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# Removal of pharmaceuticals and kinetics of mineralization by $O_3/H_2O_2$ in a biotreated municipal wastewater

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## Abstract

The ozonation of an effluent from the secondary clarifier of two Municipal Wastewater Treatment Plants was performed by using alkaline ozone and a combination of ozone and hydrogen peroxide. Alkaline ozonation achieved only a moderate degree of mineralization, essentially concentrated during the first few minutes; but the addition of hydrogen peroxide eventually led to a complete mineralization. The evolution of total organic carbon (TOC) as a measure of the extent of mineralization and the concentration of dissolved ozone were analysed and linked in a kinetic model whose parameter represented the product of the exposure to hydroxyl radicals and the kinetic constant of indirect ozonation. This rate parameter yielded the highest values during the first part of $O_3/H_2O_2$ runs. The kinetic constant for the decomposition of ozone at the end of the run was also measured and computed for the non-oxidizable water matrix and yielded essentially the same values regardless of whether or not hydrogen peroxide was used. A group of 33 organic compounds, mainly pharmaceuticals and some relevant metabolites present in the wastewater effluents, were evaluated before and after the ozonation process using a liquid chromatography-hybrid triple-quadrupole linear ion trap system (LC-QqLIT-MS). The results demonstrate that the ozonation degrades these compounds with efficiencies of over 99% in most cases, even under low mineralization conditions in alkaline ozonation.

Keywords: Advanced Oxidation Processes; Wastewater; Pharmaceuticals; Water reuse

## 1. Introduction

The presence of pharmaceutical compounds in water and wastewater has been repeatedly reported. Kümmerer (2001) reviewed the emission of drugs, disinfectants, and other chemicals by hospitals. Al-Rifai et al. (2007) and Gagné et al. (2006) recently reported the occurrence of several pharmaceutically active products in municipal wastewater. Ternes (1998) identified over 30 drugs in the influent of German Municipal Wastewater Treatment Plants (MWTP). Many of these active substances are persistent as they escape to conventional wastewater treatments and are becoming ubiquitous in the environment (Carballa et al., 2004, Tauxe-Wuersch et al., 2005). Certain compounds and, in particular, some antibiotics, anti-tumour agents and analgesics, are neither degradable nor adsorbable on sewage sludge. There has been an increasing concern about the impact of pharmaceutical compounds on public health and on the environment not only due to their acute toxicity, but also their genotoxicity, development of pathogen resistance and endocrine disruption (Halling-Sørensen et al., 1998). The occurrence of these contaminants in treated waters also endangers their reuse in diverse applications, an aspect of especial interest since the availability of good quality water is a critical issue for a sustainable economic development. Consequently, the application of more exhaustive wastewater treatment protocols, including the use of new and improved technologies; the application of wider and integrated quality control strategies, comprising chemical, microbiological and toxicological analysis; and the development of wastewater reuse strategies are all goals which have to be worked towards (Hernando et al., 2005).

Advanced Oxidation Processes (AOPs), involve the generation of hydroxyl radicals and other strong oxidant species that are able to degrade compounds characterized by high chemical stability or by strong difficulty towards complete mineralization (Andreozzi et al., 1999). These technologies involve different methods for the generation of hydroxyl radical. They include Fenton systems, ozonation, hydrodynamic and acoustic cavitation, homogeneous ultraviolet irradiation, heterogeneous photocatalysis using semiconductors, radiolysis, and a number of electric and electrochemical methods (Rajeshwar et al., 1994, Gogate and Pandit, 2004a). Proper combinations of AOPs have increased the chances of treating target recalcitrant pollutants (Esplugas et al., 2002). In particular, Fenton, photo-Fenton, $TiO_2$ photocatalysis, ultraviolet-based processes ($H_2O_2$/UV and $O_3$/UV),

$O_3/HO^-$ and $O_3/H_2O_2$ have been reported for several drugs by different authors (Ikehata et al., 2006). Other combinations such as sonophotocatalysis, ultrasounds combined with ozone of hydrogen peroxide or Photo-Fenton, among others have also been suggested or considered (Gogate and Pandit, 2004b). Many of them are in early development stages or suffer from considerable drawbacks, while ozone-based processes are a proven technology and are relatively energy efficient even in comparison with other established technologies like low-pressure UV-based oxidation (Rosenfeldt et al., 2006). The use of $O_3/H_2O_2$ system in this work pursued a deep degree of mineralization to ensure absence of oxidation intermediates and toxicity reduction as well as the removal of individual emerging pollutants identified in a real wastewater effluent. Some pharmaceutical compounds are very reactive towards molecular ozone. Some others, such as, for example, the non-steroidal, anti-inflammatory drug Ibuprofen or the lipid regulator clofibric acid are relatively refractory (Ternes et al., 2002, Ikehata et al., 2006), for degradation by the later, ozone-based Advanced Oxidation Processes (AOP) is much more efficient than ozone alone. These processes are able to completely oxidize recalcitrant compounds, making them less harmful and forming easily biodegradable products (Larsen et al., 2004). Zwiener and Frimmel (2000) reported over 98% conversion of 2 μg/L of clofibric acid, ibuprofen and diclofenac in 10 min at pH 7 using $O_3/H_2O_2$. Other investigations carried out with antibiotics, steroid hormones, beta-blockers or X-ray contrast media have demonstrated the particular capacity of ozone-based AOPs to remove these compounds in effluents, achieving an elimination rate over 90% in most cases (Hernando et al., 2007).

With the aim of developing technologies to improve the use of reclaimed water, a program financed by the Spanish Government is attempting to tackle the different aspects involved in the reuse of wastewater. As a part of the program, this work presents some results concerning the first part of a one-year sampling campaign undertaken in two MWTPs in the city of Alcalá de Henares (Madrid, Spain). Its immediate goal was to relate the efficiency of ozone-based treatments in organic carbon depletion to the removal of individual organic contaminants. The organic compounds analyzed belonged to the group of pharmaceuticals and also included some of their metabolites.

## 2. Material and methods

### 2.1. Materials and ozonation procedure

Wastewater samples were withdrawn from the secondary clarifier of the two MWTP located in Alcalá de Henares (Madrid). West-Alcalá receives urban wastewater (U), i.e., a mixture of domestic and industrial wastewater from facilities located near the city whereas East-Alcalá essentially treats domestic wastewater (D). In all cases, composite samples were collected on an hourly basis (1-L) during 24 h sampling periods at least one day per month. Samples were immediately processed or stored in a refrigerator (<4 °C) inside glass bottles.

The ozonation runs were carried out in a 5-L glass jacketed reactor whose temperature was monitored throughout the experiment by means of a Pt100 RTD and controlled by a Huber Polystat cc2 thermostatic regulator. Ozone was produced by a corona discharge ozonator (Ozomatic, SWO100) fed by oxygen (about 95% purity) produced by an AirSep AS-12 PSA (pressure swing adsorption) oxygen generation unit. Details of the experimental set-up are shown in Fig. 1. The mixture of ozone and oxygen was bubbled into the liquid by means of a porous glass disk with a gas flow of 0.36 $N\ m^3\ h^{-1}$. The reaction vessel was agitated with a Teflon four-blade impeller at 1000 rpm. During the run, some samples were withdrawn at prescribed intervals for TOC analysis. Ozone was removed from samples by bubbling nitrogen. The experiments were carried out at a pH slightly over 8.0, which was controlled when necessary by pumping a diluted solution of sodium hydroxide using a feed-back PID control loop. In most cases, the decomposition of ozone acidified the reaction mixture except during the quick first mineralization period of some runs in which pH tended to increase. This behaviour was attributed to the reactions between hydroxyl radicals and carbonate and bicarbonate ions produced during the mineralization process (Chandrakanth and Amy, 1998).

### 2.2. Analysis

The concentration of ozone in gas phase was determined with the 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 amperometric analyser Rosemount 499A OZ equipped with Pt100 RTD temperature compensation and calibrated against the Indigo Colorimetric Method (SM 4500-$O_3$ B). The signal 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 RTD 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 an LC10AS Shimadzu pump that fed sodium hydroxide solution, thus allowing pH to be controlled throughout the experiment. 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. Based on the measuring device dynamics, a sampling period of 5 s was selected.

Total Organic Carbon (TOC) analyses were carried out by means of a Shimadzu TOC-VCSH total carbon organic analyser equipped with an ASI-V autosampler. Inorganic anions were determined using a Dionex DX120 Ion Chromatograph with conductivity detector and an IonPac AS9-HC 4x250 mm analytical column

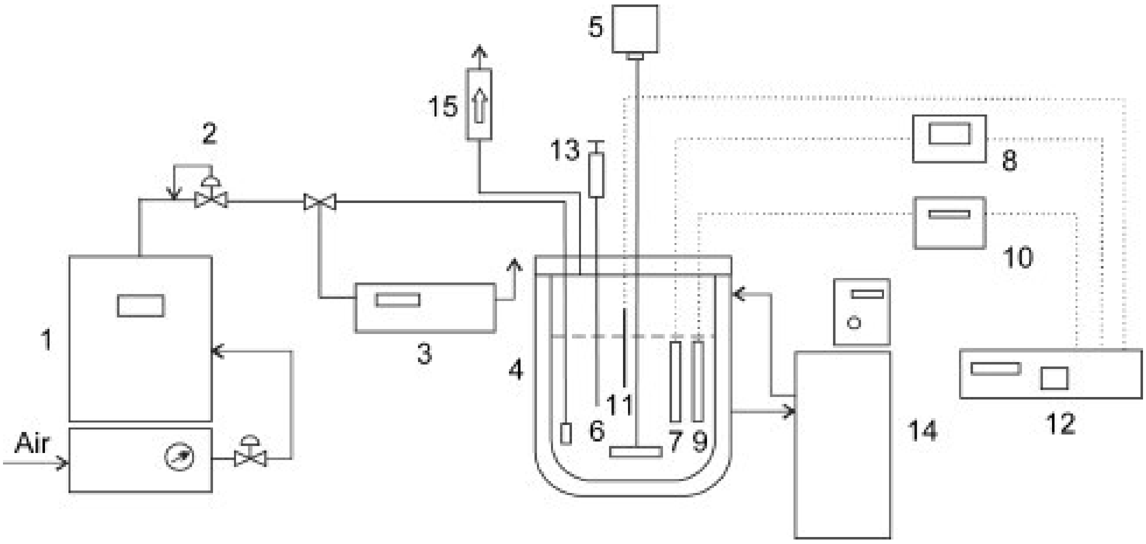

**Figure 1**. Experimental set-up showing (1) ozone generator, (2) flow control, (3) gas phase UV ozone analyser, (4) glass jacketed reactor, (5) stirrer, (6) gas diffuser, (7) dissolved ozone amperometric sensor, (8) ozone-signal analyser, (9) pH electrode, (10) pH control unit, (11) thermocouple, (12) data acquisition unit (13) sampling device, (14) thermostat–cryostat, and (15) ozone destruction unit.

Table 1: Characterization of domestic (D) and urban (U) wastewaters.

| Sample | Suspended solids (mg/L) | Conductivity (μS) | pH | TOC (mg $L^{-1}$) | COD (mg $L^{-1}$) | BOD (mg $L^{-1}$) | Alkalinity (ppm $CaCO_3$) | $SO_4^{2-}$ (ppm) | $Cl^-$ (ppm) |
|---|---|---|---|---|---|---|---|---|---|
| D070125 | 9.8 | 495 | 7.84 | 17.5 | 64 | - | 544 | 114 | 61 |
| D070206 | 12.8 | - | 7.98 | 15.5 | 44 | - | 528 | 111 | 60 |
| D070208 | 12.8 | - | 8.04 | 12.8 | 44 | - | 496 | 112 | 62 |
| D070306 | 23.9 | 544 | 7.56 | 12.1 | 112 | 24 | 468 | 104 | 60 |
| D070308 | 10.1 | 368 | 7.76 | 12.2 | 182 | 17 | 419 | 85 | 52 |
| D070417 | 0.55 | 631 | 8.12 | 8.5 | 81 | 10 | 580 | 86 | 55 |
| D070419 | 7.45 | 579 | 8.38 | 14.0 | 66 | 13 | 521 | 81 | 55 |
| D070529 | 9.4 | 605 | 7.74 | 10.2 | 90 | 7.0 | 416 | 99 | 57 |
| D070531 | 5.9 | 549 | 7.52 | 8.4 | 84 | 8.3 | 305 | 102 | 63 |
| D070612 | 9.0 | 556 | 7.76 | 9.3 | 89 | 4.7 | 399 | 105 | 60 |
| U070205 | 3.6 | - | 8.01 | 11.9 | 42 | - | 539 | 127 | 77 |
| U070208 | 12.4 | - | 8.11 | 9.0 | 35 | - | 508 | 132 | 76 |
| U070222 | ~ 0 | 407 | 7.61 | 8.6 | 62 | 6.5 | 455 | 103 | 68 |
| U070305 | 11.6 | 492 | 7.66 | 11.9 | 71 | 16 | 497 | 114 | 74 |
| U070308 | 0.65 | 446 | 7.59 | 15.5 | 54 | 12 | 415 | 91 | 61 |
| U070416 | ~ 0 | 601 | 7.65 | 8.8 | 67 | 18 | 475 | 116 | 78 |
| U070419 | ~ 0 | 548 | 7.94 | 8.4 | 52 | 16 | 345 | 101 | 81 |
| U070528 | 4.0 | 614 | 7.54 | 5.7 | 72 | 3.0 | 473 | 133 | 79 |

I, II and III refer to ozone profile as indicated in Fig. 3.

[a] Sample filtrated before ozonation to 100 μm.

(ASRS-Ultra suppressor). The eluent flow was 1.0 mL/min of 9.0 mM $Na_2CO_3$ and the sample loop volume was 1 μL. Total suspended solids were determined by Method 2540 D, "Total Suspended Solids Dried at 103–105 °C" (American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1995). COD measurements were performed using the Standard Method 5220D. Standard Methods SM 4500-P E and 4500 $NH_3$ D were followed for the determination of ortho-phosphate and ammonia nitrogen. Details of the analysis of raw wastewater samples are included in Table 1. Hydrogen peroxide was determined by the

Preconcentration of the samples prior to the chromatographic analysis was performed by solid phase extraction (SPE) with Oasis™ HLB cartridges (Waters, 200 mg, 6 cc). An automated sample processor ASPEC XL from Gilson (Villiers-le-Bel, France) was used for this purpose. The operational procedure has been described elsewhere (Martinez Bueno et al., 2007). Briefly, the cartridges were preconditioned with MeOH (6 ml) and deionized water HPLC-grade (5 ml, pH adjusted to 8 with 20% $NH_4OH$) at a flow rate of 1 ml/min. Aliquots of 200 ml of sample (pH adjusted to 8) were then loaded into the cartridge at a flow rate of 10 ml/min, rinsed with 5 ml of deionized water and finally eluted with 2 × 4 ml of MeOH at 1 ml/min. The extracts so obtained were finally evaporated until almost dryness, reconstituted with 1 ml of MeOH:water, 10:90 (*v*/*v*), filtered, and diluted 1:1 with MeOH:water (10:90) before the analysis.

The analysis of the selected organic compounds was performed by a 3200 QTRAP MS/MS system (Applied Biosystems) using a turbo ionspray source in positive and negative modes. Separation was performed in an Agilent Technologies HPLC series 1100, equipped with a reversed-phase C-18 analytical column (ZORBAX SB, 250 mm × 3.0 mm I.D.; 5 µm). For the analysis in positive mode, the compounds were separated using acetonitrile (mobile phase A) and HPLC-grade water with 0.1% formic acid (mobile phase B) at a flow rate of 0.2 ml/min. A linear gradient progressed from 10% A to 100% A in 40 min, after which the mobile phase composition was maintained at 100% A for 10 min. The re-equilibration time was 15 min. Compounds analyzed in negative mode were separated using acetonitrile (mobile phase A) and HPLC-grade water (mobile phase B) at a flow rate of 0.3 ml/min. LC gradient progressed from 30% A to 100% A, in 7 min, and it was maintained at 100% A for 8 min. The re-equilibration time was 10 min. The volume of injection was 20 µL in both modes. Specific operational conditions were optimized and have been described elsewhere (Martinez Bueno et al., 2007). The analytical methodology based on the use of an LC-MS system equipped with a modern and sensitive hybrid triple-quadrupole linear ion trap (QqLIT) mass spectrometer was applied in the determination of a group of selected compounds usually present in wastewater effluents. They include mainly pharmaceuticals of different therapeutic groups, such as analgesics/anti-inflammatories, antibiotics, lipid regulators, β-blockers, antidepressants, anti-epileptics/psychiatrics, ulcer healing compounds, diuretics and bronchodilators. Also of interest was the presence of some metabolites such as the metabolites of the analgesic/antipyretic drug dipyrone, 4-methylamino-antipyrine (4-MAA), *N*-acetyl-4-amino-antipyrine (4-AAA) and *N*-formyl-4-amino-antipyrine (4-FAA).

### 2.3. Decomposition of ozone and kinetics of TOC removal

Assuming that the decomposition of dissolved ozone follows a first-order kinetics, a general mass balance to ozone leads to the following expression:

$$\frac{dC_{O_3}}{dt} = k_L a\left(C^*_{O_3} - C_{O_3}\right) - k_d C_{O_3} \qquad (1)$$

represents the equilibrium concentration of dissolved ozone in water, $k_La$ the volumetric mass transfer coefficient and $k_d$ the first-order kinetic constant of ozone decomposition. Eventually, the concentration of dissolved ozone reaches stationary state if the rates of ozone consumption and the rate of ozone mass transfer from the gas bubbles arrive at equilibrium:

$$0 = k_L a\left(C^*_{O_3} - C_{O_3s}\right) - k_d C_{O_3s} \qquad (2)$$

Once the gas flow is stopped, and in case mass transfer with the gas in the freeboard zone is neglected, the concentration of dissolved ozone follows a first-order decay:

$$\frac{dC_{O_3}}{dt} = -k_d C_{O_3} \qquad (3)$$

The evolution of dissolved ozone together with the volumetric mass-transfer coefficient can be used to calculate ozone dosing. An ozonation model is needed, however, to link this data to the ozonation kinetics determined by the depletion rate of individual compounds of the rate mineralization measured as TOC removal. Taking into account that the elimination of dissolved pollutants by ozone is due to the combination of direct and indirect or radical reactions, Elovitz et al. (Elovitz and von Gunten, 1999, Elovitz et al., 2000) proposed a kinetic model in which the removal of specific micropollutants was determined by ozone exposure. In it, the ozonation process is characterized by a parameter $R_{ct}$ defined as the relationship between the integral ct-exposure to ozone and hydroxyl radical, the two main oxidants involved in the system:

$$R_{ct} = \frac{\int C_{HO\bullet}\,dt}{\int C_{O_3}\,dt} \qquad (4)$$

characterizes the ozonation process and, eventually, allows the estimation of the concentration of hydroxyl radical in water from the concentration of dissolved ozone. This parameter relates the removal of a given pollutant to ozone exposure. The balance to a certain pollutant (P) with $C_{P_o}$ of initial concentration in water in a volume element of reactor either in batch or plug flow during an ozonation process is expressed by the following integrated equation:

$$\ln\frac{C_P}{C_{P_o}} = k_{O_3}\int_0^t C_{O_3}\,dt + k_{HO\bullet}\int_0^t C_{HO\bullet}\,dt = \left(k_{O_3} + R_{ct}k_{HO\bullet}\right)\int_0^t C_{O_3}\,dt \qquad (5)$$

The kinetic constants $k_{O3}$ and $k_{HO\bullet}$ represent the direct and indirect second-order ozone reactions, respectively. The low concentration of hydroxyl radical in water ($C_{HO\bullet} \leq 10^{-12}$ M) makes difficult its direct measurement. The integral $\int C_{HO\bullet}\,dt$ may be determined by means of probe compounds (Hoigné, 1997) such as *p*-chlorobenzoic acid (*p*CBA) whose direct and indirect kinetic constants are known ($k_{O3/pCBA} \approx 0.15 M^{-1} s^{-1}$, $k_{HO\bullet/pCBA} \approx 5\times10^9 M^{-1} s^{-1}$). This procedure was not used in this work due to the difficulty of getting data representative for the whole mineralization process. In real wastewaters, a mixture of many compounds in low concentration is always encountered. In such a case, by analogy with the case of a single pollutant, an integrated equation similar to Eq. (5) can be used by replacing the concentration of the individual compound by an aggregate such as TOC or COD. The changes in reaction constants would be a consequence of the evolution of reaction matrix as ozonation proceeds. Depending on reaction conditions, the ozonation may take place solely by a radical mechanism, by direct reactions or by a combination of both. In general, the kinetics of TOC removal complies the following expression:

$$\ln\frac{\mathrm{TOC_o}}{\mathrm{TOC}} = \left(k_{O_3} + R_{ct}k_{HO^\bullet}\right)\int C_{O_3}\,dt = R\int C_{O_3}\,dt \qquad (6)$$

The pseudo-rate constant *R*, depends not only on the true second-order kinetic constant of the hydroxyl-mediated ozonation, but also on the specific balance of hydroxyl radicals to ozone exposure. As TOC removal is not a single chemical process but the consequence of a series of reactions, *R* is not expected to be constant in general. Rather, it should be considered a parameter that characterizes the ozonation process by connecting ozone profiles and TOC decay.

## 3. Results and discussion

### 3.1. Removal of Total Organic Carbon

Urban and domestic wastewaters were ozonated with and without addition of hydrogen peroxide. The evolution of TOC and the concentration of dissolved ozone during a representative alkaline ozonation treatment, i.e., without injecting hydrogen peroxide, are shown in Fig. 2. The wastewater corresponds to the effluent of the secondary clarifier from the domestic wastewater MWTP (Table 2, Table 3, D070208). In this run, the gas, a mixture of ozone and oxygen with a 46.1 g N m$^{-3}$ ozone concentration, was bubbled at a rate of 0.36 N m$^3$ h$^{-1}$. Equilibrium ozone concentration, $C_{O3}*$, differs somewhat from run to run due to the pulses in the PSA unit that fed ozone generator. During the experiment the pH was kept the range 8.04–8.25. Based on the concentration profile of dissolved ozone, three different zones can be observed during the run and are indicated in Fig. 2. In zone I, the rate of ozone transfer was greater than that of ozone decomposition with a strong initial increase in ozone concentration. In zone II, the concentration of dissolved ozone reached a stationary value: $C_{O3s}$ after a certain overdamping probably due to the change in composition of the wastewater during treatment. In zone III the concentration of ozone decayed after stopping the gas flow as a consequence of its self-decomposition in the water matrix.

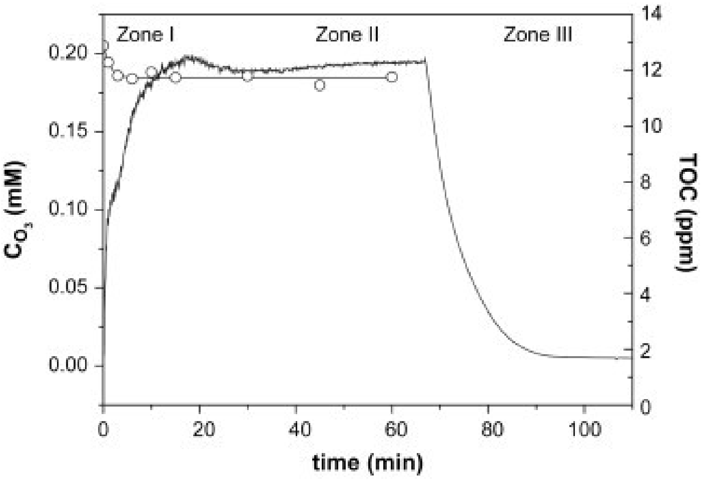

**Figure 2**. Total organic carbon (TOC in ppm) and ozone concentration (mM) during the ozonation of D070208 wastewater (Table 2, Table 3); pH, 8.04–8.25; *T*, 25 °C; gas flow rate, 0.36 N m$^3$ h$^{-1}$; gas ozone concentration, 46.1 g/N m$^3$.

Table 2: Reaction conditions and kinetic parameters of the ozonation ($O_3/H_2O_2$) of domestic (D) and urban (U) wastewater at T = 25ºC, pH = 7.6–8.2 and $k_La = 0.614 \pm 0.009$ min$^{-1}$ (f: sample filtrated before ozonation to 100 µm)

| Sample | TOC removed (%) | $C_{O3gas}$ (mM) | $C_{O3}*$ (mM) | $C_{O3I}$ (mM) | $k_{dI}$ (min$^{-1}$) | $R_I$ (mM$^{-1}$min$^{-1}$) | $C_{O3II}$ (mM) | $k_{dII}$ (min$^{-1}$) | $R_{II}$ (mM$^{-1}$min$^{-1}$) | $C_{O3III}$ (mM) | $k_{d\,III}$ (min$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| D070206 $^f$ | 91.3 | 1.010 | 0.233 | 0.038 | 3.26 | 0.823 | 0.050 | 2.32 | 0.125 | 0.198 | 0.112 |
| D070208 $^f$ | 85.8 | 1.039 | 0.240 | 0.044 | 2.74 | 1.084 | 0.055 | 2.07 | 0.375 | 0.204 | 0.109 |
| D070308 | 62.7 | 1.021 | 0.236 | 0.036 | 3.41 | 0.996 | 0.051 | 2.23 | 0.084 | 0.190 | 0.104 |
| D070417 | 85.4 | 1.019 | 0.235 | 0.049 | 1.51 | 0.337 | 0.070 | 0.94 | 0.192 | 0.199 | 0.072 |
| D070419 | 76.4 | 1.021 | 0.236 | 0.050 | 2.25 | 0.496 | 0.078 | 1.22 | 0.047 | 0.206 | 0.088 |
| D070529 | 59.0 | 0.938 | 0.217 | 0.032 | 3.56 | 1.130 | 0.061 | 1.58 | 0.031 | 0.194 | 0.073 |
| D070531 | 89.9 | 0.937 | 0.216 | 0.039 | 2.79 | 0.857 | 0.082 | 1.01 | 0.084 | 0.199 | 0.057 |
| D070612 | 59.9 | 1.002 | 0.232 | 0.045 | 2.54 | 0.965 | 0.059 | 1.79 | 0.043 | 0.210 | 0.064 |
| U070205 $^f$ | 90.5 | 1.00 | 0.231 | 0.027 | 3.20 | 1.226 | 0.043 | 1.85 | – | 0.202 | 0.061 |
| U070208 $^f$ | 100 | 1.04 | 0.239 | 0.037 | 3.20 | 2.130 | 0.056 | 1.91 | – | 0.202 | 0.107 |
| U070222 | 92.1 | 1.04 | 0.240 | 0.053 | 2.20 | 1.744 | 0.090 | 1.04 | 0.261 | 0.209 | 0.093 |
| U070305 | 88.4 | 1.07 | 0.247 | 0.054 | 2.25 | 0.513 | 0.067 | 1.69 | – | 0.210 | 0.111 |
| U070308 | 85.6 | 1.03 | 0.239 | 0.038 | 2.04 | 0.220 | 0.051 | 1.42 | 0.165 | 0.188 | 0.105 |
| U070416 | 94.2 | 1.04 | 0.239 | 0.043 | 2.77 | 1.270 | 0.065 | 1.63 | 0.159 | 0.201 | 0.115 |
| U070419 | 95.0 | 1.03 | 0.238 | 0.051 | 2.48 | 0.525 | 0.068 | 1.69 | – | 0.205 | 0.109 |
| U070528 | 89.7 | 0.904 | 0.209 | 0.026 | 4.17 | 0.789 | 0.061 | 1.44 | 0.222 | 0.181 | 0.108 |

I, II and III refer to ozone profile as indicated in Fig. 3.

The least-square fitting of the experimental data of ozone concentration to the integral form of Eq. (3), yielded $k_d$ in zone III, a value considered representative of the matrix of inorganic compounds and refractory ozonation products generated during ozonation. The value of $k_La$ was obtained from Eq. (2) in the plateau. For the operational conditions of the experiment represented in Fig. 1, the calculated values of $C_{O3*}$, $k_La$, and $k_d$ were 0.234 mM, 0.610 $min^{-1}$ and 0.139 $min^{-1}$, respectively. The kinetic constant for the decomposition of ozone measured in zone III had an average value of $0.109 \pm 0.048$ $min^{-1}$ for the whole set of reactions carried out without hydrogen peroxide. (The boundary represents the 95% confidence interval.) The evolution of TOC in experiments of alkaline ozonation exhibited in all cases the same pattern shown in Fig. 2. A reduction of organic carbon close to 10% was observed during the first few minutes of reaction, but the mineralization ends even before the concentration of ozone reached a plateau. The first TOC sample was taken after 1 min of bubbling ozone and represented a reduction of 2.7 mg/L of organic carbon, over 80% of the total TOC reduction, this pattern being similar for the rest of the runs. The behaviour of urban and domestic wastewaters was markedly different with a kinetic parameter $R$ in zone I, $R_I$, much greater for the former. In relation with this, TOC removal was considerably higher for urban than that for domestic wastewaters. Details are given in Table 3.

Fig. 3 shows the evolution of ozone and TOC during the ozonation of the same wastewater of Fig. 2 (D070208, Table 1, Table 2). Reaction conditions were pH = 8.09–8.23, $T = 25$ °C, gas flow rate 0.36 N $m^3$ $h^{-1}$ and gas ozone concentration: 45.9 g/N $m^3$, similar to those found in other runs. The average volumetric mass-transfer coefficient was $k_La = 0.616$ $min^{-1}$. During the runs using hydrogen peroxide, injections of 0.15 mL of $H_2O_2$ (30% w/v) were performed every 5 min starting just before the beginning of ozone bubbling. It is noticeable that the initial rapid decrease in TOC (from $TOC_0 = 12.8$ mg/L) is faster in runs without addition of hydrogen peroxide. This effect was attributed to the greater concentration of dissolved ozone reached in runs without hydrogen peroxide, that would favour a higher rate of direct reactions between organics and ozone. A more complete TOC removal, however, took place when the radical indirect reactions were promoted by the presence of $H_2O_2$, with a percentage of TOC refractory to mineralization below 15% of the initial organic carbon in most runs. The analysis of the lower molecular weight carboxylic acids by anion chromatography in the reaction mixture indicated that most of the dissolved carbon can be attributed to formic, acetic and oxalic acids after the first mineralization period that corresponded to the transition I–II in Fig. 3. Oxalic acid was predominant except for the early stages of reaction so that after the transition to the second mineralization period most organic carbon measured as TOC was already in form of carboxylate. At the end of the runs, the low molecular weight carboxylic compounds always accounted for the totality of the remaining organic compounds. This result is consistent with the well-known resistance of these compounds to oxidation both by ozone and hydroxyl radicals (Contreras et al., 2003).

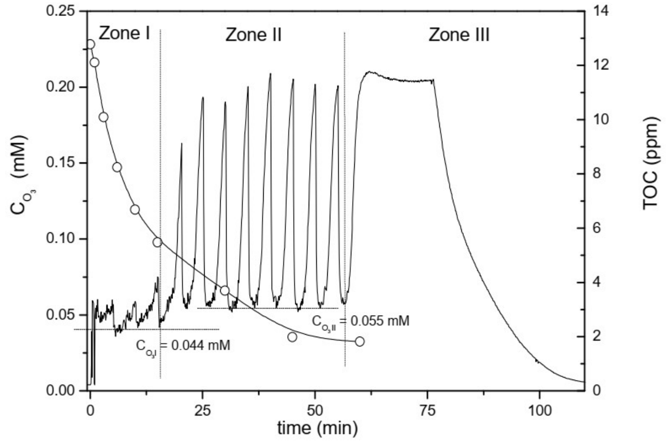

**Figure 3**. Evolution of TOC (○) and ozone concentration during the treatment of D070208 wastewater (Table 1, Table 2) with $O_3/H_2O_2$ with injections of 0.15 mL of $H_2O_2$ (30% w/v) every 5 min; pH, 8.09–8.23; *T*, 25 °C; gas flow rate, 0.36 N $m^3$ $h^{-1}$; gas ozone concentration, 45.9 g/N $m^3$.

In $O_3/H_2O_2$ runs, three zones, that corresponded to three different ozone decomposition kinetics, can be observed. In zone III, the injections of hydrogen peroxide were stopped to avoid ozone decomposition and thereby allowing the concentration of ozone to reach a stationary state ($C_{O3} = 0.204$mM in Fig. 3) before ending ozone bubbling. In it, assuming first-order decomposition of ozone, Eq. (3) can be applied to fit experimental data in order to get $k_{dIII}$, a kinetic decomposition constant linked to the refractory matrix of wastewater. The value for $k_{dIII}$ was not significantly different from that of alkaline ozonation: $0.092 \pm 0.039$ $min^{-1}$ and reflected the absence of compounds participating in ozone self-decomposition reactions disregarding the degree of mineralization. In zones I and II the intense ozone fluctuations are due to the decomposition induced by the injections of hydrogen peroxide. In these two zones two minimums ($C_{O3\text{-}I} = 0.044$mM and $C_{O3II} = 0.055$mM in the experiment of Fig. 3) may be identified. Assuming that these two values could correspond with two stationary states of the process the ozone decomposition kinetic constants for each zone can be calculated: $k_{dI} = 2.74$ $min^{-1}$ and $k_{dII} = 2.07$ $min^{-1}$. For the assembly of the runs, $k_{dI}$ and $k_{dII}$ show a good positive correlation with $k_{dI}$ systematically greater than $k_{dII}$. Fig. 4 shows the logarithmic plot of TOC removal as a function of the integral ozone exposure following Eq. (6). Two different TOC removal zones can be observed which corresponding slopes are $R_I = 1.084$ $mM^{-1}$ $s^{-1}$ and $R_{II} = 0.375$ $mM^{-1}$ $s^{-1}$. The transition (15 min in D070208) corresponded approximately with the boundary between the zones I and II identified from ozone profile. The results pointed to the depletion of the more easily oxidizable compounds as the reason underlying the change in ozone reaction represented by the reduction of the corresponding kinetic constant from $k_{dI}$ to $k_{dII}$. The results for other wastewater samples are shown in Table 1 and suggest that the parameter $R$ may allow a kinetic characterization of the ozonation processes when a global parameter to measure the amount of pollutants in water such as TOC is used. The comparison of $R$-parameters for $O_3/HO^-$ and $O_3/H_2O_2$ runs shows much higher values of $R_I$ for the later, the difference being bigger in domestic wastewaters. The main effect of hydrogen peroxide is to promote mineralization during the first part of the run, in which a low amount of ozone is still found in solution.

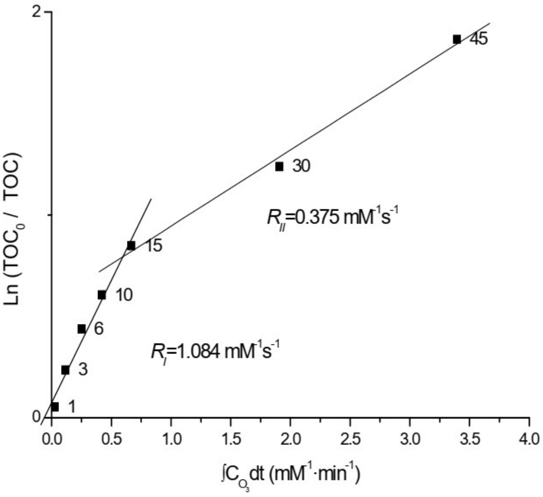

**Figure 4**. Determination of kinetic parameters $R_I$ and $R_{II}$ for the ozonation of D070208 wastewater (Table 1, Table 2) with $O_3/H_2O_2$ with injections of 0.15 mL of $H_2O_2$ (30% w/v) every 5 min; pH, 8.09–8.23; $T$, 25 °C; gas flow rate, 0.36 N m$^3$ h$^{-1}$, gas ozone concentration, 45.9 g/N m$^3$. The numbers represent sampling time in minutes.

The amount of ozone required for a given degree of TOC removal can be calculated by means of Eq. (6). On the other hand, for a given contact time, the total dose of ozone transferred to the water can be obtained from a mass balance to the gas phase:

$$D_{O_3} = \int_0^t k_L a\,(C^*_{O_3} - C_{O_3})\,dt \qquad (7)$$

Both $C_{O3*}$ and $\int C_{O3}$ dt can be readily calculated from gas phase and dissolved ozone concentration recorded during the run. After 5 min of ozonation and for wastewater D070208, the dose of ozone consumed was 18.8 mg/L and 29.7 mg/L for $O_3/OH^-$ and $O_3/H_2O_2$ runs, respectively. During this period, a quick mineralization takes place with TOC removal in the order of 40% for ozone/hydrogen peroxide treatment (Fig. 3). Muroyama et al. (2005) used a similar residence time for the ozonation of drinking water in a big-scale bubble column (27.2 m height, 3.95 m diameter). The ozone doses used for Muroyama et al. (2005), ~3 mg/L, are much lower than those used in this work of ours, but both the nature of treated water (drinking water and wastewater) and the objective (removal of odours and mineralization of organic matter from wastewater) are so different that doses are difficult to compare. The ratio of ozone consumed, and TOC removed for $O_3/HO^-$ and $O_3/H_2O_2$ in D070208 wastewater were 18.8 mgO$_3$/mg TOC and 5.94 mgO$_3$/mg TOC, respectively. These figures, even when corresponding to a laboratory reactor not designed for an efficient ozone transfer, are relatively close to those commonly encountered in surface water ozonation in processes where TOC removal is not the main target. These are usually in the 1–2 mgO$_3$/mg TOC with a limited degree of mineralization (Larson, 1989, Seredynska-Sobecka et al., 2005).

Wastewater quality parameters listed in Table 2 showed little influence on pseudo-rate constants $R_I$ and $R_{II}$. The time series of sulphate and chloride content exhibited a significant positive cross-correlation with both constants in $O_3/H_2O_2$ runs, the variance explained by the former being specially important. The effect seemed to be opposite in $O_3/HO^-$ runs, with a negative correlation of $R_I$ with conductivity, chloride and sulphate, but in this case, the effect is difficult to assess due to the shortage of data but has been pointed out by elsewhere (Muthukumar and Selvakumar, 2004, Chu and Lau, 2007). The influence of sulphate and chloride on ozonation rates could be linked to the formation of weak oxidants such as chlorine, sulphate radical or peroxydisulphate ion from hydroxyl radicals whose role could be to extend the effect of the oxidant mixture rather than to reduce the exposure to hydroxyl radicals. More research is needed, however, on this issue. Contrary to expected results, alkalinity showed no statistically significant influence on mineralization rate constants. This does not mean that they are physically independent. First, alkalinity in wastewaters was similar in all samples with the exception of D070417 (highest value) and U070419 or D070531 (lowest values). For the first, $R_I$ was particularly low, whereas for the second, where a high value could be expected, the result may have been hindered by a particular circumstance affecting this wastewater. In U070419 wastewater, and probably as a consequence of its high BOD to COD ratio as indicated in Table 2, TOC profile for $O_3/H_2O_2$ ozonation of wastewater U070419 exhibited an induction period of about 3 min during which mineralization did not significantly take place. For the case of runs carried out without injection of hydrogen peroxide the extent of mineralization occurred only to a limited extent with an average of 52% in urban and 19% in domestic wastewaters. These results are compatible with a scenario in which indirect reactions are responsible for most or the mineralization even in the absence of a significant effect of alkalinity.

### 3.2. Removal of individual compounds

Table 4 shows the concentrations found in the effluent used for ozonation treatments before two representative runs, by applying the previously described analytical method whose validation parameters have been described elsewhere (Martinez Bueno et al., 2007). The concentration of individual pharmaceutical compounds ranged from 3 to 2100 ng/L and represented a total charge of 10 μg/L. The table includes data from intermediate samples analysed after different processing times (5, 10, 20 and 30 min) in conditions of alkaline ozonation and with injection of hydrogen peroxide. The data showed that practically all pharmaceuticals oxidized even in conditions of low TOC removal, with an average disappearance greater than 99% during the first 5 min of treatment irrespective of the use are not of hydrogen peroxide. The fluoroquinolones ciprofloxacin and ofloxacin exhibited removal efficiencies lower than 95% after 5 min and the only compound with less than 90% removal after 5 min of $O_3/H_2O_2$ was the antidepressant fluoxetine. The ozonation of pharmaceuticals is very rapid, both in the presence and in the absence of hydrogen peroxide, a result due to the very large second-order kinetic constants for the reaction of most pharmaceuticals with ozone (Huber et al., 2003). $O_3/H_2O_2$ enhances mineralization, but after 5 min, the total concentration of analysed pharmaceuticals was 150 ng/L, while in alkaline ozonation at the same time, only 8 ng/L was detected. Moreover, the latter did not decrease with more prolonged treatment whereas in $O_3/H_2O_2$ runs, a further decrease to about 50 ng/L took place during the following first minutes. This behaviour was attributed to the lower concentration of dissolved ozone that inhibited direct reactions. In runs with injection of hydrogen peroxide, the radical route was privileged, and mineralization improved.

Table 4. Evolution of the concentration of pharmaceutical compounds (ng/L) determined in the WWT effluent as a function of processing time when treated with $O_3/H_2O_2$ and $O_3/HO^-$.

| Compound | $O_3/H_2O_2$ | | | | | $O_3/HO^-$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Time (min) | 0 | 5 | 10 | 20 | 30 | 0 | 5 | 10 | 20 | 30 |
| 4-methylaminoantipyrine (4-MAA) | 22 | 0 | 0 | 0 | 0 | 22 | 0 | 0 | 0 | 0 |
| Antipyrine | 20 | 0 | 0 | 0 | 0 | 21 | 0 | 0 | 0 | 0 |
| Atenolol | 849 | 8 | 0 | 0 | 0 | 717 | 0 | 0 | 0 | 0 |
| Bezafibrate | 139 | 0 | 0 | 0 | 0 | 126 | 0 | 0 | 0 | 0 |
| Carbamazepine | 65 | 2 | | 0 | 0 | 61 | 2 | | | |
| Carbamazepine epoxide | 14 | 0 | 0 | 0 | 0 | 13 | 0 | 0 | 0 | 0 |
| Ciprofloxacin | 741 | 70 | 44 | 50 | 49 | 572 | 6 | 6 | 9 | 10 |
| Codeine | 329 | 0 | 0 | 0 | 0 | 351 | 0 | 0 | 0 | 0 |
| Diazepan | 3 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 |
| Diclofenac | 369 | 0 | 0 | 0 | 0 | 216 | 0 | 0 | 0 | 0 |
| Erythromycin | 126 | 0 | 0 | 0 | 0 | 120 | 0 | 0 | 0 | 0 |
| Fluoxetine | 54 | 15 | 3 | 0 | 0 | 135 | 0 | 0 | 0 | 0 |
| Furosemide | 101 | 0 | 0 | 0 | 0 | 71 | 0 | 0 | 0 | 0 |
| Gemfibrozil | 608 | 0 | 0 | 0 | 0 | 618 | 0 | 0 | 0 | 0 |
| Hydrochlorothiazide | 1301 | 15 | 0 | 0 | 0 | 1470 | 0 | 0 | 0 | 0 |
| Indomethacine | 47 | 0 | 0 | 0 | 0 | 40 | 0 | 0 | 0 | 0 |
| Ketoprofen | 346 | 0 | 0 | 0 | 0 | 335 | 0 | 0 | 0 | 0 |
| Ketorolac | 40 | 0 | 0 | 0 | 0 | 42 | 0 | 0 | 0 | 0 |
| Mefenamic Acid | 85 | 0 | 0 | 0 | 0 | 71 | 0 | 0 | 0 | 0 |
| Mepivacaine | 5 | 0 | 0 | 0 | 0 | 5 | 0 | 0 | 0 | 0 |
| Metoprolol | 18 | 0 | 0 | 0 | 0 | 16 | 0 | 0 | 0 | 0 |
| Metronidazole | 212 | 0 | 0 | 0 | 0 | 188 | 0 | 0 | 0 | 0 |
| N-acetyl-4-amino-antipiryne (4-AAA) | 2163 | 0 | 0 | 0 | 0 | 2065 | 0 | 0 | 0 | 0 |
| Naproxen | 389 | 0 | 0 | 0 | 0 | 334 | 0 | 0 | 0 | 0 |
| N-formyl-4-amino-antipiryne (4-FAA) | 1096 | 0 | 0 | 0 | 0 | 1029 | 0 | 0 | 0 | 0 |
| Ofloxacin | 565 | 33 | | | | 464 | | | | |
| Omeprazole | 181 | 0 | 0 | 0 | 0 | 164 | 0 | 0 | 0 | 0 |
| Propanolol hydrochloride | 30 | 0 | 0 | 0 | 0 | 27 | 0 | 0 | 0 | 0 |
| Ranitidine | 297 | 7 | 0 | 0 | 0 | 224 | 0 | 0 | 0 | 0 |
| Salbutamol | 6 | 0 | 0 | 0 | 0 | 5 | 0 | 0 | 0 | 0 |
| Sotalol | 13 | 0 | 0 | 0 | 0 | 11 | 0 | 0 | 0 | 0 |
| Sulfamethoxazole | 150 | 0 | 0 | 0 | 0 | 117 | 0 | 0 | 0 | 0 |
| Trimethoprim | 69 | 0 | 0 | 0 | 0 | 59 | 0 | 0 | 0 | 0 |

The amount of ozone consumed by the ozonation of measured pharmaceuticals has not been assessed and was probably much lower than the total amount of ozone transferred during the first 5 min. TOC data suggested that the fact that most drugs disappeared oxidized in less than 5 min with or without the addition of hydrogen peroxide does not mean that they have been converted to less harmful compounds. The conversion to carboxylic acids and, eventually, total mineralization assessed by TOC removal can ensure adequate reuse conditions.

## 4. Conclusions

The mineralization of wastewater from the secondary clarifier of urban and domestic MWTP was studied by using ozone in alkaline conditions ($O_3/HO^-$ at pH ~ 8) and ozone-hydrogen peroxide ($O_3/H_2O_2$). In the absence of hydrogen peroxide, a TOC decay of about 15% was obtained after 1 h, from which most part (~ 80%) took place during the first five reaction minutes. On the other hand, by injecting pulses of hydrogen peroxide (0.15 mL of $H_2O_2$ 30% w/v in a 5-L reactor every 5 min), the degree of mineralization reached an average over 90%.

The evolution of TOC during hydrogen peroxide ozonation was fitted to a model that assumed a second order reaction of the organic matter measured as TOC and the hydroxyl radicals produced from the peroxide-induced ozone decomposition. The rate constant of the model, *R*, includes information on the hydroxyl-to-ozone ratio and the true second-order kinetic constant between hydroxyl radicals and the individual organic compounds being ozonated. In most runs, a transition was observed from about 1 $mM^{-1}$ $min^{-1}$ to a value one order of magnitude lower. This transition corresponded to a decrease in the ozone decomposition pseudo-first order kinetic constant that was reduced in all cases by a factor close to two. This behaviour was attributed to a change in the organic compounds in the wastewater associated with the depletion of the most reactive moieties. In fact, most refractory organic matter at the end of the runs could be accounted for as low-weight carboxylic acids such as acetic and oxalic. The model parameter R showed a statistically significant positive dependence on the content of sulphate and chloride in wastewater during $O_3/H_2O_2$ runs. This was probably linked to the balance between oxidant species in the reaction mixture. In alkaline ozonation runs, the rate constants of the model were considerably lower, especially for the case of domestic wastewater.

After stopping the gas flow, the decomposition of ozone obeyed a first-order kinetics, whose reaction constant was essentially the same irrespective of the sample considered and of whether or not hydrogen peroxide was used. These results suggest that the decomposition of ozone is not directly linked to the presence of residual organic matter but to the inorganic matrix.

Alkaline ozonation and $O_3/H_2O_2$ treatments yielded high removal efficiencies for pharmaceuticals whose concentrations in wastewater were in the 3–2100 ng/L with a total concentration of 10 μg/L. After 5 min, removal efficiencies were over >99% for most compounds irrespective of the use or not of hydrogen peroxide. Only fluoroquinolones and fluoxetine were relatively resistant to ozonation with removal in the 90–95% range. The total concentration of the analysed pharmaceuticals after 10 min reached, for the most unfavourable conditions less than 0.5% of the initial load. By the kinetic transition observed in $O_3/H_2O_2$ runs, most of the organic carbon was in the form of carboxylates, especially oxalate. Both alkaline and hydrogen peroxide ozonation represent a promising alternative for reducing the total charge of pollutants in biotreated effluents. Target pharmaceuticals disappeared during early stages of ozonation, but only TOC removal is able to ensure the absence of reaction intermediates.

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## Nomenclature

| | |
|---|---|
| $C_{HO\bullet}$ | concentration of hydroxyl radical (M) |
| $C_{O_3}^*$ | equilibrium concentration of dissolved ozone (M) |
| $C_P$ | concentration of a given compound (M) |
| $C_{O_3}$ | concentration of dissolved ozone (M) |
| $C_{O_3s}$ | stationary concentration of dissolved ozone (M) |
| $D_{O_3}$ | dose of ozone transferred to the liquid (mg/L or M) |
| $k_d$ | kinetic constant of ozone decomposition ($s^{-1}$) |
| $k_{HO\bullet}$ | kinetic constant for reactions with hydroxyl radical (L $mol^{-1}$ $s^{-1}$) |
| $k_La$ | volumetric mass transfer coefficient ($s^{-1}$) |
| $k_{O_3}$ | kinetic constant for direct reaction with ozone (L $mol^{-1}$ $s^{-1}$) |
| *R* | kinetic constant for TOC removal during ozonation (L $mol^{-1}$ $s^{-1}$) |
| $R_{ct}$ | hydroxyl ozone ratio defined by Eq. (4) (–) |

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