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Abstract

This study investigates the ozonation of naproxen and carbamazepine during catalytic and non-catalytic semicontinuous oxidation experiments performed at 25ºC and in the range of pH 3-7. The results showed that naproxen and carbamazepine were completely consumed in the first few minutes of reaction. The extent of mineralization during non-catalytic runs reached about 50% and essentially took place during a period covering the first 10-20 min. Catalytic runs were carried out on a commercial catalyst consisting of fumed colloidal TiO_2 particles. The catalyst increased the extent of mineralization by up to 75% of the initial organic carbon. The results showed that the catalyst enhanced mineralization both in acidic and neutral solutions, but the best results were obtained in a slightly acidic media. This effect was probably linked to the adsorption of reaction intermediates on Lewis acid catalytic sites. The catalyst enhanced the decomposition of ozone in an acid medium but inhibited it in a neutral solution. This seems to exclude a mechanism based on the surface formation of hydroxyl radicals followed by their migration and bulk reaction with organic compounds. The evolution of the total organic carbon measured in samples taken during the run was modelled as a function of the integral ozone exposure. The kinetic regression model considered that the ozonation products from naproxen or carbamazepine consisted of either oxidizable or refractory compounds, where the latter were necessarily produced from the former. The model assumed a second order reaction between organic compounds and ozone. The higher non-catalytic rate constants for the first mineralization period were $1.048 \times 10^{-2} \pm 9.3 \times 10^{-4}$ L mmol^{-1} s^{-1} for naproxen and $6.16 \times 10^{-3} \pm 5.6 \times 10^{-4}$ L mmol^{-1} s^{-1} for carbamazepine, both at pH 7. The corresponding pseudohomogeneous catalytic rate constants were $7.76 \times 10^{-3} \pm 3.9 \times 10^{-4}$ L mmol^{-1} s^{-1} and $4.25 \times 10^{-3} \pm 9.7 \times 10^{-4}$ L mmol^{-1} s^{-1} for naproxen and carbamazepine respectively at pH 5 and with a catalyst load of 1 g/L. The evolution of carboxylic acids during reaction revealed that the catalyst avoided the accumulation of oxalate especially in comparison with non-catalytic runs, in which it accounted for up to 30% of the final organic carbon. Specific ultraviolet absorbance at 254 nm was also followed during the run. The products from naproxen reached a high absorbance from the beginning of the ozonation that was maintained throughout the run. For carbamazepine, however, the absorbance rapidly decreased revealing a different chemical structure of reaction products.

Keywords: Pharmaceuticals, Mineralization, Ozonation, Catalysis, Adsorption, Titanium Oxide.

1. Introduction

Human and veterinary drugs and their bioactive metabolites are continuously released into the environment and may lead to long-term adverse effects for aquatic and terrestrial organisms [1]. Ternes reported the existence of a number of drug residues in the discharge waters of German Municipal Sewage Treatment Plants as a consequence of their relatively high persistence in biological treatments performed with non-adapted microorganisms [2-3]. Some pharmaceuticals showed resistance even to advanced water treatment systems such as adsorption on granular activated carbon or ozonation, thus proving that there is a risk of exposure through drinking water supplies, especially in water reuse situations [4]. In fact, significant concentrations of these compounds have already been reported in rivers and other surface waters [5]. A combination of high residence-time biological treatment and ozonation seems to be a promising technology to be applied in wastewater treatment plants [6]. To overcome the relatively high-energy intensity of ozonation and the fact that some compounds are relatively refractory to ozonation treatments, several advanced oxidation processes have also been proposed [7, 8]. The homogeneous rate of hydroxyl radicals produced from ozone is strongly enhanced under alkaline conditions in which an important drawback exists in the case of water with bromide levels higher than 50 μg/L due to the formation of bromate as an oxidation by-product [9]. Bromate formation can be avoided by limiting ozone exposure and by using pH < 7 [10]. Catalytic ozonation can be used to promote ozone decomposition, ozonation reactions or both in acidic conditions, in which the formation of hydroxyl radicals and the rate of mineralization would otherwise be too low. Moreover, the use of a catalyst has been repeatedly proposed to remove carboxylic acids, a class of organic compounds particularly refractory to the oxidation by ozone and produced during the ozonation of complex organic molecules [11, 12].

Supported and unsupported metals and metal oxides are the most commonly tested catalysts for the ozonation of organic compounds in water. Titanium oxide has been repeatedly reported as an active material able to accelerate the ozonation processes of different compounds [12-14]. Its role in the mineralization of low molecular weight carboxylic acids has been reported by Beltrán et al. [15-16] showing conversions forty times higher than that corresponding to non-catalytic homogeneous ozonation. Gracia et al. [17] reported a high activity of TiO_2 supported in alumina in the removal of organic carbon in natural waters by ozone. On the other hand, Cooper and Burch [18] found no significant differences between pure alumina and TiO_2/Al_2O_3 for the ozonation of oxalic acid. Concerning the mechanism of catalytic ozonation, there is still controversy regarding the ability of the catalyst to adsorb the organic substrate, especially on ionizable surfaces. Catalytic ozonation may proceed with the adsorption of ozone, the organic pollutant or both and the process may or may not involve surface equilibrium. It has been demonstrated that dissolved ozone adsorbs and decomposes on many solid surfaces other than activated carbon, the resulting radicals being responsible for indirect oxidation reactions [19]. The proposed mechanisms for heterogeneous ozone decomposition usually extrapolate the results obtained in the gas phase. For example, Dhandapani and Oyama [20] reported that the ozone decomposition on p-type oxides is consistent with the formation of superoxide (O_2^-) or peroxide (O_2^{2-}) species on the surface. Bullanin et al. [21] suggested that ozone dissociates after adsorption on strong Lewis sites yielding a surface oxygen atom, whereas on weaker sites, ozone molecules coordinate via one of the terminal oxygen atoms. Besides the liquid phase reaction of surface-produced radicals, the adsorption of organic molecules on the catalyst surface leads to additional mechanisms: an adsorbed organic compound may react with ozone or radicals from the bulk aqueous phase or with an adsorbed ozone molecule or the products of surface ozone decomposition [22]. The prevailing mechanism is not clear. Moreover, it has to be taken into consideration that the formation of surface oxidation sites or the adsorption of neutral compounds on oxides is difficult in aqueous solutions due to the competitive adsorption of water molecules. Adsorption is easier for ionizable organic compounds in water if the surface is charged allowing ion exchange. In fact, the surface of metal oxides exhibits ion exchange properties and the hydroxyl groups formed behave as Brönsted acid sites and dissociate depending on the pH of the solution [23]. Finally, a mechanism has been proposed based on the initiation of ozone decomposition by hydroxide ions linked to the negatively charged surface of metal oxide [24].

The aim of this work is the study of the aqueous phase catalytic ozonation of naproxen, a non-steroidal anti-inflammatory drug, and carbamazepine, an antiepileptic agent (Fig. 1). These compounds were selected as representative of two different families of drugs the occurrence of which has previously been reported in water and wastewater [2]. The catalytic reactions were performed in a semi-continuous regime using a commercial Degussa P25 TiO_2 catalyst commonly used in photocatalysis and in photocatalytic ozonation [25]. Moreover, the activity of P25 TiO_2 in decomposing dissolved ozone has been previously reported by our group in unsteady absorption-reaction experiments that allowed the determination of reaction constants and activation energies for ozone decomposition and suggested that P25 could be a good choice as an ozonation catalyst for the mineralization of organic pollutants in water [26]. The main characteristics influencing the TiO_2 activity are surface area, crystalline phase, particle size and the aggregate size in suspension [27]. With respect to the last of these, nanosized P25 TiO_2 particles exist in agglomerates in solution as a consequence of Van der Waals attractive forces, which can be affected by hydrolyzation of TiO_2 surface. The hydrolyzation occurs at pH below pH_{PZC} and therefore in acidic conditions so originating repulsive forces between particles [28]. The effect of pH on the size of particle aggregates of TiO_2 has been reported by some authors, but values do not generally agree. Fernández-Ibáñez et al. [29] reported aggregates from 250 to 600 nm in acidic solutions with significant differences among agitation protocols. Yurkadal et al. [30] obtained much larger values from 2.2 to 2.5 μm for pH in the 3-8 range with a low influence of pH but with an important effect of catalyst concentration on the size of agglomerates at least for low concentrations. Gumy et al. reported 370 nm at pH 6 [31]. Whereas agglomeration has been shown to be an important factor for the catalyst's activity, its measurement is difficult and published data do not agree. An activity decrease could be expected by bringing surface close to neutrality.

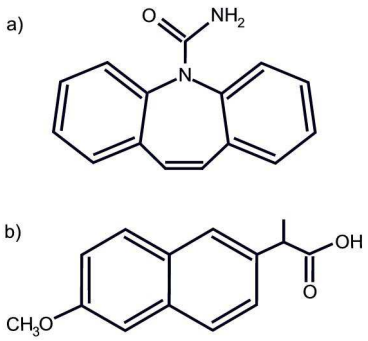

Figure 1. Chemical structures of carbamazepine (a) and naproxen (b).

Concerning the interaction with catalytic surface, the most significant difference between carbamazepine and naproxen was that the former (pK_a = 14.0) was protonated in the whole pH range whereas naproxen (pK_a = 4.60) dissociated, allowing ion exchange on positively charged surfaces. Special attention was paid to the

kinetics of mineralization and to the presence of oxalic acid, a common end-product refractory to ozonation. Specific ultraviolet absorbance (SUVA) was also determined as a measure of the aromaticity and the unsaturated character of the products and, therefore, their toxicity potential.

2. Experimental

2.1. Materials and ozonation procedure

Naproxen and carbamazepine were supplied by Sigma-Aldrich (98% purity). The catalyst used was titanium dioxide P25 Degussa (80/20 anatase-to-rutile ratio). The powder consists of primary particles of about 20 nm forming aggregates of several hundred nanometers that can be removed by filtration using 0.45 μm Teflon filters. The BET specific surface was 50 m^2/g. The point of zero charge (PZC), that is, the pH at which the surface is neutral, was determined by potentiometric titration as described by Halter [32]. The value obtained, pH_{PZC} = 6.6, squared well with similar data published elsewhere [33].

Reaction runs were carried out in a 1 L glass jacketed reactor whose temperature was controlled by a Huber Polystat cc2 thermostatic regulator. The temperature of the liquid inside the reactor was monitored throughout the experiment by means of a Pt100 thermocouple. Ozone was produced by a corona discharge ozonator (Ozomatic, SWO100) fed by oxygen (about 95% purity) produced by an AirSep AS-12 PSA oxygen generation unit. Fig. 2 shows details of the experimental set-up.

The mixture of ozone and oxygen was bubbled into the liquid by means of a porous glass disk with a gas flow of 0.20 Nm^3/h. The reaction vessel was agitated with a magnetic rod at 700 rpm. The ozone decomposition experiments were conducted in a semicontinuous mode using a fixed volume of distilled water containing 15 mg/L of naproxen or carbamazepine (6.51×10^{-5} M and 6.35×10^{-5} M respectively). Catalytic runs were performed at a fixed bulk concentration of 1g/L. During the run, certain samples were withdrawn at prescribed intervals. Ozone was quenched in samples by adding a concentrated solution of sodium thiosulfate or by bubbling nitrogen. In the case of catalytic runs, the catalyst was previously removed by filtration. The experiments were carried out at pH in the 3-7 range, controlled by pumping a diluted sodium hydroxide using a feed-back PID control. The decomposition of ozone tended to acidify the reaction mixture in all cases except for neutral pH during the quick mineralization period that appeared at the beginning of the run. In this case the pH tended to increase and was controlled with the addition of hydrochloric acid. This behaviour was probably due to the reactions between hydroxyl radicals and carbonate and bicarbonate ions produced during the mineralization process [34]. Fig. 3 shows the evolution of dissolved ozone concentration during a representative run performed at 25ºC and pH 3. The relatively large mass transfer volumetric coefficient ($k_La = 0.0123 \pm 0.0017$ s^{-1}) accounts for the rapid increase observed at the beginning of the run. After 120 min, the prescribed reaction time for all runs, the flow of gaseous mixture of ozone and oxygen was stopped, and the decay of dissolved ozone was used to supply information on the ozone decomposition reactions due to the organic compounds remaining in the liquid.

2.2. Analysis

The concentration of ozone in the gas phase was determined with a non-dispersive UV Photometer Anseros Ozomat GM6000 Pro calibrated and tested against a chemical method. The concentration of ozone in the liquid was measured using the Rosemount 499A OZ amperometric analyser equipped with Pt 100 RTD temperature compensation and calibrated against the Indigo Colorimetric Method (SM 4500-O_3 B). The signal

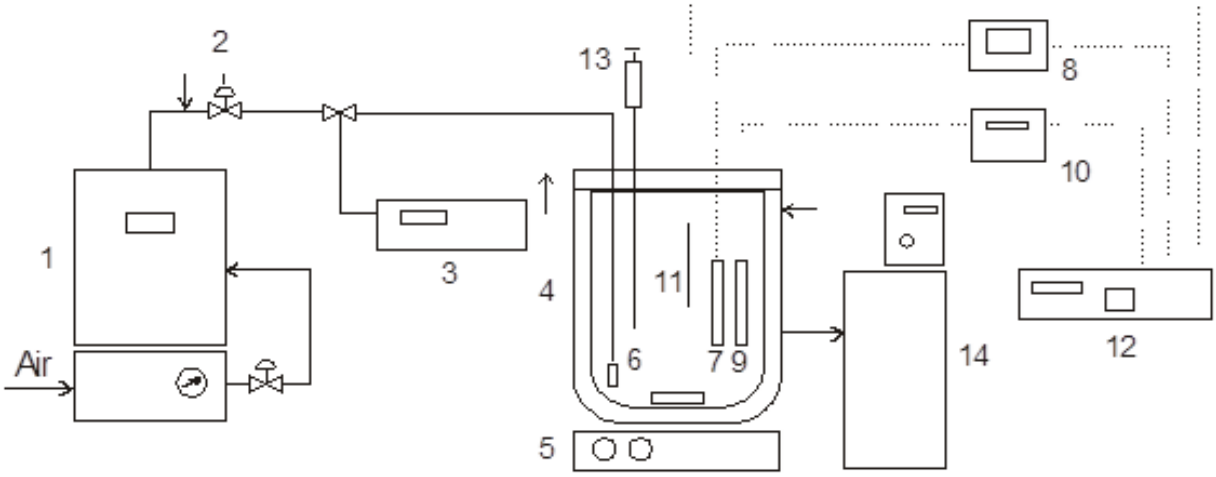

Figure 2. Experimental equipment: 1, ozone generator; 2, flow control; 3, gas-phase UV ozone analyser; 4, reactor; 5, magnetic stirrer; 6, diffuser; 7, ozone amperometric sensor; 8, ozone analyser; 9, pH electrode; 10, pH control unit; 11, thermocouple; 12, data acquisition unit; 13, sampling device; 14, thermostat-cryostat.

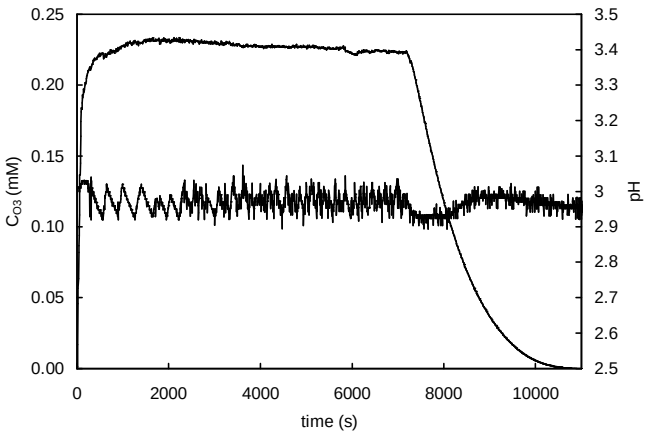

Figure 3. Concentration of ozone and pH during the non-catalytic ozonation of naproxen at 25ºC. At 7200 s the flow of ozone was stopped.

was transmitted to a Rosemount 1055 SoluComp II Dual Input Analyser connected to a data acquisition unit. The temperature inside the reactor was monitored with a Pt100 thermocouple and the pH was measured by means of a CRISON electrode connected to a Eutech αlpha-pH100 feed-back control device. The final control element for pH was a LC10AS Shimadzu pump that delivered a solution of hydrochloric acid or sodium hydroxide allowing a control of pH inside ±0.1 units throughout the experiment (Fig. 3). The signals from the concentration of dissolved ozone, pH and temperature were monitored and recorded using an Agilent 34970 Data Acquisition Unit connected to a computer. TOC analyses were carried out by means of a Shimadzu TOC-VCSH total carbon organic analyzer equipped with an ASI-V autosampler. Carboxylic acids were determined using a Dionex DX120 Ion Chromatograph with conductivity detector and an IonPac AS9-HC 4x250mm analytical column (ASRS-Ultra suppressor). The eluent flow was 1.0 mL/min of 9.0 mM Na_2CO_3 and the volume of sample loop was 1 μL. UV absorbance at 254 nm was recorded by means of a Shimadzu SPD-6AV spectrophotometric detector. Specific ultraviolet absorbance ($SUVA_{254}$) was obtained by dividing ultraviolet absorption at 254 nm by the total organic carbon of the sample (TOC) in mg/L. $SUVA_{254}$ is commonly accepted as a measure of the content of humic substances in drinking water, or on the other hand, an indirect measure of the aromaticity and unsaturated character of the organic matter [35]. The analyses of naproxen and carbamazepine were performed by HPLC using a Hewlett Packard 1100 apparatus equipped with a C18 250mm column. The mobile phase was a mixture of acetonitrile and water (70:30) adjusted to pH 2.5 using orthophosphoric acid with an isocratic flow of 1.0 mL/min at room temperature. The UV detection was carried out at 268 nm.

3. Results and discussion

The extent of mineralization was tracked by determining the TOC of samples taken during the run. Fig. 4 shows the evolution of total organic carbon for selected catalytic and non-catalytic runs. The data show the existence of two mineralization periods. During the first few minutes, a rapid decay of TOC was considerably accelerated by the presence of a catalyst. The second period was essentially independent of pH and corresponded to the mineralization of the less reactive intermediates. In both cases, the parent compounds disappeared during the first few minutes of reaction due, at least, to the direct second order reaction with molecular ozone. The second-order rate constant for the ozonation of carbamazepine determined by Huber et al. [36] at pH 7 and 20ºC was about 3×10^5 M^{-1} s^{-1}. Considering that the concentration of ozone in the liquid rapidly reached a plateau value of about 0.23 mM, the half-life time of carbamazepine should be in the order of 10^{-2} s. In practice, small amounts of naproxen and carbamazepine could be detected after the first minute of reaction, a period in which the concentration of dissolved ozone in still low. No data are available for the direct rate constant of naproxen [37] but it always became undetectable after a maximum of three minutes after the beginning of the run, even with dissolved ozone concentrations far from its equilibrium value.

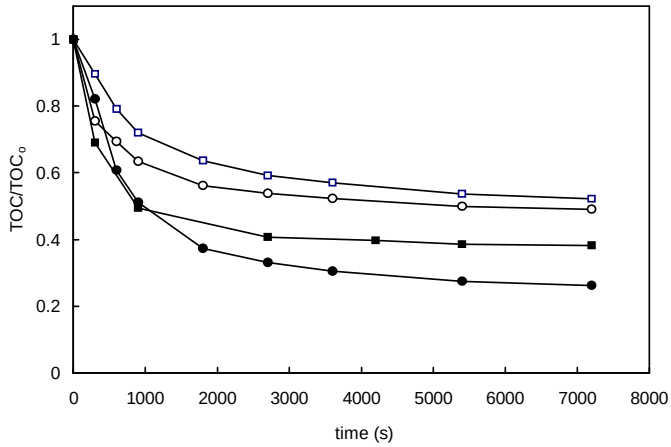

Figure 4. Mineralization of naproxen at pH = 5 (■, □) and carbamazepine at pH = 5 (●) and pH = 7 (○). Gas flow rate 0.20 Nm^3/s, ozone concentration in gas 38-40 g/Nm^3, temperature 25ºC. Empty symbols represent non-catalytic runs.

3.1. Non-catalytic ozonation

As indicated previously, the primary reaction of naproxen and carbamazepine with dissolved ozone proceeded at a high rate. Therefore, the compounds analysed as TOC corresponded in any case to ozonation products absent from the initial reaction mixture. In general, the homogeneous rate of reaction of a certain organic compound is the consequence of the second order parallel reactions with dissolved ozone and with hydroxyl radicals:

$$-\frac{dc_i}{dt} = k_{HO^\bullet}\, c_{HO^\bullet}\, c_i + k_{O_3}\, c_{O_3}\, c_i \qquad (1)$$

Elovitz and von Gunten introduced a parameter, R_{ct}, that represents the ratio of hydroxyl radicals and ozone at any time during the reaction [38].

$$R_{ct} = \frac{c_{HO^{\bullet}}}{c_{O_3}} \qquad (2)$$

In natural water, it has been shown that R_{ct} is a constant for most of the ozonation process, while during the ozonation of wastewater it behaves as a parameter that characterizes the oxidation process [39]. Combining Eqs. (1) and (2) and integrating the differential equation, the integral ozone exposure becomes the independent variable for the logarithmic decay of the concentration of a given compound:

$$\ln \frac{c_{io}}{c_i} = \left(k_{HO^{\bullet}} R_{ct} + k_{O_3}\right) \int c_{O_3}\, dt = k_R \int c_{O_3}\, dt \qquad (3)$$

where k_R is expected to be constant only for a given compound and in conditions at which the ratio R_{ct} does not change. In this work, it was assumed that if the aggregate TOC (in mM or mg/L of organic carbon) is used instead of the concentration of a single compound, a similar kinetic expression could represent the process. In this case, k_R would be expected to decay as a consequence of the formation of more refractory products while ozonation proceeds and the extent of mineralization increases. Figs. 5 and 6 show experimental data corresponding to the ozonation of naproxen (*NAP*, c_o = 6.51 x 10^{-5} M) and carbamazepine (*CAR*, c_o = 6.35 x 10^{-5} M) both in several catalytic and non-catalytic runs as a function of the time-integrated concentration of ozone. The results suggest the existence of two mineralization periods that can be modelled by considering that the organic carbon in the reaction products can be sorted into two classes according to its reactivity. The experimental values of TOC could be explained by means of a kinetic model in which a first set of easily oxidizable intermediates (A) yielded a second group of refractory products (B). The results showed that the formation of B from A was not specifically linked to the mineralization of the later and required a specific interconversion constant, k_{Ri}:

$$NAP, CAR \rightarrow A \xrightarrow{k_{R,1}} CO_2 + H_2O \qquad (4)$$

$$A \xrightarrow{k_{R,i}} B \qquad (5)$$

$$B \xrightarrow{k_{R,2}} CO_2 + H_2O \qquad (6)$$

Except for the first few minutes of reaction, the organic carbon measured as TOC always corresponded to the carbon contained in the ozonation products of naproxen and carbamazepine, grouped in A and B, respectively expressed in mM or mg/L as c_A and c_B or as total carbon: $TOC = c_A + c_B$. According to the preceding mechanism, the kinetic expressions for the ozonation of A and B are as follows:

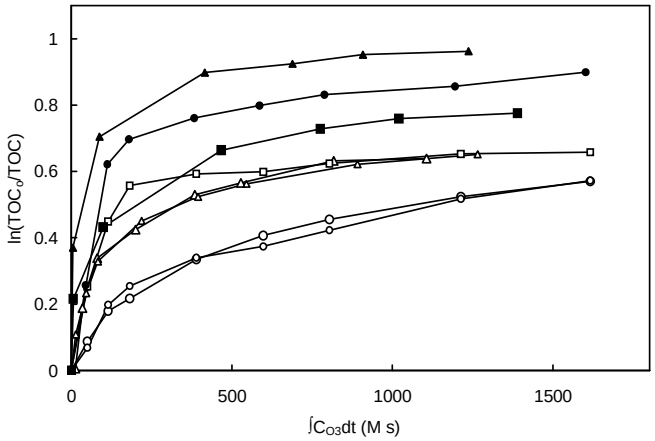

Figure 5. Ozone exposure plot for non-catalytic mineralization of naproxen at pH = 3 (○), 5 (Δ) and 7 (□). Gas flow rate 0.20 Nm^3/s, ozone concentration in gas 38-40 g/Nm^3, temperature 25ºC. Filled symbols represent catalytic runs in the same conditions using 1 g/L of TiO_2 P25. Some runs have been replicated.

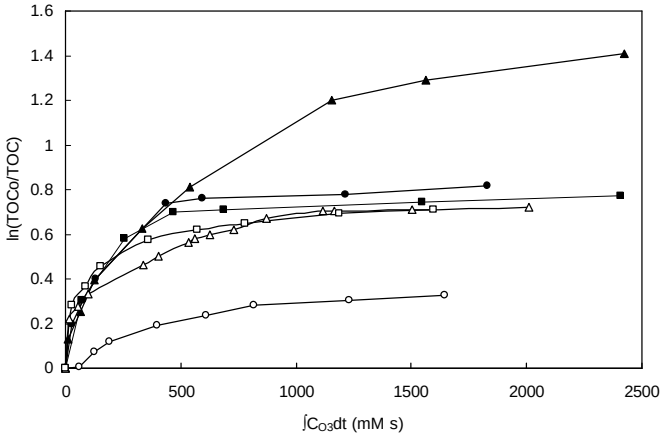

Figure 6. Ozone exposure plot for non-catalytic mineralization of carbamazepine at pH = 3 (○), 5 (Δ) and 7 (□). Gas flow rate 0.20 Nm^3/s, ozone concentration in gas 38-40 g/Nm^3, except for non-catalytic run at pH = 5 that represents a combination of experiments performed under different ozone gas concentrations. temperature 25ºC. Filled symbols represent catalytic runs in the same conditions using 1 g/L of TiO_2 P25.

$$-\frac{dc_A}{dt} = k_{R,1}\, c_{O_3}\, c_A + k_{R,i}\, c_{O_3}\, c_A \qquad (7)$$

$$\frac{dc_B}{dt} = k_{R,i}\, c_{O_3}\, c_A - k_{R,2}\, c_{O_3}\, c_B \qquad (8)$$

Least squares fitting included a fourth order Runge-Kutta routine for the integration of Eqs. (7) and (8). Fig. 7 shows the experimental and predicted values of TOC and reaction intermediates for the ozonation of naproxen at pH 5. The calculated rate constants are shown in Table 1. The results revealed that increasing the pH of the mixture considerably accelerated the fast mineralization period. This accords well with the well-known role of hydroxide anion in the initiation of ozone decomposition and the

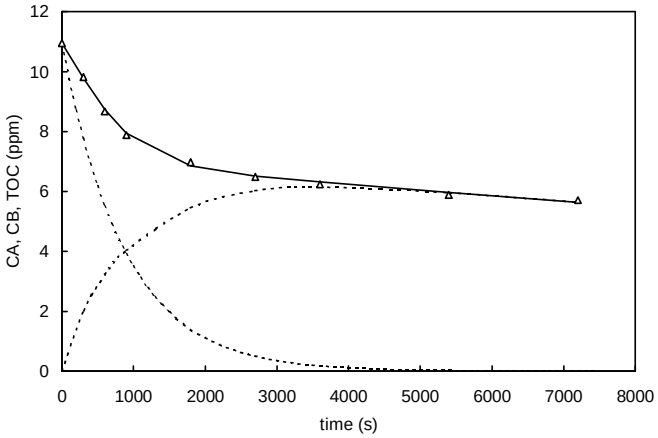

Figure 7. Ozonation of naproxen at pH = 5 without catalyst and model predictions for TOC and reaction intermediates. Symbols correspond to experimental data and lines to model results.

subsequent production of hydroxyl radicals. The influence of pH on the interconversion reaction was lower whereas the mineralization of refractory products was slow and practically unaffected. An increasing acidity of oxidation intermediates could explain these differences, as the dissociated forms of weak acids are more reactive towards ozonation reactions.

Table 2 compares the rate of ozone decomposition in distilled water with the same in the reaction mixture at the end of the run (120 min.) for the experimental conditions used in this work. The data were obtained by stopping the gas flow as indicated in Fig. 3 and in all cases, a good fitting was obtained by assuming a first order for the kinetics of ozone decomposition. Data showed large differences in the decomposition rate depending on the matrix. In an acidic medium, the reaction products of the ozonation of naproxen and carbamazepine increased the rate of ozone decomposition by up to one order of magnitude with regard to the water matrix. The effect could be attributed to the presence of promoters among the refractory final products of the ozonation reactions. For increasing pH the difference is lower and, under neutral conditions, the ozonation products even inhibited the decomposition of ozone. The behaviour can be rationalized by taking into consideration the formation of promoters and inhibitors involved in ozone decomposition reactions. For example, formic acid, a radical chain promoter, reached up to 2 mg/L in the products of reaction at pH 3, while at pH 7 was almost undetectable. The inhibition detected at neutral pH might be related to the accumulation of carbonate and bicarbonate ions from the mineralization process. Fig. 8 shows the effect of the addition to the reaction mixture of 50 mM of sodium phosphate, a well-known radical scavenger [40]. Solid lines corresponded to the values indicated in Table 2 except for $k_{R,1}$, that decreased to about half ($k_{R,1}$ = 0.0015 L mmol^{-1} s^{-1}). This result showed that the main mineralization reactions proceeded via a radical mechanism. The fact that a good fitting was achieved with the same parameter $k_{R,i}$ from Table 2 might indicate that interconversion reactions are not stoichiometrically linked to the fast mineralization period. In fact, the ratio $k_{R,i}$ /$k_{R,1}$ decreased steadily as pH increased in all cases.

Table 1. Kinetic constants for the mineralization model represented by Eqs. (4-6).

Non-catalytic reactions (L mmol^{-1} s^{-1})			
	k_{R1}	k_{Ri}	k_{R2}
Naproxen			
pH = 3	0.00167	0.0034	1.7 x 10^{-4}
pH = 5	0.00437	0.0046	1.6 x 10^{-4}
pH = 7	0.0105	0.0048	1.3 x 10^{-4}
Carbamazepine			
pH = 3	0.00068	0.0019	2.1 x 10^{-4}
pH = 5	0.00285	0.0055	1.9 x 10^{-4}
pH = 7	0.00616	0.0069	1.6 x 10^{-4}
Catalytic ozonation (L mmol^{-1} s^{-1})			
	k_{Rc1}	k_{Rci}	k_{Rc2}
Naproxen			
pH = 3	0.00587	0.0031	6.2 x 10^{-5}
pH = 5	0.00776	0.0041	8.1 x 10^{-5}
pH = 7	0.00458	0.0045	9.1 x 10^{-5}
Carbamazepine			
pH = 3	0.00277	0.0024	*
pH = 5	0.00425	0.0012	*
pH = 7	0.00271	8.9 x 10^{-4}	*

* Not significantly different from zero

Table 2. First-order kinetic constant for the decomposition of ozone in the distilled water matrix and for ozone decay at the end of the ozonation reactions of naproxen and carbamazepine (120 min.). The catalyst load was 1 g/L in catalytic runs.

	pH		
Non-catalytic decomposition $k_d(s^{-1})$	3	5	7
Distilled water	3.07×10^{-4}	9.93×10^{-4}	8.83×10^{-3}
Naproxen	9.9×10^{-4}	1.2×10^{-3}	1.8×10^{-3}
Carbamazepine	2.6×10^{-3}	3.2×10^{-3}	4.2×10^{-3}

	pH		
Catalytic decomposition $k_{cd}(m^3\ kg^{-1}\ s^{-1})$	3	5	7
Distilled water	4.72×10^{-4}	1.45×10^{-3}	1.27×10^{-3}
Naproxen	9.9×10^{-4}	1.04×10^{-3}	n.d.
Carbamazepine	9.6×10^{-4}	1.10×10^{-3}	n.d.

n.d.: not determined.

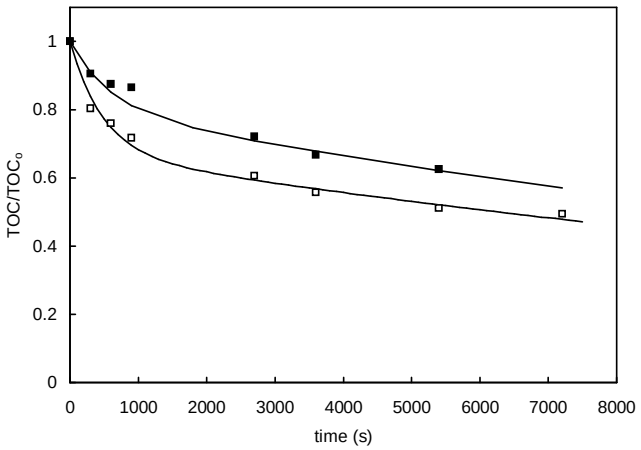

Figure 8. Non-catalytic ozonation of carbamazepine and model predictions for TOC at pH = 5 in pure distilled water (□) and with addition of Na_3PO_4 50 mM (■).

3.2. Adsorption of naproxen and carbamazepine on P25 TiO_2

Neutral organic compounds in aqueous solution may adsorb on the surface of metal oxides if the surface is not charged and therefore the pH is near the pH_{PZC} (point of zero charge) of the solid. Otherwise, the coordination layer would prevent any adsorption. Furthermore, it is also necessary that the adsorbate is a Lewis base strong enough to displace adsorbed water molecules. In the case of ionizable substances such as carboxylates the adsorption takes place on positively charged surfaces by exchanging the corresponding counteranion [23]. Fig. 9 shows the results for the adsorption of naproxen (pK_a = 4.60) and carbamazepine (pK_a = 14.0) on TiO_2 Degussa P25 (pH_{PZC} = 6.6). The results showed that the adsorption of naproxen is favoured in acidic conditions in which the surface behaves as an anion exchanger. Similar results have been published for other acidic solutes that may be adsorbed by an ion-exchange mechanism [15, 16]. Carbamazepine was protonated in the whole pH range and its adsorption on a neutral or positively charged surface should take place by displacing coordination water in Lewis sites. The extent of adsorption was similar for pH in the 3-7 range. The adsorption kinetics was slow enough to suspect that its rate may play a significant role in the ozonation process. For both drugs, the equilibrium required several hours, and the extent of adsorption reached only 5-15% during the first hour (c_s = 1 g/L). This is in line with several data showing that the adsorption of acid pollutants on metal catalysts supported on alumina is slow, taking from hours to days to reach equilibrium [12, 15].

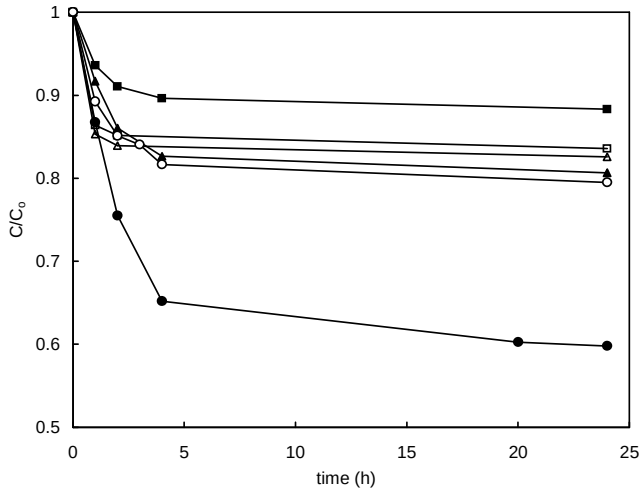

Figure 9. Dimensionless concentration of naproxen at pH = 3 (●), pH = 5 (▲) and pH = 7 (■) and carbamazepine at pH = 3 (○), pH = 5 (Δ) and pH = 7 (□) corresponding to adsorption experiments on P25 TiO_2 at 25ºC. The initial concentration was 6.35×10^{-5} M for carbamazepine and 6.51×10^{-5} M for naproxen. Catalyst load 1 g/L.

3.3. Ozonation on TiO_2 catalyst

There is still a considerable lack of information regarding the role of metal oxides in the aqueous phase of ozonation reactions, in particular regarding the ozone

decomposition reaction. It has been suggested that ozone can be adsorbed on a catalyst surface to yield different oxidizing species [15]. However, the bonding of an adsorbate to a vacant site, must involve the displacement of coordination water prior to adsorption. As indicated earlier, the ion exchange of charged species is much easier. Therefore, with the exception of systems such as those based on activated carbon in which the catalyst behaves merely as a promoter in the decomposition of ozone, the ozonation mechanism should involve the adsorption or ion exchange of an organic compound on a surface site [41]:

$$A + S \rightleftarrows A - S \qquad (9)$$

where S represents a free active site on the catalyst surface. Once adsorbed, the solute may react with a previously oxidized surface site (Ox-S):

$$O_3 + S \rightarrow Ox - S \qquad (10)$$

$$Ox - S + A - S \rightarrow AOx + 2\,S \qquad (11)$$

Alternatively, hydroxyl radicals or any other oxidant such as molecular ozone might react from the bulk with adsorbed organic compounds:

$$HO^{\bullet} + A - S \rightarrow AOx + S \qquad (12)$$

The rate of ozonation combines the homogeneous reaction with ozone or hydroxyl radicals and the heterogeneous reaction following any of these mechanisms. The rate expression for a situation in which adsorption equilibrium exists and the adsorbed organic compounds react with hydroxyl radicals from the bulk but do not interact with oxidized sites is as follows:

$$-\frac{d\,c_A}{d\,t} = k_{HO^{\bullet}}\, c_{HO^{\bullet}}\, c_A + k_c\, c_s\, c_{HO^{\bullet}} \frac{k_a\, c_A}{k_a\, c_A + k_{-a}} \qquad (13)$$

Where k_a and k_d are the adsorption and desorption kinetic constants for the organic compound.

If surface coverage is small, the denominator of Eq. (13) becomes independent on the concentration of adsorbate. Finally, by using the R_{ct} ratio of Elovitz and von Gunten, the concentration of hydroxyl radicals can be expressed as a function of the concentration of dissolved ozone:

$$-\frac{d\,c_A}{d\,t} = \left(k_{HO^{\bullet}}\, R_{ct} + k_c\, R_{ct}\, K_a\, c_s\right) c_{O_3}\, c_A \qquad (14)$$

The integration of the former expression leads to:

$$\ln \frac{c_{A,o}}{c_A} = \left(k_{HO^{\bullet}}\, R_{ct} + k_c\, R_{ct}\, K_a\, c_s\right) \int c_{O_3}\, dt = k_{Rc} \int c_{O_3}\, dt \qquad (15)$$

A Langmuir-Hinshelwood rate expression would represent a situation in which an elementary step occurring on the surface is rate controlling and adsorption equilibrium exists at any time for both oxidant and organics. On the assumption that the equilibrium constant for the oxidation of surface sites is low enough, an integrated expression similar to Eq. (15) can be derived. A surface redox reaction mechanism has sometimes been described by means of a Mars-van Krevelen rate expression. In such case, the rate of catalytic reaction would depend on the rate of the surface oxidation process and on the rate of the organic compound's reaction with the oxidized catalyst. If the catalyst oxidation is slow, the catalytic reaction would be independent of the concentration of oxidant. In contrast, for a high rate of surface oxidation, the reaction rate should be first order in the organic compound. Although relatively common in catalysis, the Mars-van Krevelen rate expression, lacking as it does a solid fundamental background, finally proved to be physically incorrect [42].

The logarithmic decay of the organic carbon was fitted to the linear expression on the ozone integral exposure indicated by Eq. (15) in which the pseudo-homogeneous catalytic kinetic constant is expected to follow a complex dependence probably dominated by the R_{ct} parameter. The evolution of TOC in the catalytic reactions performed in this work is shown in Figs. 5 and 6 for naproxen and carbamazepine respectively. The trend is similar to that encountered in non-catalytic runs with a rapid initial TOC decay followed by a period in which the rate of mineralization was very low. Therefore, the same model used in non-catalytic runs and based on splitting the organic carbon into two categories according to its rate of mineralization was also used for catalytic ozonations. The interpretation of the apparent kinetic constant, $k_{Rc,}$ depends on the underlying reaction mechanism, but discriminating between rival models was not the objective of this research. With regard to the effect of adsorption of naproxen and carbamazepine on the ozonation process, some experiments were performed in which they were allowed to reach adsorption equilibrium before beginning the run. Results show no significant differences between ozonation with a 24 h contact time and runs performed with direct addition of the catalyst just before passing ozone.

Another question suggested by the slow adsorption kinetics observed for naproxen and carbamazepine is whether the adsorption kinetics of the intermediate products of ozonation could control the overall reaction rate. The contribution of an adsorption process in parallel with the catalytic reaction would include in the rate expression a term independent of the concentration of oxidant:

$$-\frac{d\,c_A}{d\,t} = k_{HO^{\bullet}}\, R_{ct}\, c_{O_3}\, c_A + k_a\, c_s\, c_A \qquad (16)$$

The integration of Eq. (16) leads to an expression in which the logarithmic decrease of the organic compound is not linear in the time-integrated concentration of ozone. The corresponding model can be discriminated from those based on surface equilibrium by using data in which the integral ozone exposure and time are not

correlated. Fig 10 shows the logarithmic TOC decay for the ozonation of naproxen at pH 7 with a concentration of dissolved ozone ten times lower than the corresponding to the experiment reported in Fig. 6. This represented a plateau concentration of about 0.02 mmM (1 mg/L of ozone) instead of 0.22 mM (about 10 mg/L) from the previous run. If the adsorption of reaction intermediates on acid sites were relevant, the plot of the logarithmic decay of TOC as a function of the integral ozone exposure would reflect a deviation from Eq. (15) as indicated by Eq. (16), whose integration yields a contribution to logarithmic TOC reduction linear with time. The result indicated that the mineralization can be explained by a pure catalytic mechanism and that a possible competitive adsorption of reaction products was not important at a neutral pH. For runs performed under acidic conditions, the situation was somewhat different. Fig. 10 shows the result of ozonation of naproxen (pH 3) and carbamazepine (pH 5) in runs in which the ozone flow was stopped at 30 min. From about 40 min to the end of the sampling period (120 min), the concentration of dissolved ozone was not detectable in both runs. The results are compared in Fig. 10 with runs performed with continuous gas flow (filled symbols). Again, if adsorption of reaction intermediates was significant, the plot would show sharp increase after 40 min corresponding to the adsorption of acids produced during ozonation. Results showed, however, a limited increase in dissolved carbon during the part of the runs carried out in the absence of ozone. This effect, greater at pH 3, was probably linked to the development of Brnsted catalytic sites during ozone decomposition. After ceasing the ozone flow, certain acidic sites could revert with the subsequent desorption of organic compounds to the bulk.

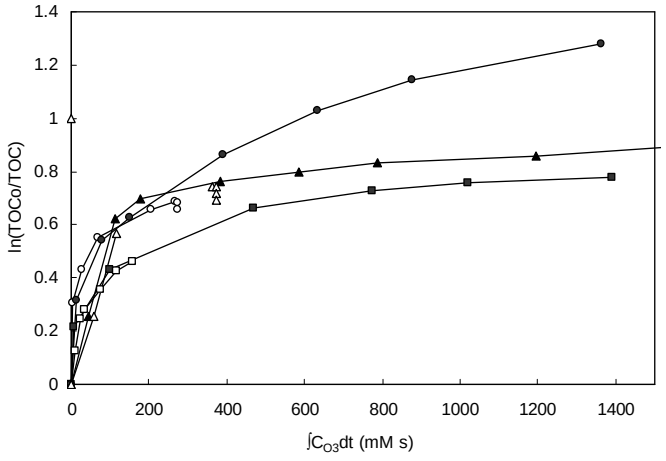

Figure 10. Ozonation of naproxen at pH 7 with marks representing samples for low (□) and high (■) ozone concentration and experiments with ozone stopped-flow for carbamazepine at pH 5 (○) and naproxen at pH 3 (Δ). Filled symbols correspond to runs under constant ozone gas flow.

The kinetic constants estimated by the least squares fitting of experimental data are shown in Table 2. Figs. 5 and 6 show the experimental and theoretical values together with the corresponding results of non-catalytic runs as indicated above. In general, the catalyst accelerated the first mineralization reaction period for the runs carried out in acidic media. At neutral pH the rate of catalytic reaction, k_{Rc1}, decreased to about half the value of the non-catalytic corresponding constant, k_{R1}. Anyway, the catalyst caused a deeper mineralization even at neutral pH because the conversion from oxidizable to refractory compounds (A $\rightarrow$ B) seemed to be inhibited by the catalyst, especially in the case of carbamazepine. The best results for the removal of reaction intermediates were obtained for slightly positive surface charge (pH = 5) suggesting that the adsorption of organics on Lewis sites could be involved in the mechanism of catalytic ozonation. For a higher pH, the lower rate constant could be attributed to the role of hydroxide ions that, being a strong Lewis base, should inactivate acidic catalyst sites. The results shown in Table 2, also indicate that the presence of a catalyst inhibited the decomposition of ozone, lowering the decomposition kinetic constant from $8.83 \times 10^{-3} \pm 4 \times 10^{-5}$ s^{-1} to $1.27 \times 10^{-3} \pm 1 \times 10^{-5}$ s^{-1} for reaction in the distilled water matrix. This result could be due to the role of a catalytic surface in chain termination reactions. The boundaries correspond to 95% confidence intervals. The order of kinetic constants k_{Rc1} was the same as that encountered for the catalytic decomposition of ozone in water, pointing towards a mechanism based on the adsorption of organics and ozone on the same sites. The ratio k_{Rc1}/k_{cd} decreased with increasing pH, following a trend that suggested a greater interaction of the catalytic surface with organic compounds than with molecular ozone. The ratio k_{Rc1}/k_{R1} changed from 3.5-4.0 to less than 0.45 as pH increased from 3 to 7 showing that the mineralization rate was affected more than the ozone decomposition reaction while increasing the concentration of hydroxide. Both observations suggested that the adsorption of organics effectively plays a role in the reaction and that the mineralization is not merely the consequence of an enhanced production of hydroxyl radicals from ozone. The second period of mineralization was characterized by a very reduced rate constant, not significantly different from zero for the ozonation of carbamazepine. The interconversion constant, k_{Rci}, was very similar for catalytic and non-catalytic runs in the case of naproxen, but significantly decreased for carbamazepine as pH increased. This behaviour suggests that the reactions of organic compounds that do not lead to mineralization can exhibit a complex pattern linked to the interaction with a catalytic surface. For homogeneous runs, however, interconversion reactions were favoured by high pH as expected for a hydroxyl-mediated oxidation process.

Fig. 11 shows the evolution of the concentration of oxalate measured by ionic chromatography in samples taken at certain intervals during the runs. In the interests of clarity only some representative results are shown. In non-catalytic runs, oxalate steadily increased during the

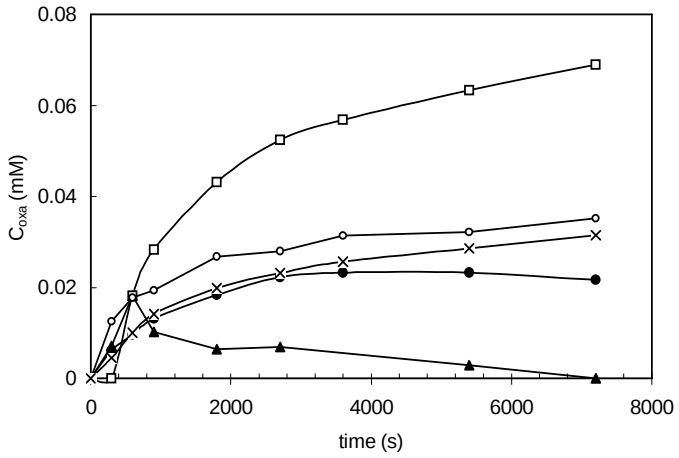

Figure 11. Evolution of the concentration of oxalic acid in several runs. Empty symbols represent non-catalytic ozonation of naproxen ad at pH = 3 (○) and pH = 7 (□). Filled symbols correspond to the catalytic ozonation of carbamazepine at pH = 3 (●) and pH = 5 (▲). Crosses correspond to catalytic ozonation of naproxen at pH = 3.

ozonation especially for the higher values of pH that corresponded to the greater mineralization rates. Catalytic runs exhibited a different behaviour, and the accumulation of oxalate was only observed at pH 3. In less acidic media and in the presence of a catalyst, the disappearance rate of oxalate increased so that no oxalate was observed in any case at neutral pH. Results showed that, even on a neutral surface, oxalate was oxidized in conditions at which the mineralization was not particularly deep, a behaviour that can be explained by the higher affinity of organic anions for catalytic sites. Oxalate accounted for as much as 30% of the organic carbon remaining in the reaction mixture in non-catalytic runs and no more than 12% in catalytic runs. Consequently, the use of a catalyst favours not only the reactions leading to oxalate but also the mineralization of oxalate itself, avoiding its accumulation in the reaction mixture. The mineralization of oxalate is not particularly enhanced by a positive surface charge and, therefore, results seem to exclude a mechanism based solely on the ion exchange of oxalate. To support this conclusion, in certain runs the catalyst was washed with an alkaline solution at the end of the reaction, and the extract analyzed by TOC and ionic chromatography in search of adsorbed but not oxidized organic compounds. In all cases, the amount of organic carbon detected was very low showing that a adsorption by anion exchange was not the reason for the disappearance of oxalate. The degree of mineralization was not directly linked to the accumulation of other low molecular weight carboxylic acids. In particular, low levels of acetate and formiate were detected in most runs, but without an accumulation pattern clearly linked to the pH or the evolution of TOC.

Figs. 12 and 13 show the evolution of $SUVA_{254}$ with the integral ozone exposure for the ozonation of naproxen and carbamazepine. The pattern was very different in both cases. During the reaction of carbamazepine, the absorbance decreased almost steadily with ozone exposure, but the products of the ozonation of naproxen exhibited a greater absorbance than the parent solution. For runs with a high degree of mineralization, $SUVA_{254}$ showed the highest values. This reflected the formation of aromatic or unsaturated products and their preferential accumulation in the reaction mixture even under relatively deep mineralization conditions and may be favoured by the condensed structure of naproxen. The non-saturated character of the products will probably be linked to an increased toxicity of the reaction mixture even if TOC becomes considerably reduced. The chemical structure of the parent compounds, which is relatively less important for the catalytic ozonation rate, determined the nature of the reaction products and must be taken into account even under strong oxidant conditions.

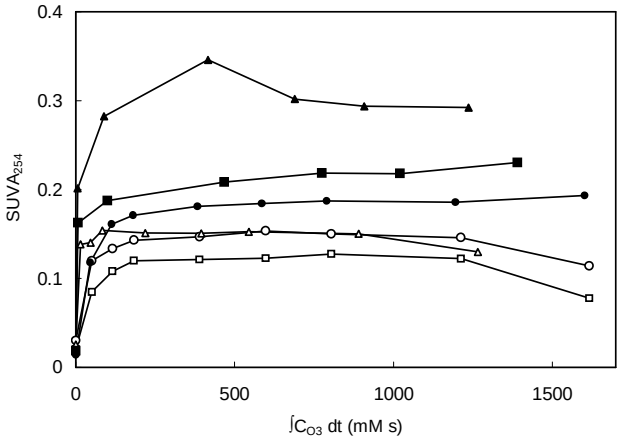

Figure 12. Specific ultraviolet absorption at 254 nm for the ozonation of naproxen at pH = 3 (○), pH = 5 (Δ) and pH = 7 (□) in the absence of catalyst ant at pH = 3 (●), pH = 5 (▲) and pH = 7 (■) using 1 g/L TiO_2.

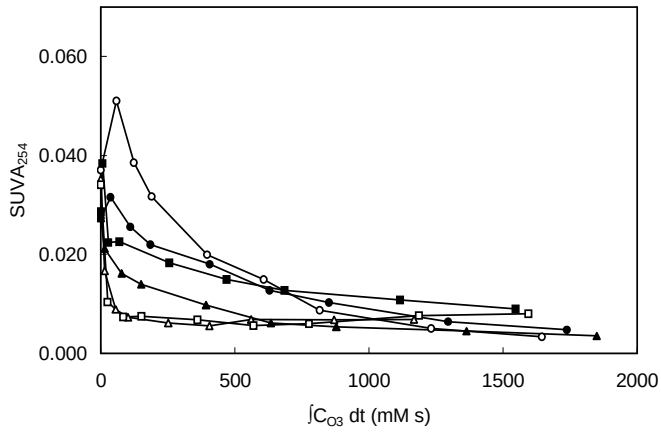

Figure 13. Specific ultraviolet absorption at 254 nm for the ozonation of carbamazepine at pH = 3 (○), pH = 5 (Δ) and pH = 7 (□) in the absence of catalyst ant at pH = 3 (●), pH = 5 (▲) and pH = 7 (■) using 1 g/L TiO_2.

4. Conclusions

The catalytic ozonation of naproxen and carbamazepine in aqueous solution reduced the total organic carbon to

about one third of its initial value for reactions carried out at 25ºC with a catalyst load of 1 g/L. Best results, with TOC reduction of 62% for naproxen and 73% for carbamazepine were obtained in slightly acidic conditions with pH 5 and an initial concentration of 15 mg/L. In the same conditions, the non-catalytic ozonation of naproxen and carbamazepine yielded a mineralization degree of only 50% with a maximum reaction rate obtained at neutral pH. Naproxen and carbamazepine reacted during the first few minutes in contact with ozone and, therefore, the organic carbon measured during the run corresponded to ozonation products. Most of the mineralization takes place during the first 10-20 minutes in a rapid ozonation period followed by a slow mineralization of the more refractory compounds. The initial rate of non-catalytic reaction decreased in the presence of sodium phosphate, proving that at least the initial rapid mineralization reactions are an indirect hydroxyl radical-mediated oxidation.

The evolution of the mineralization process was modelled by assuming a different kinetic behaviour for the organic carbon belonging to easily oxidizable substances and to refractory final reaction products. It was also considered that the later were oxidation products from the ozonation of the former. A regression model allowed an estimate of the pseudo-homogenous reaction constants for catalytic and non-catalytic runs. The catalytic rate constant was maximum for pH 5 with a value of $7.76 \times 10^{-3} \pm 3.9 \times 10^{-4}$ L mmol^{-1} s^{-1} for naproxen and $4.25 \times 10^{-3} \pm 9.7 \times 10^{-4}$ L mmol^{-1} s^{-1} for carbamazepine. The results also showed that the catalyst promotes the decomposition of ozone under acidic conditions, while at neutral pH it behaved as an inhibitor of the ozone decomposition in comparison with the homogeneous ozone self-decomposition in pure water. The effect of an increase of pH was greater on the rate constant of the first mineralization period than on the catalytic reaction of ozone decomposition and the rate of mineralization decreased with the increasing concentration of hydroxide. These results suggest that the adsorption of organics could play a significant role in the reaction and indicate that the surface interaction is greater with organic compounds than with molecular ozone. The enhancement of mineralization would not merely be the consequence of a greater surface production of hydroxyl radicals from ozone. The catalyst promotes mineralization especially in slightly acidic conditions, a result that is probably linked to the adsorption of reaction intermediates on acid catalytic sites. The experiments partially carried out in the absence of ozone indicated that the adsorption of intermediates did not play a role in the reduction of dissolved organic carbon during the ozonation reaction. Moreover, the absence of ozone was associated with a desorption of organic compounds probably linked to a decrease in acidic catalyst sites.

The catalyst not only modified the mineralization rate, but also, the composition of the mixture at the end of the process. Oxalate, which accumulates in the reaction mixture from non-catalytic runs, mineralized in catalytic runs particularly in neutral conditions. The amount of oxalate in the products of catalytic experiments accounted for no more than 12% of the organic carbon. Therefore, the catalyst enhanced mineralization reactions of oxalate itself, avoiding its accumulation in the reaction mixture. The reaction products exhibited a markedly different pattern concerning ultraviolet absorption at 254 nm. $SUVA_{254}$ decreased steadily with ozone dosage for the ozonation products of carbamazepine, while they maintained a high value, even greater than the one corresponding to the parent solution, for naproxen. This was linked to the aromatic condensed structure of naproxen and suggests that toxicity could be higher even after a deep mineralization reaction.

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Notation

c_A c_B	concentration of organic carbon in compounds A and B, mM or mg/L^{-1}
c_i	concentration of a given organic compound, mol L^{-1}
$c_{HO\bullet}$	concentration of hydroxyl radicals, mol L^{-1}
c_{O_3}	concentration of dissolved ozone, mol L^{-1}
c_o	initial concentration, mol L^{-1}
c_s	bulk concentration of solids in the liquid phase, kg_{solids} L^{-1}
k_a	adsorption kinetic constant, L kg_{solids}^{-1} s^{-1}
k_{-a}	desorption kinetic constant, mol kg_{solids}^{-1} s^{-1}
k_c	intrinsic catalytic kinetic constant, L kg_{solids}^{-1} s^{-1}
k_d	kinetic constant of the ozone homogeneous decomposition, s^{-1}
k_{cd}	kinetic constant of the ozone heterogeneous decomposition, L kg_{solids}^{-1} s^{-1}
K_a	adsorption equilibrium constant, L mol^{-1}
$k_{HO\bullet}$. k_{O_3}	second order kinetic constant of homogeneous ozone reactions, L mol^{-1} s^{-1}
k_R	homogeneous kinetic constant defined in Eq. (3), L mol^{-1} s^{-1}
k_{Rc}	pseudo-homogeneous catalytic kinetic constant defined in Eq. (15), L mol^{-1} s^{-1}
R_{ct}	ratio of $c_{HO\bullet}$ to c_{O_3} at a given time during the reaction, dimensionless

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