH 3 and 5 on TiO_2 Degussa P25 (pH_{PZC} 6.6). The adsorption kinetics was slow and took place essentially during the firsts 2–4 h, although equilibrium was achieved after a considerably longer period and the extent of adsorption reached only 5–15%. At pH 7 adsorption did not take place in any

Table 1
Kinetic constants for the ozonation and mineralization reactions.

Ozonation of clofibric acid			
	Non-catalytic (k_R , $\text{L mmol}^{-1} \text{s}^{-1}$)	Catalytic (k_{RC} , $\text{L mmol}^{-1} \text{s}^{-1}$, $c_s = 1 \text{ g/L}$)	
pH 3	$8.16 \times 10^{-3} \pm 5.4 \times 10^{-4}$	$2.17 \times 10^{-2} \pm 5.6 \times 10^{-3}$	
pH 5	$1.77 \times 10^{-1} \pm 3.0 \times 10^{-2}$	$6.80 \times 10^{-1} \pm 2.4 \times 10^{-2}$	
Mineralization constants for the two-stage mineralization model			
	k_{R1}	k_{Ri}	k_{R2}
Non-catalytic ($\text{L mmol}^{-1} \text{s}^{-1}$)			
pH 3	$1.22 \times 10^{-3} \pm 3.2 \times 10^{-4}$	$7.03 \times 10^{-3} \pm 4.4 \times 10^{-4}$	$5.4 \times 10^{-4} \pm 7 \times 10^{-5}$
pH 5	$7.43 \times 10^{-3} \pm 8.5 \times 10^{-4}$	$1.59 \times 10^{-1} \pm 2.0 \times 10^{-2}$	$3.5 \times 10^{-4} \pm 6 \times 10^{-5}$
Mineralization constants for the two-stage mineralization model			
	k_{RC1}	k_{RCi}	k_{RC2}
Catalytic (pseudo-homogeneous constant at $c_s = 1 \text{ g/L}$, $\text{L mmol}^{-1} \text{s}^{-1}$)			
pH 3	$4.52 \times 10^{-3} \pm 4.7 \times 10^{-4}$	$1.66 \times 10^{-2} \pm 1.5 \times 10^{-3}$	$4.3 \times 10^{-4} \pm 4 \times 10^{-5}$
pH 5	$1.68 \times 10^{-2} \pm 1.1 \times 10^{-3}$	$6.49 \times 10^{-1} \pm 2.8 \times 10^{-2}$	$2.9 \times 10^{-4} \pm 7 \times 10^{-5}$

measurable extension, a result consistent with a negatively charged surface. Similar results have been published for other acidic solutes that may be adsorbed by an ion-exchange mechanism [15,16].

The rate of catalytic ozonation of a certain compound is given by the rate of its homogeneous reaction with ozone or hydroxyl radicals and that of the heterogeneous catalytic reaction. Considering that the reaction between adsorbed species and hydroxyl radicals from the bulk is the limiting process, the rate expression would be:

$$-\frac{dc_i}{dt} = k_{HO} \cdot c_{HO} \cdot c_i + k_c c_s c_{HO} \cdot \theta \quad (5)$$

where θ is the fraction of surface sites occupied with adsorbate and c_s is the bulk concentration of solids. Assuming adsorption equilibrium and including the R_{ct} concept as indicated before, the combined rate becomes:

$$-\frac{dc_i}{dt} = k_{HO} \cdot c_{HO} \cdot c_i + k_c c_s c_{HO} \cdot \frac{k_a c_i}{k_a c_i + k_{-a}} \quad (6)$$

in which k_a and k_{-a} are the adsorption and desorption kinetic constants for the organic compound respectively. In the case of small surface coverage $k_a c_i \ll k_{-a}$ and the following equation is obtained in which the adsorption equilibrium constant, $K_a (=k_a/k_{-a})$ can be included in a group of constants with a linear dependence on cata-

lyst load:

$$-\frac{dc_i}{dt} = (k_{HO} \cdot R_{ct} + k_c R_{ct} K_a c_s) c_{O_3} c_i \quad (7)$$

The integration of the former equation yields a linear relationship between the logarithmic decay of the concentration of any given compound and the integral exposure to ozone:

$$\ln \frac{c_{i,0}}{c_i} = (k_{HO} \cdot R_{ct} + k_c R_{ct} K_a c_s) \int c_{O_3} dt = k_{RC} \int c_{O_3} dt \quad (8)$$

A Langmuir-Hinshelwood mechanism would lead to the same expression on the assumption that the equilibrium constant for the oxidation of surface sites is low enough [27]. The pseudo-homogeneous kinetic constant k_{RC} for the ozonation of clofibric acid obtained from the fitting of experimental data to Eq. (8) is shown in Fig. 3 for several catalyst loads and for runs performed both at pH 3 and 5. The kinetic constants were linear with the concentration of catalyst, as expected from the previously outlined model. The catalytic constant was $2.17 \times 10^{-2} \pm 5.6 \times 10^{-3} \text{ L mmol}^{-1} \text{s}^{-1}$ (pH 3) and $6.80 \times 10^{-1} \pm 4.1 \times 10^{-2} \text{ L mmol}^{-1} \text{s}^{-1}$ (pH 5) for a catalyst load of 1.0 g/L. It must be noted that this rate constant includes the R_{ct} parameter that was not independently determined in this work. The fact that non-catalytic reaction constants match with the intercepts of catalytic constants extrapolated to zero catalyst load, suggests

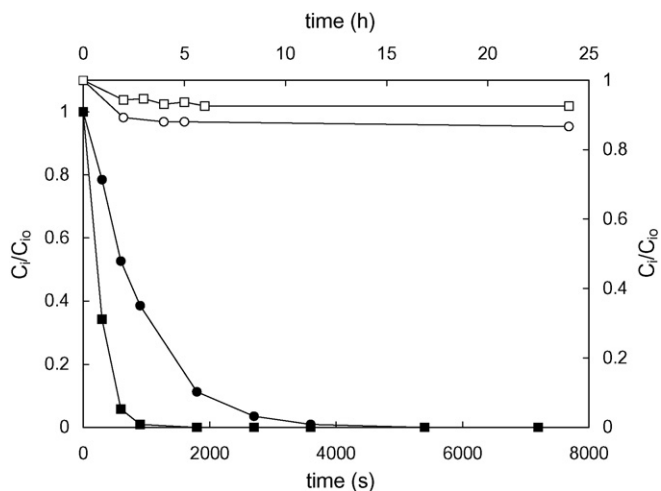


Fig. 2. Adsorption of clofibric acid at pH 3 (○) and pH 5 (□) on 1 g/L of TiO_2 (upper scale) and evolution of clofibric acid during catalytic ozonation runs at pH 3 (●) and pH 5 (■) (lower scale) also using 1 g/L of TiO_2 . Initial concentration of clofibric acid: 50 mg/L.

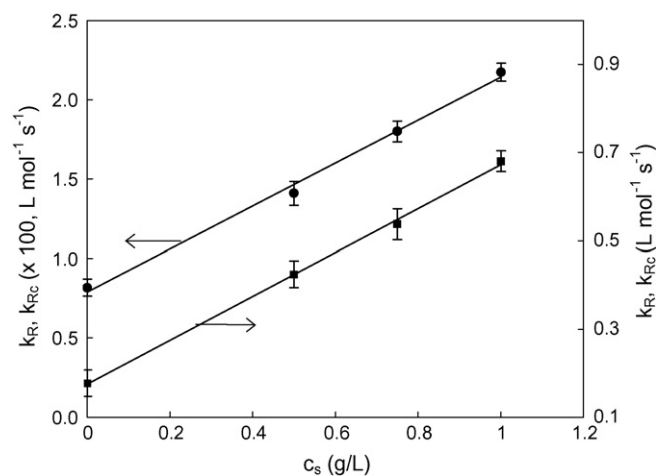


Fig. 3. Pseudo-homogenous kinetic constant for the ozonation of clofibric acid in catalytic runs as a function of catalyst concentration at pH 3 (●, left scale) and pH 5 (■, right scale). The error bars represent 95% confidence intervals.

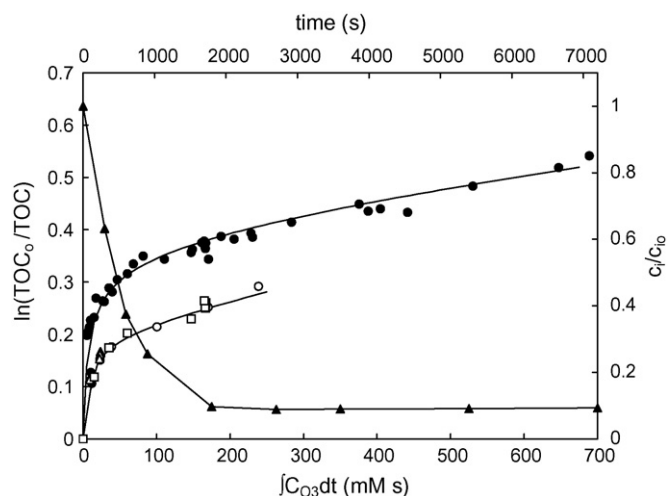


Fig. 4. Dissolved organic carbon as a function of the integral ozone exposure for catalytic runs performed at pH 5 (●) and at pH 3 (○, □, and △), where the latter represent runs with stopped flow of ozone. The evolution of clofibric acid at pH 3 is also shown for a run in which the flow of ozone ceased after 10 min (▲, left and upper scales; the TOC for this run corresponded to the empty triangles).

that the catalyst surface does not play an important role in changing the ratio ozone-to-hydroxyl radicals in solution.

3.2. Mineralization kinetics

The mineralization process was followed by determining TOC in samples withdrawn during the runs. The evolution of TOC for representative non-catalytic runs is shown in Fig. 1 and for several catalytic experiments at pH 3 and 5 in Fig. 4. In all cases, as shown in Fig. 4, the logarithmic decrease of the organic carbon was not linear with the time-integrated concentration of ozone. A rapid initial TOC decay was always followed by a much lower rate of mineralization. During all this first ozonation period, there were still measurable amounts of clofibric acid in solution as indicated in Figs. 1 and 4. Filled squares in Fig. 4 represent the concentration of clofibric acid in a run performed at pH 3 with 10 min ozone flow. At this moment, the flow of ozone ceased and the dissolved ozone started to decay. Ozone was still measured in solution for about 20 more min, but the rest of the run, that lasted 120 min, took place in the absence of ozone. Once ozone was completely depleted, there was still about 4 ppm of clofibric acid, a concentration that did not decrease during the last part of the run. The integral exposure to ozone was limited in this run to 25 mM s (empty triangles) and in the absence of ozone the amount of dissolved carbon (TOC) did not evolve. These results showed that adsorption of both clofibric acid and reaction intermediates was not substantially modified by the absence of ozone under reaction conditions and could not be the reason for the decay of organics in solution. The second and slower mineralization period corresponded to the reaction of the less reactive intermediates, the transition corresponding to the depletion of clofibric acid. The experimental values of TOC were fitted to a kinetic model that considered a first set of easily oxidizable compounds (A) which, on ozonation, yielded a second group of refractory products (B). The kinetics of mineralization did not match with a simple series $A \rightarrow B \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ due to the relatively rapid decay of dissolved carbon during the first part of the runs. This suggested that the formation of intermediates should not be a prerequisite for mineralization and suggested the following model:

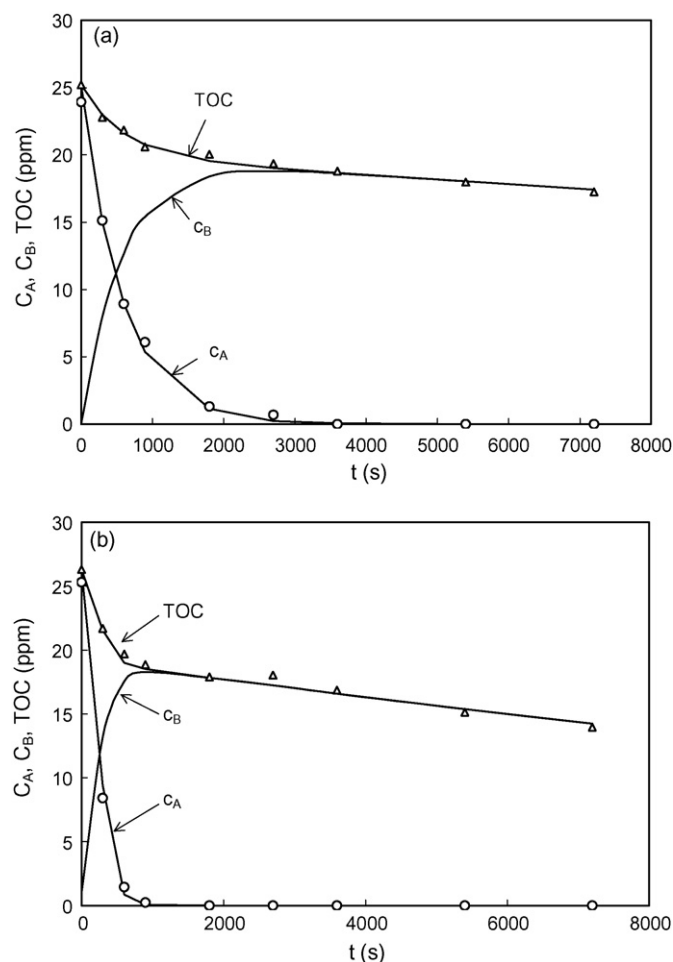
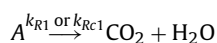
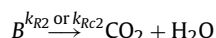
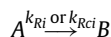


Fig. 5. Catalytic ozonation (1 g/LP25) of clofibric acid at pH 3 (a) and 5 (b) and model predictions for clofibric acid (c_A), TOC and reaction intermediates (c_B). Symbols correspond to experimental data and lines to model results. Empty circles represent the organic carbon in clofibric acid measured in samples.



Assuming that the reactions considered in the model are ozone-mediated transformations, Eqs. (4) and (8) can be applied for non-catalytic and catalytic runs respectively. The corresponding homogeneous kinetic constants for the three reactions considered have been labelled k_{R1} , k_{Ri} and k_{R2} (k_{Rc1} , k_{Rci} and k_{Rc2} in the case of catalytic runs) for the three individual steps yielding the following kinetic expressions for the ozonation of A and B:

$$-\frac{dc_A}{dt} = k_{R1}C_{O_3}C_A + k_{Ri}C_{O_3}C_A \quad (9)$$

$$\frac{dc_B}{dt} = k_{Ri}C_{O_3}C_A - k_{R2}C_{O_3}C_B \quad (10)$$

The observed experimental value, TOC, corresponds to $c_A + c_B$ at any time. The calculated profile of A essentially corresponded to that of the parent compound clofibric acid, and therefore c_A was considered a directly measurable variable coincident with the concentration of clofibric acid. The modelling by least square fitting included a fourth order Runge–Kutta routine for the integration of Eqs. (9) and (10). Fig. 5 shows experimental and predicted values of TOC for the catalytic ozonation of clofibric acid at pH 3(a) and 5(b) with a catalyst load of 1 g/L. In the same figure, the experimen-

tal concentration of clofibric acid, which remains detectable up to about 15 min (pH 5) and 50 min (pH 3), is also shown together with the theoretical profiles of c_A and c_B . The fact that clofibric acid can be identified at least as the most significant contribution to the group of oxidizable compounds included in A, indicates that no accumulation of reactive intermediate oxidation products is taking place. The calculated rate constants corresponding to the model described by Eqs. (9) and (10) are shown in Table 1 together with their 95% confidence intervals. The fitting achieved confirms that the parameter R_{ct} should not significantly change during the ozonation of the group of compounds that characterize both ozonation periods, namely clofibric acid and acidic oxidation derivatives. The results indicated that an increase of pH accelerated the first mineralization period both in catalytic and non-catalytic runs. This observation is consistent with the role of hydroxide anion in the production of hydroxyl radicals and also agrees with previously published data on the catalytic ozonation of other drugs [27]. The mineralization of the final refractory products was somewhat slower in catalytic runs, but the differences have low statistical significance due to the overlap of their respective confidence intervals. As expected comparing Eqs. (4) and (9), $k_{R1} + k_{Ri}$ was essentially coincident with k_R and the same for the corresponding catalytic runs as shown in Table 1.

The role played by the adsorption of clofibric acid in explaining TOC decay is not expected to be important in view of its slow adsorption kinetics as indicated in Fig. 2 and the kinetic mineralization data reported in Table 1. Moreover, the rate constant of the initial TOC decay in catalytic runs is considerably greater at pH 5 than at pH 3, at which the adsorption of the dissociated form of clofibric acid is more favoured. A related question is whether the adsorption kinetics of the intermediate products formed during ozonation may control the overall reaction rate invalidating the equilibrium-based mechanisms outlined before (Eq. (7)). The contribution of an adsorption process in parallel with the catalytic reaction would include a term not dependent on the concentration of oxidant in the rate expression:

$$-\frac{dc_A}{dt} = k_{HO} \cdot R_{ct} \cdot c_{O_3} \cdot c_A + k_a c_s c_A \quad (11)$$

The integration of Eq. (11) gives an expression in which the logarithmic decrease of the organic compound is not linear with the time-integrated concentration of ozone. The situation underlying this model can be discriminated from those models based on surface equilibrium with data in which the integral ozone exposure and reaction time are not correlated. The data shown in Fig. 4 reflect the logarithmic TOC decay during the ozonation of clofibric acid at pH 5 in four independent runs, in three of which the flow of ozone was stopped several times during the run and for different periods in order to obtain TOC data with different $\int c_{O_3} dt$ in samples taken at the same time intervals. The data are shown together with their theoretical fitting curve obtained from Eqs. (9) and (10) and indicate that an adsorption-based mechanism like that of Eq. (11) was not governing the observed mineralization kinetics. A different approach leading to the same conclusion is shown in Fig. 4, whose data correspond to runs performed at pH 3. In these runs, the ozone flow was stopped after 10, 30 and 120 min in runs represented by triangles, squares and circles respectively. The gas flow was not restored thereafter and ozone remained detectable in solution for about 10 min after stopping gas flow. If the kinetic expression contained a time-dependent term like that in Eq. (11), the TOC decay curve would turn upwards sharply in the part of the run where adsorption of intermediates in the absence of ozone could take place. The same conclusion may be drawn for clofibric acid if it remains in solution from the data shown in Fig. 4 that correspond to a run in which the flow of ozone was stopped after 10 min. Fig. 6 shows the evolution of mineralization with the time-integrated concentration of ozone in runs performed at pH 3

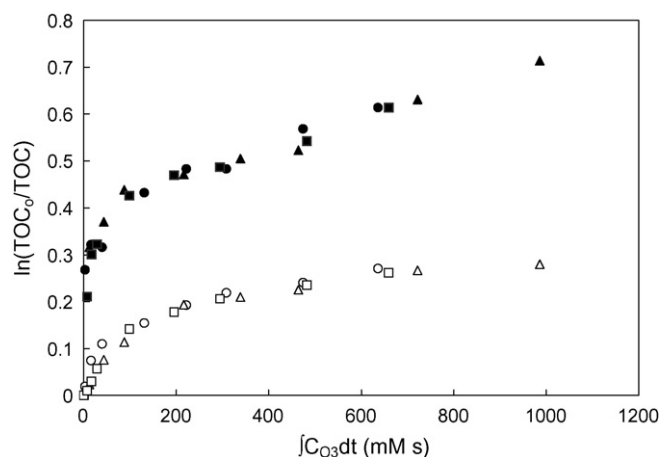


Fig. 6. Organic carbon as a function of the integral ozone exposure for catalytic runs performed at pH 3 (empty symbols) and pH 5 (filled symbols) and for different initial concentrations of clofibric acid: 25 mg/L (○ and ●), 50 mg/L (□ and ■), 100 mg/L (△ and ▲), and $c_s = 1$ g/L.

and 5 while varying the initial concentration of clofibric acid. The fact that the logarithmic TOC decay is not dependent on the initial amount of dissolved carbon supports the assumptions underlying the kinetic expressions based on Eqs. (6)–(8). It must be noted, however, that the mechanism cannot be considered proved as other mechanisms such as a reaction between adsorbed organic compounds and oxidized catalyst sites, are compatible with the same kinetic expressions [36]. Finally, a series of reactions were also carried out for several concentrations of catalyst in the 0.25–1.25 g/L range at pH 5. The results shown in Fig. 7, indicate that kinetic constants k_{R1} and k_{Ri} are linear with the bulk concentration of catalyst. Concerning k_{R2} , it is difficult to draw conclusions due to the high uncertainty associated with this constant. A good fit was obtained using values in the order of 10^{-4} L mmol $^{-1}$ s $^{-1}$. Fig. 7 also shows the first-order decomposition constant of ozone in the presence of TiO $_2$ P25 as a function of the amount of catalyst in suspension. The increase in the ozone decomposition rate associated to the use of catalyst has a minor importance with a shift from 8.98×10^{-4} s $^{-1}$ (non-catalytic run) to 1.01×10^{-3} s $^{-1}$ (1.5 g/L).

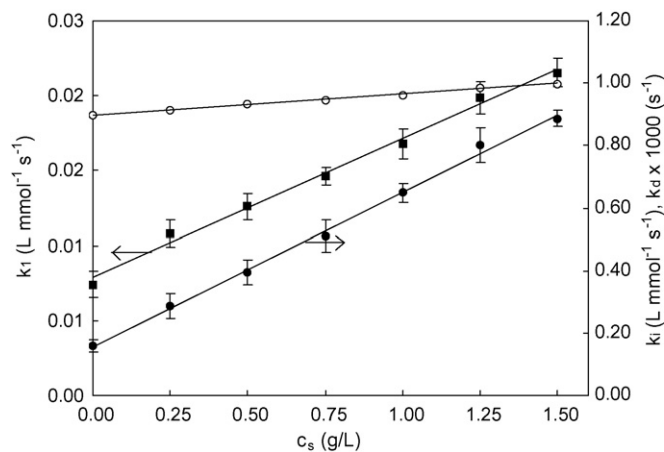


Fig. 7. Pseudo-homogeneous kinetic constants for the catalytic ozonation of clofibric acid at different catalyst loads: k_{R1} (■, left scale) and k_{Ri} (●, right scale) and first-order kinetic constant for the catalytic decomposition of ozone, k_d (○, right scale).

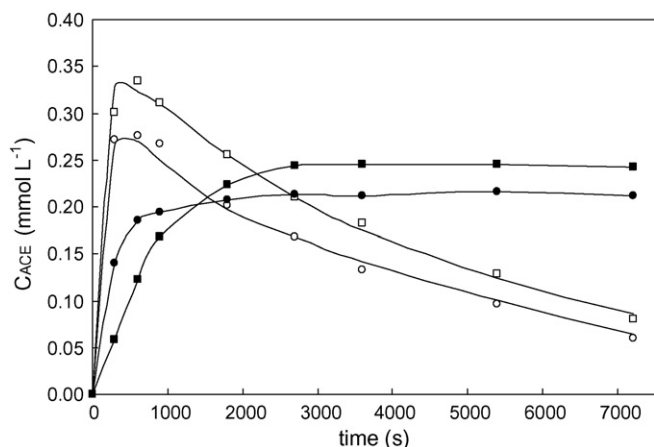


Fig. 8. Evolution of acetate during the catalytic ozonation of 50 mg/L of clofibric acid at pH 3 (● and ■) and pH 5 (○ and □). Circles: non-catalytic; squares: runs using 1 g/L of P25.

3.3. Ozonation products

Except for the first few minutes, carboxylic acids are the main products of the ozonation of clofibric acid both in catalytic and non-catalytic runs. The three measured carboxylates accounted for over 60% of the organic carbon that remained in solution at the end of runs performed using 1 g/L of catalyst. For the same conditions but in the absence of catalyst, the organic carbon in the form of carboxylates was less than 50% of the total dissolved organic carbon. After 5 min, the amount of organic carbon attributed to carboxylates was 50% and 40% for catalytic and non-catalytic ozonation respectively at pH 5. At pH 3, the difference between catalytic and non-catalytic runs was greater, with 60% and 40% respectively of the organic carbon in the form of carboxylates. The concentration of oxalate, a well-known final product of the ozonation of organic compounds, tend to increase steadily during the runs, particularly at higher pH. The concentration of acetate showed a different profile in runs performed at pH 5, in which a rapid accumulation is followed by a slower decay as shown in Fig. 8.

The rapid formation of acetate from clofibric acid was probably a consequence of the oxidation of 2-hydroxyisobutyric acid from the parent compound or other ring-opening products. If it could be assumed that all the acetates are produced from clofibric acid, the following kinetic expression applies:

$$\frac{dc_{ACE}}{dt} = k_A c_{O_3} c_A - k_{ACE} c_{O_3} c_{ACE} \quad (12)$$

where k_A and k_{ACE} are the second order constants for the ozonation of clofibric acid (c_A) and acetic acid (c_{ACE}). They include both direct and indirect ozonation and correspond to Eqs. (4) and (8), although in the case of catalytic reactions, the subscript "R" has been dropped for clarity. The values of k_A were not coincident with k_R or k_{RC} from Table 1. For example, for a catalyst load of 1 g/L at pH 5, the fitting of experimental data to Eq. (12) led to a rate constant $k_A = 0.36 \text{ L mmol}^{-1} \text{ s}^{-1}$, almost half of the pseudo-homogeneous rate constant are listed in Table 1. This result suggests that a significant fraction of the observed acetic acid is produced from relatively stable reaction intermediates. Even in the absence of reliable data from c_A , accurate values of k_{ACE} can be obtained from the concentration profile of acetic acid. The reason is that during most of the run the kinetic evolution of acetic acid corresponds to a second order consumption dominated by the second term of the right hand side of Eq. (12).

The rate constant for the ozonation of acetate, k_{ACE} , was $1.57 \times 10^{-3} \pm 2.6 \times 10^{-4} \text{ L mmol}^{-1} \text{ s}^{-1}$ for non-catalytic ozonation

and $2.09 \times 10^{-3} \pm 1.3 \times 10^{-4} \text{ L mmol}^{-1} \text{ s}^{-1}$ when using 1 g/L of P25 catalyst. By contrast, at pH 3 the rate of disappearance of acetate was very low and rate constants could not be determined. The results for representative runs are as shown in Fig. 8. The data from experiments in which the flow of ozone was stopped before the end of the run, show an almost constant concentration of carboxylates during the period that took place in the absence of ozone. These data indicate that the concentration of carboxylates in solution was not appreciably affected by a parallel adsorption or desorption process either due to anion exchange or induced by changes in catalytic surface associated to the presence of dissolved ozone. The results exclude a reaction mechanism based on a modified oxidized surface reacting with organics from the bulk.

For all reaction conditions studied in this work, the rate of accumulation of oxalic acid was always positive and showed no decay after 120 min, the prescribed reaction time in all cases. The reactions leading to oxalate were predominant during the last part of the ozonation runs. Where a previous work [26] determined that the catalyst favours not only the reactions leading to carboxylates but also the mineralization of carboxylates, in this work this effect has not been clearly observed, probably hindered by a large concentration of organic substrate. In any case, for the larger reaction times, the individual concentration of organic acids was not far different in catalytic and non-catalytic runs, while the former exhibited a greater TOC decay.

4. Conclusions

Clofibric acid can be completely removed by catalytic ozonation in less than 60 min at pH 3 and less than 10 min at pH 5 in runs performed at 25 °C with a bulk catalyst concentration of 1 g/L. With an initial concentration of clofibric acid of 50 mg/L and using a concentration of dissolved ozone lower than 0.10 mM, non-catalytic ozonation at pH 3 only reached a conversion of 85% in 1 h with an integral ozone exposure of 1500 mM s. The use of 1 g/L of TiO_2 allowed a complete ozonation in the same time using with ozone exposure of 400 mM s. The data of ozone and clofibric acid concentration collected during the runs were fitted to a second order kinetic expression in which the oxidant was assumed to be either ozone or hydroxyl radicals produced from ozone. The kinetic constant of the non-catalytic ozonation of clofibric acid was $8.16 \times 10^{-3} \pm 3.4 \times 10^{-4} \text{ L mmol}^{-1} \text{ s}^{-1}$ at pH 3 and $1.77 \times 10^{-1} \pm 1.5 \times 10^{-2} \text{ L mmol}^{-1} \text{ s}^{-1}$ at pH 5. Catalytic runs, performed on a Degussa P25 titanium dioxide catalyst, linearly enhanced the rate of ozonation of clofibric acid. It has also been proved that the disappearance of clofibric acid was not a consequence of its adsorption on the catalyst surface. The mechanism involved in the reaction is probably a interaction of bulk oxidants or oxidized surface sites with adsorbed organics.

The evolution of total organic carbon in samples taken during the run was modelled as a function of the integral ozone exposure. It was considered that clofibric acid yielded carboxylic acids and other compounds more difficult to oxidize among which, several simple carboxylic acids were identified. The extent of mineralization during non-catalytic runs ranged from 50% at pH 7 to 20% at pH 3, the reaction taking place essentially during the first 10–20 min. The catalyst decreased TOC in solution with an additional mineralization of 5–10% with respect to non-catalytic ozonation runs at pH in the 3–5 range. The most important consequence of the use of TiO_2 P25 was to enhance the first mineralization period with pseudo-homogeneous rate constants of $4.52 \times 10^{-3} \text{ L mmol}^{-1} \text{ s}^{-1}$ at pH 3 and $1.68 \times 10^{-2} \text{ L mmol}^{-1} \text{ s}^{-1}$ at pH 5, up to three times over the corresponding non-catalytic constants for a catalyst load of 1 g/L. The catalyst led to a higher rate of carboxylate formation during the first period of the run in which the oxidation

of clofibrac acid is taking place. The ozonation of acetate is also accelerated by the presence of catalyst, with a kinetic constant changing from $1.57 \times 10^{-3} \text{ L mmol}^{-1} \text{ s}^{-1}$, when no catalyst is used, to $2.09 \times 10^{-3} \text{ L mmol}^{-1} \text{ s}^{-1}$ for 1 g/L of P25.

Stopped-flow experiments showed that the disappearance from solution of clofibrac acid and its reaction intermediates was not a consequence of a slow adsorption process on the surface of the solid. It was also shown that the catalyst only moderately enhanced the decomposition of ozone with decomposition rate constants linearly increasing catalyst load. The results suggest that the adsorption and subsequent reaction of organics on catalyst sites is responsible for the enhancement of ozonation rate observed in catalytic runs. The enhancement is not likely to obey to a greater surface production of hydroxyl radicals from ozone.

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