Ozonation of Emergent Contaminants

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Programa de doctorado: "Ingeniería del Medio Ambiente y del Producto", bienio 2003-2005.

4 Results and discussions

4.1 4-chlorophenol abatement by ozonation coupled with a sequencing batch biofilm reactor (SBBR)

Although this wok focused the treatment of emerging contaminants, a section devoted to the ozonation with posterior biological treatment of 4-chlorophenol is also presented. Nowadays, the behaviour of chlorophenols submitted to ozonation is well known from the available literature. However, this preliminary study aimed to start up the ozonation devices as well as the analytical methods used in the whole investigation. On the other hand, the coupling ozonation with biological treatment, using a SBBR, is considered an innovative work.

In this first section, results from the chemical part (ozonation) of the 4-CP treatment are presented along with the mineralization results obtained by the combination of ozonation-SBBR.

4.1.1 Detailed experimental procedure

4.1.1.1 Ozonation runs

In this part of the work, ozonation experiments were carried out in two different devices. For the kinetic study, the runs were carried out in a 1-L reactor, where the gas flow (50 L h^{-1}) was bubbled in and the solution was continuously stirred. The ozone concentration was adjusted to 5.44 g h^{-1}, which was the minimum stable concentration achieved by the ozonator. Before performing the runs, 4-CP solutions were adjusted to pH 3 and, although at this pH it can be assumed that the interference of the radical mechanism is so weak, 0.1 mL of t-butanol was added in the 4-CP solutions. Thus, solutions with 4-CP concentrations in a range from 200 to 500 mg L^{-1} were ozonated and samples where withdrawn in the first minutes of ozonation and quickly analysed.

To perform the biodegradability evaluation of the pre-treated solution, a pilot plant with a 21-L gas-liquid contact reactor, previously described in the experimental section, was used. Two different ozonation flow rates were applied to treat the 4-CP solutions (5.44 and 7.57 g h^{-1}). 4-CP solutions with concentrations of 100 and 200 mg L^{-1} were charged and the liquid was recirculated at a flow rate of 200 L h^{-1}. In order to calculate the reacted ozone, the gaseous outlet from the two devices was quantified by an ozone analyser and led to a killer, where the remaining ozone was destroyed by means of a KI

aqueous solution. Ozonation reactions lasted one or two hours, and during this period samples were withdrawn from the reactor. Thus, 4-CP concentration, total organic carbon (TOC), chemical oxygen demand (COD), chloride content and biological oxygen demand (BOD) were analysed.

TOC was analyzed by means of a Shimadzu 5055 TOC analyzer. The concentration of 4-chlorophenol was quantified by means of a high performance liquid chromatography (HPLC) supplied by Waters Corporation (Massachusetts, USA). The column used was a TR-016059 supplied by Tecknokroma S. Coop. C. Ltd (Barcelona, Spain) with a length of 250 mm and an inner diameter of 4.6 mm. The mobile phase used was a mixture of acetonitrile (Panreac Quimica, S.A., Spain) and millipore water at a 40:60 volume ratio, acidified until a pH 3 by the addition of phosphoric acid (Panreac Quimica, S.A., Spain). The wavelength used in the detector was 287 nm.

4.1.1.2 Combination ozonation-SBBR

To carry out the combination ozonation-biologic treatment, 4-CP solutions were ozonated during 60 minutes. After the pre-treatment with ozone, in order to ensure that there was not remaining ozone dissolved in the pre-ozonated solution, the reactor was charged 24 hour after performing ozonation runs. The biological reactor, of 2 L of capacity, was an aerobic sequencing batch biofilm reactor (SBBR) and the biomass was supported onto volcanic stones. During the cycles, a continuous oxygen flow of 10 L h^{-1} was fed into the reactor. The activated sludge came from a previous biological reactor that was degrading pre-treated 4-CP solution from photo-Fenton experiment (Bacardit et al., 2005). The pH of the pre-ozonated solutions was adjusted near 7 before feeding the reactor with a NaOH solution and afterwards NH_4Cl, $CaCl_2$, $FeCl_3$, and $MgSO_4$ salts solutions were added as nutrients (Standard method, 5210 D). The pH of the reactor was kept near 7 and adjusted with diluted solutions of NaOH and H_3PO_4. The hydraulic retention time was decreased from four to one day. The temperature of the reactor was kept at 27 ^oC with a thermostatic bath. In the course of the cycles, to recharge the SBBR with the pre-treated 4-CP solution, the air flow and the recirculation were switch off and the supernatant was slowly pumped out of the biological reactor. Subsequently, 1 L of the pre-ozonated solution was fed into the reactor and the recirculation and the aeration were switched on. Samples were withdrawn at the beginning of each cycle and daily in order to follow the TOC removal, pH and volatile suspended solids. In any case, the total samples volume did not exceeded 10 % of the reactor volume.

4.1.2 4-CP, TOC removal and chloride releasing by ozonation

In order to assess the 4-CP removal and the byproducts mineralization, aqueous solutions with different 4-CP concentration were treated by ozonation and samples were withdrawn along the ozonation time. The runs were carried out in a 1 L reactor with an ozone flow rate of 5.44 g h^{-1}. Figure 4-1 shows the ozonation profile of 100 and 200 mg L^{-1} 4-CP solutions, where the 4-CP removal is plotted against the time along with the chloride content released in the medium. According to the results, in both cases the 4-CP is completely removed from the solution in 15 and 30 minutes, respectively. However, after the point where the 4-CP disappears, an additional ozonation time should be applied to ensure the absence of chlorinated byproducts in the medium.

The ozonation of 300 and 500 mg L^{-1} 4-CP solutions showed similar behaviour, and 60 minutes of ozonation were enough to reach the chloride stoichiometric concentration corresponding to the initial 4-CP concentration.

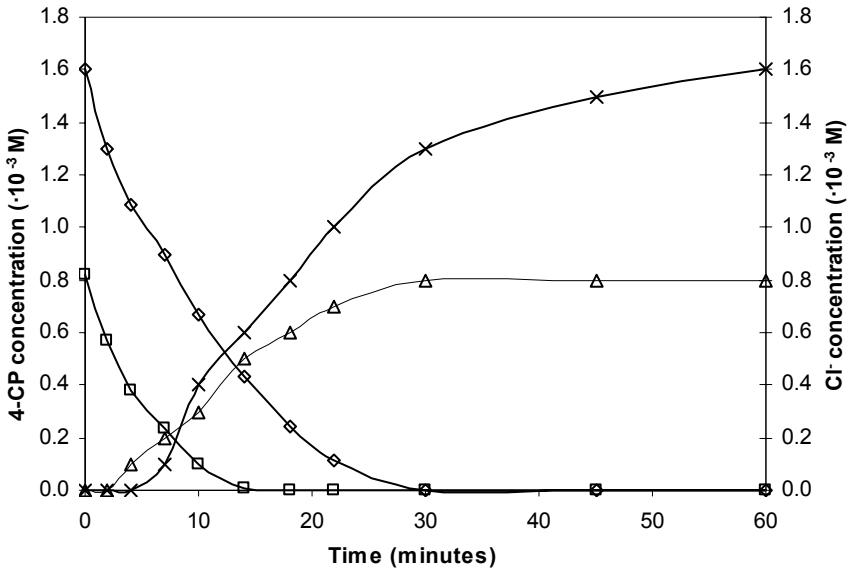


Figure 4-1 - 4-CP removal vs. chloride formation for 100 and 200 mg L^{-1} solutions. □ = [4-CP] - 100 mg L^{-1}; ◊ = [4-CP] - 200 mg L^{-1}; Δ = [Cl^-] - 100 mg L^{-1}; X = [Cl^-] - 200 mg L^{-1}.

Regarding the byproducts mineralization along the reaction time, the TOC analysis showed that at the end of the ozonation time (60 minutes) 40 % of mineralization

was the highest value achieved. According to Figure 4-2, the mineralization rate decreases with the increment of the 4-CP initial concentration. During the reaction, the pH of the solutions decreased to a range around three and remained acid until the end of the ozonation time.

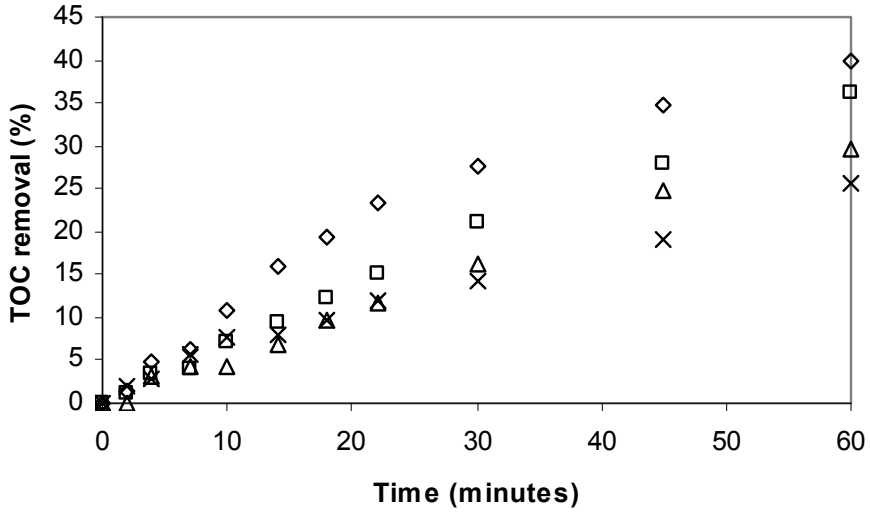


Figure 4-2 - TOC removal vs. time for runs at different 4-CP initial concentration. ◊ = 100 mg L^{-1}; □ = 200 mg L^{-1}; Δ = 300 mg L^{-1}; x = 500 mg L^{-1}.

In this part of the investigation, the 21-L pilot plant was charged with 4-CP solutions and the biodegradability of intermediates along with the mineralization of the 4-CP was studied. The results of 4-CP ozonation at different ozone flow rate (5.44 and 7.57 g h^{-1}) and 4-CP concentration (100 and 200 mg L^{-1}) are presented from Figure 4-3 to Figure 4-6. According to the data, 4-CP was completely removed from the solution. Therefore, according to the ozone concentration measured in the outlet, the average ratio of ozone needed to achieve a complete 4-CP removal was approximately 1.1 mol of ozone per mol of 4-CP. For all runs performed, two hours of ozonation were not able to achieve a total 4-CP mineralization, being the maximal TOC removal about 60 % in the case of runs with 100 mg L^{-1} of 4-CP (Figure 4-3 and Figure 4-4). Besides, at the point where the 4-CP is completely removed, in any case the percentages of TOC abatement exceeded 33 %.

4.1.3 Biodegradability of the pre-ozonated solutions

In order to assess the biodegradability improvement of 4-CP solutions by means of ozonation, samples were withdrawn throughout the 4-CP removal time and the COD and BOD_5 were analyzed. The analysis showed an increment of biodegradability with the ozone dose, achieving for all experiments a final BOD_5/COD ratio between 0.22 and 0.37. The highest BOD_5/COD value was achieved with a combination of highest ozone dose and lowest 4-CP concentration (Figure 4-4).

With regard to the biodegradation profile in the course of the ozonation time, Figure 4-5 and Figure 4-6 show that before the complete 4-CP abatement, biodegradability ratios near 0.1 could be achieved even with a concentration of 4-CP around 40 mg L^{-1}. Since the 4-CP is a non-biodegradable compound for the bacteria used in the BOD test (Grimwood and Mascarenhas, 1997), the increment of biodegradability could be attributed to the intermediates of 4-CP oxidation. After the 4-CP removal, the oxidation of these first byproducts promotes the formation of low molecular weight (organic acids) or hydroxylated compounds, which are presumed to be more biodegradable or less toxic than their parent compounds (Neng-Chou at al., 2006).

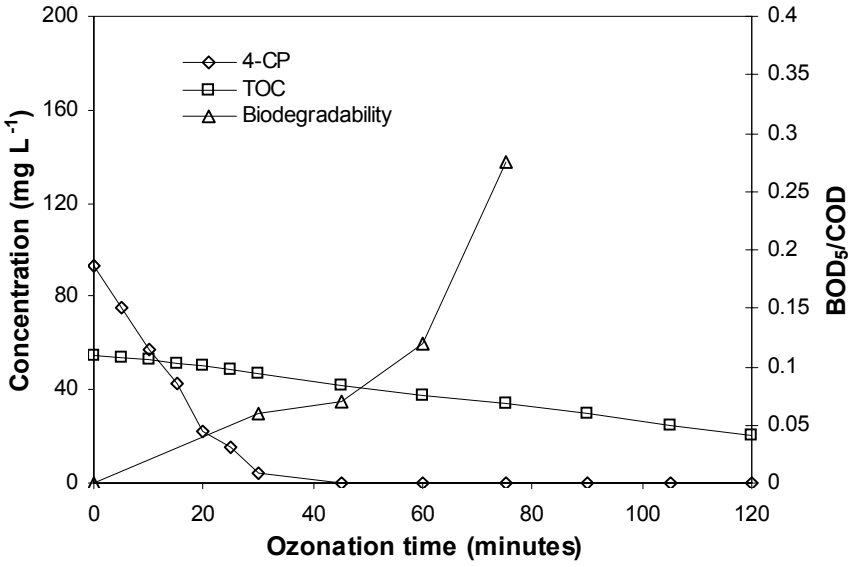


Figure 4-3 - Ozonation of a 100 mg L^{-1} 4-CP solution with a 5.44 g h^{-1} of ozone flow rate.

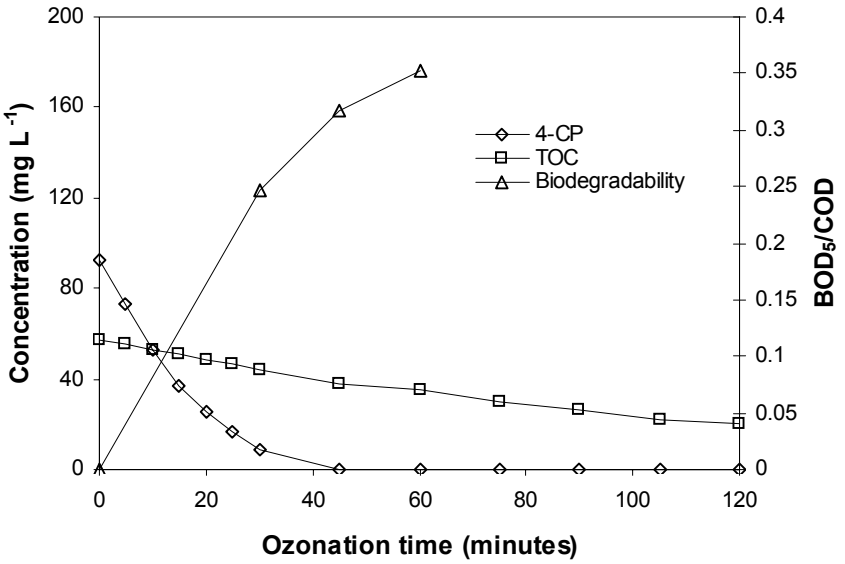


Figure 4-4 - Ozonation of a 100 mg L^{-1} 4-CP solution with a 7.57 g h^{-1} of ozone flow rate

With the purpose of comparing the different conditions applied to treat 4-CP, the data collected at the 4-CP abatement time are presented in Table 4-1. According to the presented data, none of the conditions were able to achieve a TOC removal higher than 33 % at the 4-CP removal time. Nevertheless, a COD removal of 71 % is observed for the experiment with 100 mg L^{-1} of 4-CP and 7.57 g h^{-1} of ozone. In addition, this condition presents as well a higher biodegradability ratio. The difference observed between COD and TOC removal can be explained by the presence of oxygenated organic compounds that usually are produced by ozonation with high ozone doses (Shiyun et al., 2002). Moreover, these compounds are also more biodegradable (Gilbert, 1987).

Table 4-1 - Summary of ozonation results at the 4-CP abatement point.

[4-CP] (mg L^{-1})	Ozone flow rate (g h^{-1})	TOC removal (%)	O_3 consumed / 4-CP removed (moles)	Time needed (minutes)	COD removal (%)	BOD_5/COD
100	5.44	23	1.08	45	32	0.070
100	7.57	33	1.12	45	71	0.370
200	5.44	27	1.18	90	55	0.219
200	7.57	21	1.11	60	49	0.213

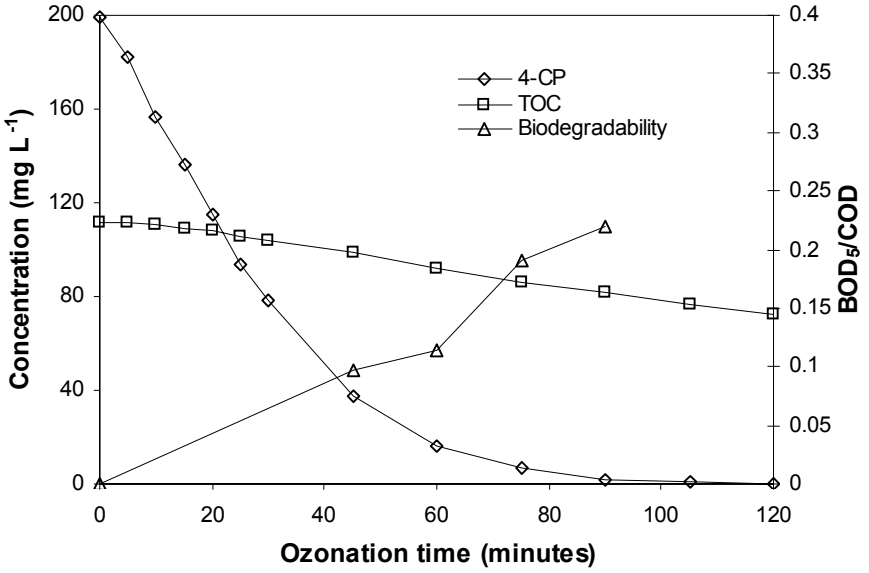


Figure 4-5 - Ozonation of a 200 mg L^{-1} 4-CP solution with a 5.44 g h^{-1} of ozone flow rate.

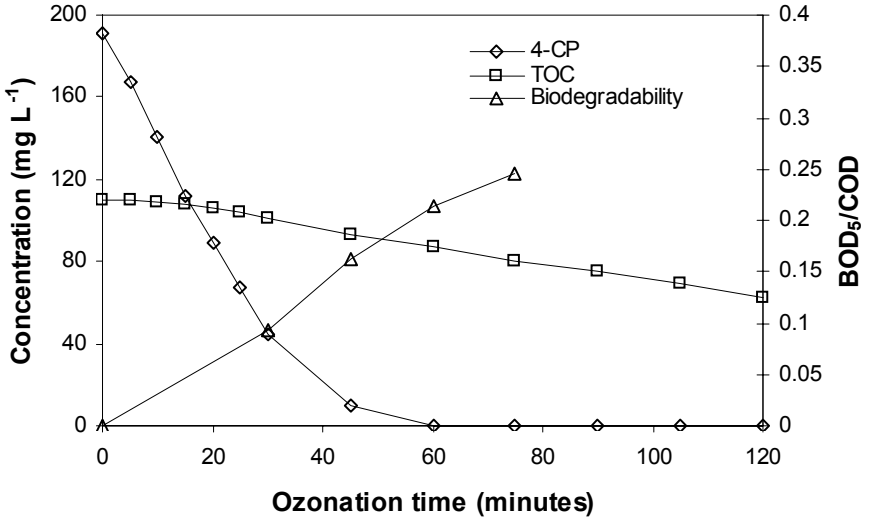


Figure 4-6 - Ozonation of a 200 mg L^{-1} 4-CP solution with a 7.57 g h^{-1} of ozone flow rate.

After a careful analysis of the different condition, 60 minutes of ozonation of a 200 mg L^{-1} of 4-CP with an ozone flow rate of 7.57 g h^{-1} (Figure 4-6) was chosen to be the starting point of the biological process. At this point, the solution presented a low TOC removal (21 %) and biodegradability ratio higher than 0.2.

4.1.4 Identification of byproducts

In Figure 4-7, the formation of byproducts during the 4-CP ozonation is presented. To perform the identification, 100 mg L^{-1} of 4-CP was treated with an ozone dose of 7.57 g h^{-1} and the chromatograms of the samples were compared with standards by means of a HPLC. Hydroquinone and quinone were identified as byproducts and their formation during the 4-CP ozonation is shown.

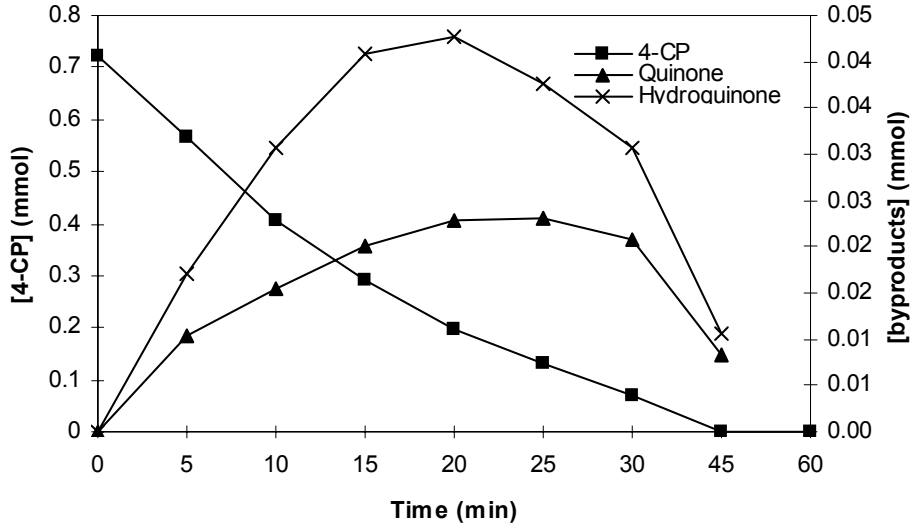


Figure 4-7 - Quinone and hydroquinone formation during ozonation of a 100 mg L^{-1} 4-CP solution with a 7.57 g h^{-1} of ozone flow rate.

According to Figure 4-7, before a total 4-CP removal both hydroquinone and quinone start undergoing oxidation to short chains acids which are biodegradable molecules probably responsible for the biodegradability indicator improvement. This fact is in agreement with the increment of biodegradation before a total 4-CP abatement previously observed. Another important fact to remark is that since the biodegradability

improvement is enhanced by ring hydroxylation, the formation of quinone and hydroquinone could also be considered as a positive factor to the biodegradability improvement (Dieckmann and Gray, 1996; Adams et al., 1997). After the time where the 4-chlorophenol disappears, it could not be identified any by-product by the method applied. It is supposed that from this point, the intermediates are short chain organic acids which could not be separated properly by the chromatography column employed. However, the growth of the biodegradability continues when quinone and hydroquinone disappear.

4.1.5 Bioassay (Final TOC removal)

For the bioassay study, the feed was prepared from a 200 mg L^{-1} 4-CP ozonated solution with a 7.57 g h^{-1} of ozone flow rate and the ozonation time was fixed at 60 minutes, as described previously. At this time of treatment, the 4-CP was completely removed and the ratio BOD_5/COD was 0.213 and a 21 % of TOC removal was achieved. To perform the biodegradation of the remaining TOC, 1-L of the pre-ozonated solution was filled into the biological reactor. The hydraulic retention times (HRT) applied for the initial cycles were four days. After twenty days of treatment, taking into account the increment of TOC removal rate along the cycles, a HRT reduction to one day was performed. During the cycles, one sample was withdrawn daily 15 minutes after filling the reactor. In the last cycles, the TOC removal after 15-120 minutes achieved values up to 85 % of mineralization, indicating a possibility of a reduction on the HRT to some hours (i.e. 8 hours). Nevertheless, due to limitations in terms of system automation HRT lower than one day was not carried out.

In Figure 4-8, the TOC removal achieved at the end of the each cycle is presented. Doted lines were introduced on the graphic in order to represent the average of initial TOC concentrations of the pre-treated solution and the TOC removed by means of ozonation. According to the results, the combination ozonation-SBBR had a good performance to remove the TOC, achieving since the first cycle (four days) a TOC removal higher than 90 %. The last cycle, with the HRT of one day was able to reach a final TOC value of 4 mg L^{-1} equivalent to about 97 % of TOC removal of the 4-CP initial solution. A factor that could contributes to the high efficiency of the SBBR comes from the fact that the bacteria community present in the reactor were already adapted to intermediates from the photo-Fenton degradation of 4-CP. Thus, the similarity of the

byproducts from the photo-Fenton process and ozonation may improve the adaptation of the biomass.

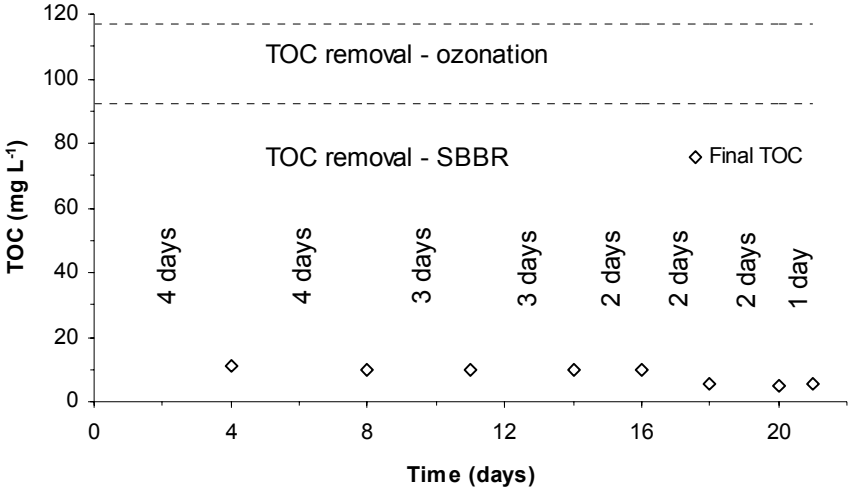


Figure 4-8 - TOC removal of coupled ozonation-SBBR.

One additional cycle without air supply and another without feeding solution were carried out in order to evaluate the SBBR recuperation in terms of TOC removal. For the stage without air supply, the reactor was filled with a 4-CP solution and left eight days without aeration. After this period, the aeration was turned on and the reactor was filled with 4-CP pre-ozonated solution. Nevertheless, TOC removals higher than 90 % were achieved after three cycles of 3, 2, 2 days, indicating a good recuperation of the bacteria community in front of the absence of the air supply. In the Figure 4-9, TOC measurements performed 15 minutes after charging the reactor and at the end of each cycle are presented. The graphic shows the performance of the SBBR reactor before and after being submitted to air absence. According to the results, since the first cycle after the air absence, the SBBR achieved a high mineralization of the organic matter content present in the pre-treated solutions.

The absence of feed took place for a period of 48 days. In the course of this stage, the reactor was filled with 4-CP solution and left for 48 days with continuous aeration. After the end of the stage, the reactor was filled with a new 4-CP pre-ozonated solution and after four cycles of 2, 2, 2 an 1 day, the combination ozonation-SBBR was enough to reach more than 90 % of TOC removal.

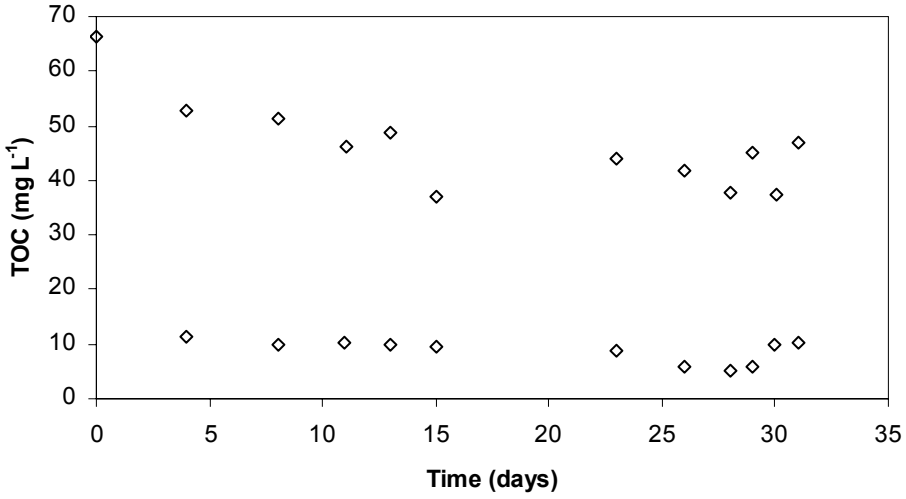


Figure 4-9 – Initial (15 minutes) and final TOC measurement during biological treatment (SBBR) of pre-treated 4-CP solutions.

4.1.6 Determination of the kinetic constant

It is well known that the kinetic model of a reaction between ozone and a pollutant, during an ozonation where the ozone is bubbled in aqueous solutions, is controlled by the ozone mass transfer from the gas phase to the aqueous solution (Beltran, 2004). However, to simplify the calculation of the kinetic constant for the direct attack of ozone on the 4-CP molecule, it was used the pseudo first order approximation. Thus, to calculate the second order kinetic constant of the ozone reactions of 4-CP solutions, buffered solutions with 1 mmol L^{-1} of t-butanol were ozonated and the 4-CP concentration was recorded in the first minutes of reaction. Assuming that the 4-CP degradation in the presence of t-butanol is based in the direct attack of ozone, the determination of the kinetic constant for this reaction was attempted as follows:

Considering the following overall kinetic to describe the ozonation of the 4-CP:

$$v = k[4CP][O_3] \qquad \textbf{equation 4-1}$$

Where [4CP] is the concentration of 4-chlorophenol and [O_3] is the ozone concentration. If it is considered that the [O_3] is much higher than [4CP] in the course of the ozonation, the concentration of [O_3] will not change during the course of the reaction. This means that the [O_3] remain constant. Thus, the rates dependence based on [4CP] can be written:

$$v = -\frac{d[4CP]}{dt} = k'[4CP] \qquad \textbf{equation 4-2}$$

Where,

$$k' = k[O_3] \qquad \textbf{equation 4-3}$$

In this case, k´ is the pseudo first order constant. As the decrease of the organic compound can be followed with the time, it is possible to calculate k´ with the use of the following equation:

$$\ln\left[\frac{[4CP]}{[4CP]_0}\right] = k' \cdot t \qquad \textbf{equation 4-4}$$

Plotting the neperian logarithm of the normalised organic compound concentration against time, the slope of the resulting straight line represents the k´. Thus, the pseudo first order method was applied with the use of the available data recorded from the ozonation of different 4-CP concentration solutions (200-500 mg L^{-1}). Then, a graphic of neperian logarithm of the normalized 4-CP concentration vs. time was created (Figure 4-10).

According to the results, the data fitted with the pseudo first order model. Nevertheless, it is known that the ozonation mechanism of chlorophenols is much more complex (Benitez, 2000).

The kinetic constant k´ calculated for the ozonation of 4-CP is shown in the table 6. The calculated value is in agreement with the literature survey (Pera-Titus et al., 2004).

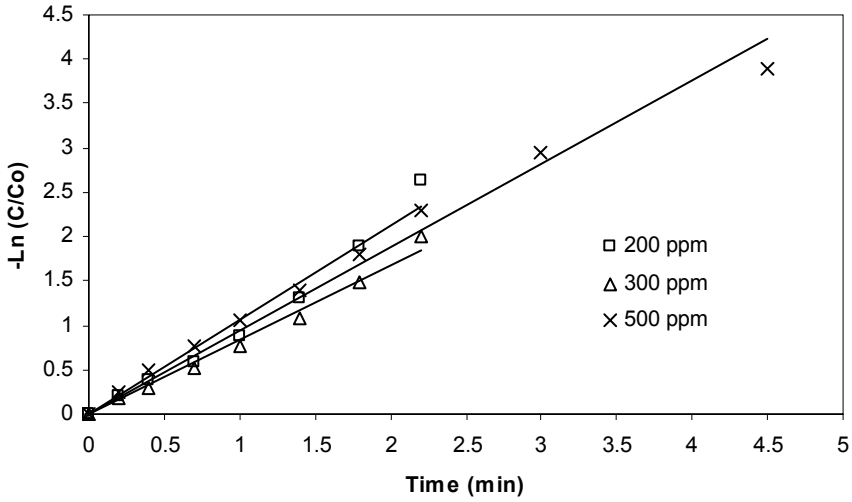


Figure 4-10 - Neperian logarithm of the relative concentration vs. time

Table 4-2 – Kinetic constant for the direct attack of ozone on the 4-CP molecule.

[4-CP]	$-r_A(s^{-1})$	pH
200 to 500 mg L^{-1}	$9.7 \cdot 10^{-2} \pm 4.5 \cdot 10^{-3}$	3

4.2 Mineralization assessment of quaternary ammonium compounds by ozonation and photo-Fenton process

The second part of this work deals with the mineralization of quaternary ammonium compounds by means of ozonation and photo-Fenton process. These compounds belong to the group of cationic surfactants, which are present in formulations of diverse personal care products (PCPs). Nevertheless, few works aiming the removal of cationic surfactants, especially those dealing with the treatment by ozonation or/and advanced oxidation process, could be found in literature.

The ozonation of cationic surfactants entails some experimental problems. Thus, along with experimental results, a discussion about experimentation is given. As an attempt to propose an alternative method to mineralize QACs, photo-Fenton runs were carried out.

4.2.1 Detailed experimental procedure

In order to assess the mineralization of the quaternary ammonium compounds in aqueous phase by ozonation, 16-BAC (Benzyl-dimethyl-hexadecylammonium-chloride), 18-BAC (Benzyl-dimethyl-stearylammonium-chloride) solutions (both with 97 % of purity) (Figure 4-11) were ozonated and samples were withdrawn at known intervals of time. The QACs solutions were prepared with distilled water and stirred during 12 hour to achieve the total QACs dissolution. The concentrations of all the aqueous solutions were in the vicinity of 50 mg L^{-1} in TOC. For ozonation experiments, in order to avoid foam formation during the gas bubbling, 3 drops of antifoam (in 1-L of solutions) were added. The concentration of the antifoam was similar to the surfactant concentration. A TOC measurement of a blank antifoam solution was performed to certify that its addition did not interfere on TOC measurements.

4.2.1.1 Ozonation runs

Ozonation experiments were carried out in a 1.2-L reactor with a continuous supply of O_2/O_3 mixture. 1-L of QACs solutions were charged into the reactor and the O_2/O_3 was continuously bubbled in. The ozone was generated from pure O_2 by means of a Sander Labor Ozonator which was set to produce 5.44 and 7.57 g O_3 h^{-1} with a flow

rate of 400 L h^{-1}. Experiments were performed in batch operation mode using a stirred reactor and the temperature was 25 ºC. Total organic carbon (TOC) and pH were measured along the reaction. The reactions were carried out at room temperature and without pH adjustment.

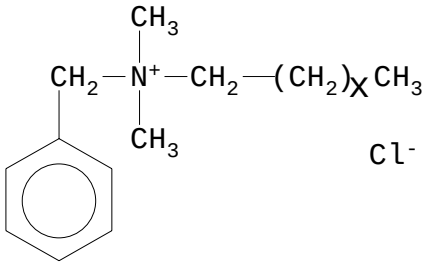


Figure 4-11 - Structure of QACs, where, x = 16 (18-BAC) and 14 (16-BAC).

4.2.1.2 Photo-Fenton runs

The photo-Fenton reactions were carried out in a 2-L glass round bottom reactor with an immersion UV lamp (Heraeus TQ 150, 230 V, 50 Hz middle-pressure) emitting from 190 up to 600 nm through a quartz glass. Experiments were performed in batch operation mode using a stirred reactor and the temperature was 25 ºC. From the lamp spectra, the photon flux to reactor (wavelength lesser than 400 nm) was estimated to be 25 μEinstein s^{-1}. For the experiments with simulated solar light, a solar box equipped with a Xe lamp Philips XOF-15-OF (λ > 235 nm) of 1000 W was used. The quartz reactor was a cylinder providing a length of 26 cm with an inner diameter of 2.1 cm and outer diameter of 2.5 cm. The reactor volume is 90 cm^3 and was connected to a 1.5-L vessel containing the 1-L aqueous surfactant solution which was continuously recycled to the solar box. Through a uranyl oxalate actinometry, a photon flux with wavelength lower than 400 nm of 0.454 μEisnteins s^{-1} (Rodriguez et al., 2005) was obtained. The experimental devices are presented in previous work (Canton et al., 2003).

4.2.2 Mineralization by ozonation

To carry out the ozonation of QACs, the gas ozone-containing was bubbled into a QACs solution at two different ozone flow rate (5.44 and 7.57 g h^{-1}). Samples were

withdrawn at known intervals of time and TOC was analyzed. The results for ozone experiments showed that after one and a half hours of ozonation, only a partial TOC removal could be achieved (between 25 and 50%). Figure 4-12 shows the final TOC removal for both surfactants tested. According to the results, the two compounds showed a similar behaviour in front of ozonation and, as expected, the TOC removal increased with the ozone dose. Nevertheless, only a 50% of TOC removal could be reached after 90 min of ozonation. In addition the compound 18-BAC seemed to be more reactive towards the ozone. The pH of the ozonation experiments was kept in a range between 5 and 6 along the runs.

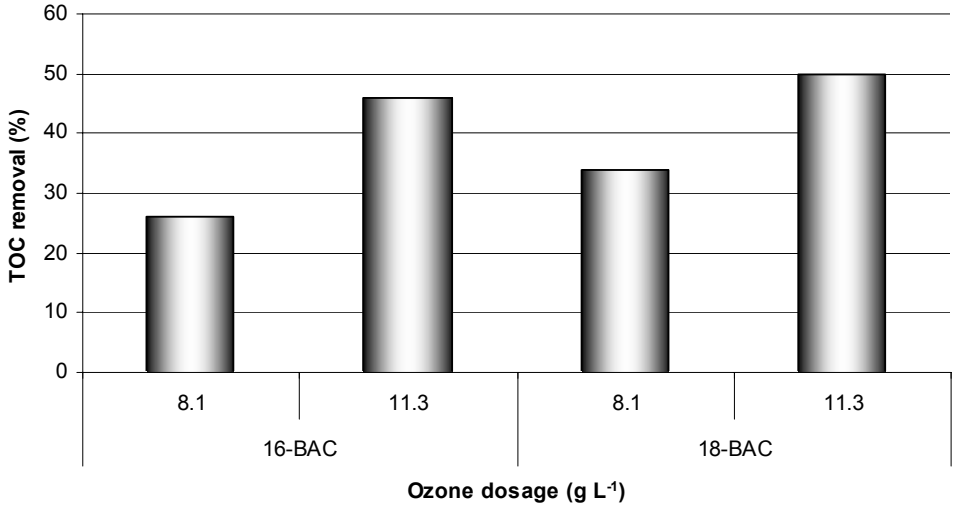


Figure 4-12 - TOC removal of 16 and 18-BAC after 90 minutes of ozonation.

It is important to mention that according to the literature, the ozone has an influence in the dissolution of surfactants (Brambilla et al., 1997). Consequently, on one hand intermediates react with ozone promoting its mineralization, and on the other hand non-dissolved molecules, which are at the surface of the solution, may dissolve by the presence of ozone. Thus, the presence of ozone in the medium may increase the 18-BAC solubility and therefore promotes the increment of its reaction rate.

As the ozone has a direct influence on the QACs water solubility, TOC measurements were affected by the oscillation in the solubility of both compounds. Due

to the great oscillation of the TOC measurements and to make the results more comprehensible, only the final TOC is presented, instead of mineralization profile curves.

In order to better observe the organic matter oxidation in the course of the QACs ozonation, COD measurement were carried out. In Figure 4-13 the oxidation of the organic matter is represented by the COD removal along the reaction time. According to the graphic, the surfactants are oxidised along the reaction time. However, after 90 minutes of reaction the highest COD removal value was around 27 %, reached during 18-BAC solution ozonation. These results confirms the higher reactivity with ozone showed by the 18-BAC.

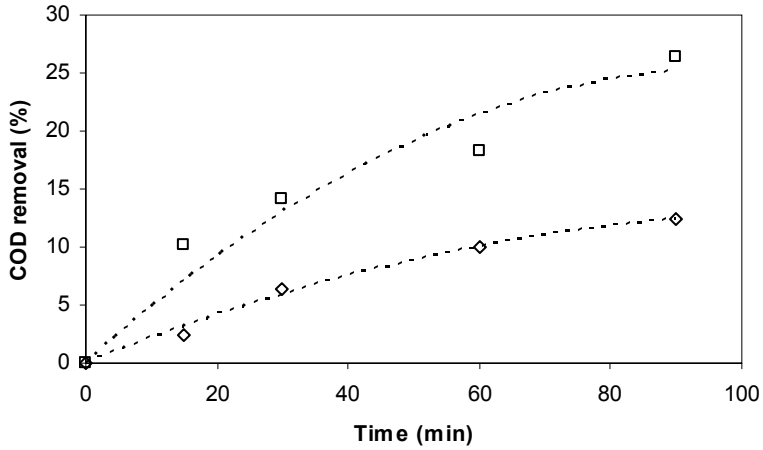


Figure 4-13 – COD removal vs. time for the ozonation of 50 mg L^{-1} (in TOC) solution of (□)18 and (◊)16-BAC. Ozone flow rate 5.44 g h^{-1}.

The influence of QACs initial concentration was studied. For this purpose, 10, 20 and 50 mg L^{-1} BAC solution were ozonated and the TOC of the sample was measured along the ozonation time. Figure 4-14 shows a run where a 16-BAC solution was ozonated during 90 minutes. Firstly, the data recorded shows that the initial TOC concentration of the surfactant untreated solution was lower than 10 mg L^{-1}. This fact supposes that some molecules of surfactant are not dissolved. Besides 90 minutes of ozonation was not capable to achieve TOC concentration below the initial value measured for the raw solution. The increment of the TOC measurements observed in the graphic could be attributed to the dissolution of the non-dissolved surfactant molecules by the ozone effect.

An important fact to remark is that when low QACs concentrations were ozonated at the used condition, TOC measurements did not allow the proper monitory of the organic matter oxidation. Ozonation of solution with TOC concentration below 20 mg L^{-1} had the TOC measurements highly disturbed, thus presenting a constant increment of TOC and even COD measurements along the ozonation time. The pH of the solution remained constant during the reaction time.

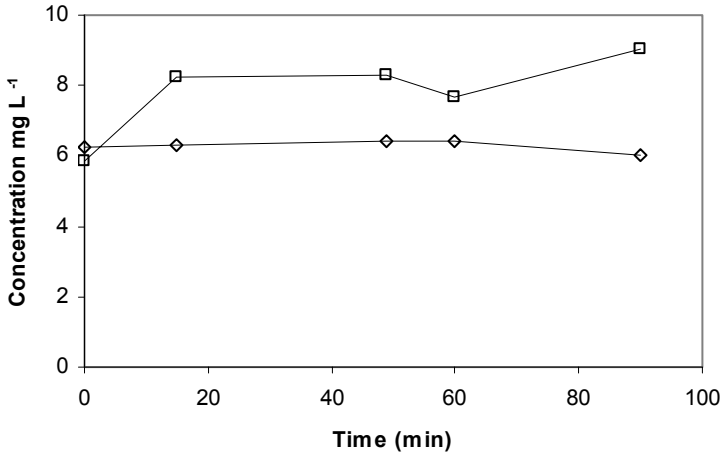


Figure 4-14 – Ozonation of 10 mg L^{-1} (in TOC) 16-BAC solution. pH = ◊; 16-BAC concentration = □. Ozone flow rate of 5.44 g h^{-1}.

Due to experimentation problems observed during the QACs ozonation, such as foam formation and disturbs on the analytical measurements (e.g. fluctuation in TOC measurements), photo-Fenton runs were carried out as an attempt to propose a alternative method to mineralize water contaminated with QACs.

4.2.3 Mineralization by photo-Fenton

Photo-Fenton experiments were carried out with a Fe^{3+} concentration fixed to 20 mg L^{-1}. Different initial concentrations of H_2O_2 were tested, which represented molar ratios of 1/4, 1/2 and 1 of the theoretical stoichiometric amount needed to remove all the TOC present in the solutions. In a course of the photo-Fenton oxidation, in order to follow the mineralization of QACs, the TOC of the samples was analyzed.

Experimental results showed that ninety minutes of photo-Fenton treatment were able to achieve a high QACs mineralization, reaching values up to 85 % when the stoichiometric hydrogen peroxide concentration was used (Figure 4-15). It is important to mention that the compound 16-BAC presented a higher mineralization rate than 18-BAC for the half and stoichiometric H_2O_2 concentrations (Figure 4-16). Regarding the structure of the two studied compounds, the difference between the TOC removal rates could be explained by their water solubility. Since the compound 16-BAC presents in its aliphatic carbon chain two carbons less than 18-BAC, it is expected a higher water solubility, consequently with the increment of the reaction rate with the dissolved reactants.

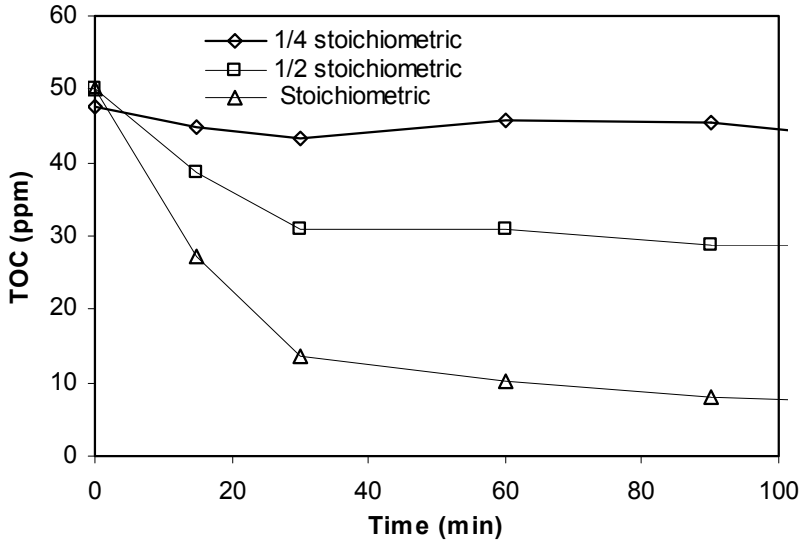


Figure 4-15 - Mineralization of 16-BAC solutions by photo-Fenton process at different H_2O_2 concentration (initial pH = 6, [Fe] = 20 mg L^{-1}, T = 25 ºC).

Figure 4-15 presents the mineralization profile of the compound 16-BAC at different hydrogen peroxide concentration. From this graphic, it could be observed that the TOC removal profile of the runs performed with a H_2O_2 concentration below the stoichiometric value shows that a major removal occurs whitin the first 30 minutes of treatment. After this period of time, TOC values remains practically at the same level until the end of the reaction. The analysis of the H_2O_2 concentration carried out by iodometry showed that for the experiments with stoichiometric hydrogen peroxide concentration, 90 minutes of reaction were needed to consume all the H_2O_2. Nevertheless, in the experiments performed with 1/4 and 1/2 of stoichiometric H_2O_2 concentration, the

hydrogen peroxide was consumed at 10 and 30 minutes, respectively. In this case, as the absence of H_2O_2 determines the end of the photo-Fenton reaction, the small extent of mineralization could be attributed to the insufficient H_2O_2 concentration. Thus, it could be stated that since this point the present compounds are only under the effect of photo-degradation. That, in the present study did not promote important changes on the TOC values during the remaining reaction time.

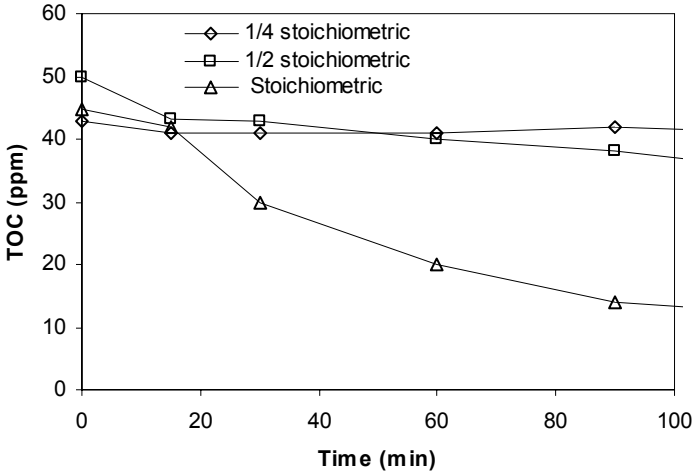


Figure 4-16 - Mineralization of 18-BAC solutions by photo-Fenton process at different H_2O_2 concentration (initial pH = 6, [Fe] = 20 mg L^{-1}, T = 25 ºC).

With reference to the pH evolution, the analysis showed that in the first minutes of oxidation, all photo-Fenton runs presented a decrease of pH, standing in a range between 3 and 4 (Figure 4-17). A remarkable fact is that along the photo-Fenton oxidation when the pH reached values near 4, a precipitate of $Fe(OH)_3$ was formed. It is possible that the formation of this precipitate disturbed the absorption of UV light by the surfactants molecules. Oxidation reduction potential (ORP) measurements were performed to confirm the oxidation of the compounds during the reaction. A change of ORP with the time confirms that a major oxidation of the compounds was observed mainly in the first 30 minutes of treatment (Figure 4-18). At the example shown in Figure 4-18, the ORP decrease observed after 30 minutes of reaction could be related with the decrease of ·OH concentration.

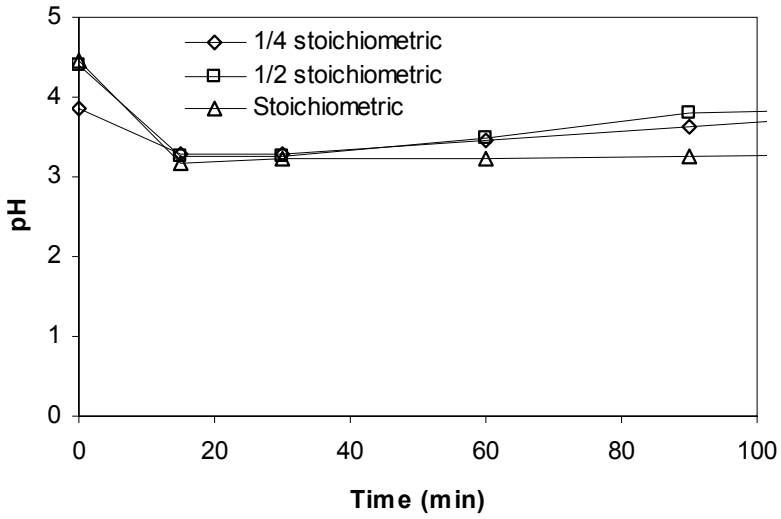


Figure 4-17 - PH evolution during mineralization of 16-BAC by photo-Fenton with UV lamp

Results from photo-Fenton process with Xe lamp showed a lower mineralization of QACs in contrast with the use of the UV lamp. Figure 4-19 presents the final TOC removal of photo-Fenton runs carried out with two lamps along with different hydrogen peroxide concentration. For experiments with Xe lamp, the highest final TOC removal (achieved after 90 minutes of treatment) was at most about 42%. In this case, there was a low difference between the mineralization with stoichiometric and half stoichiometric H_2O_2 concentration. The lower influence of hydrogen peroxide concentration on TOC removal could indicate that the xenon lamp causes a lower H_2O_2 photolysis than the UV lamp. On the other hand, when UV lamp was used, it was observed a high increment of mineralization with the increase of H_2O_2. As for the UV lamp, the compound 16-BAC presented a higher mineralization degree at the end of the treatment. The pH of the experiments with the Xe lamp remained in a range around four in the course of the reaction and it was not observed important difference between the pH evolutions for the two lamps.

It is important to state that the QACs concentration used in this work (ozonation and photo-Fenton process) was below the critical micellar concentration (Bereket and Yurt, 2002). After this point, disturbances in analytical measurements could be present (Salaguer and Fernández, 2004). Because of the difficult QACs quantification by HPLC at the concentration used, only TOC was used as degradation parameter. In any case, the

experiments were repeated many times due to fluctuation observed on TOC measurements to ensure reproducibility in the tests.

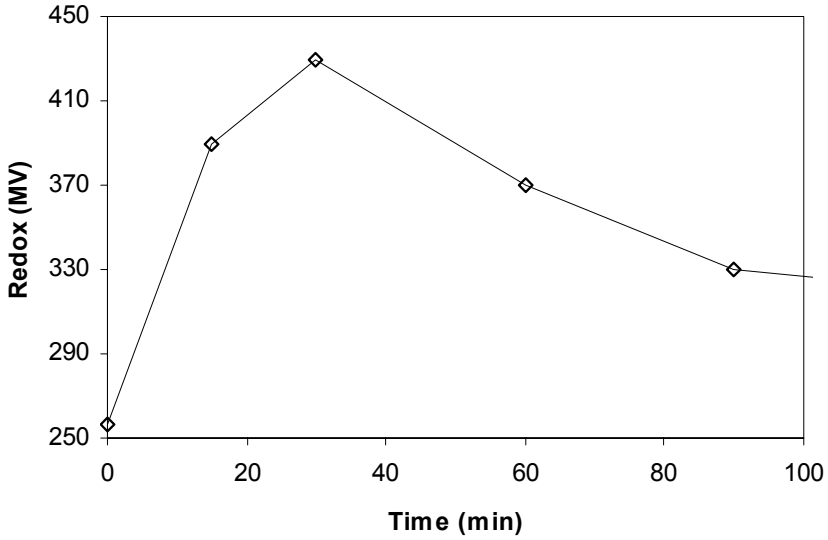


Figure 4-18 - ORP evolution during mineralization of 16-BAC by photo-Fenton (UV lamp) with 1/2 stoichiometric H_2O_2 concentration.

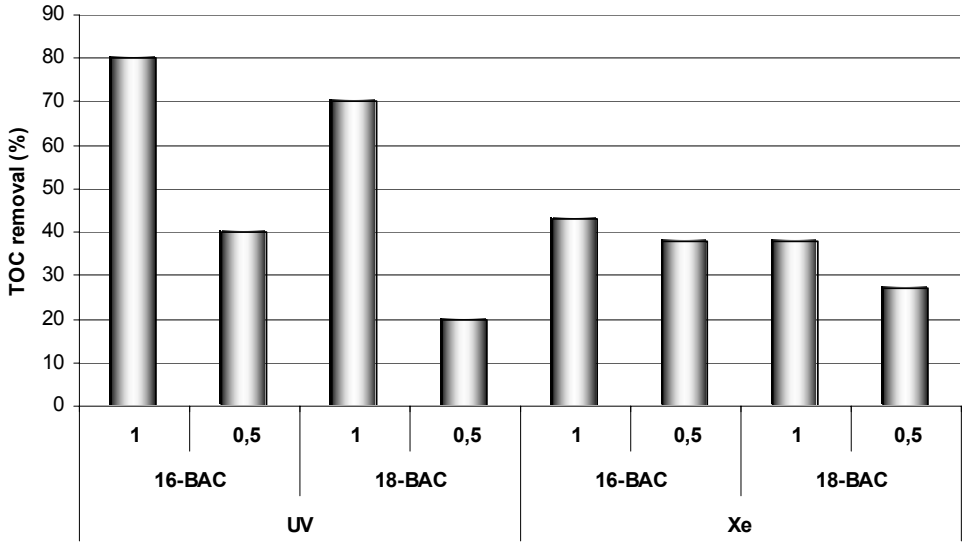


Figure 4-19 - TOC removal after 90 minutes of photo-Fenton treatment with different ratio H_2O_2/surfactant (mol/mol).

4.3 Ozonation of sulfamethoxazole

The ozonation of the pharmaceuticals sulfamethoxazole and bezafibrate constitute the most important parts of this work. In the following sections, the ozonation study is presented in a more accurate form and a complete assessment of the products is attempted.

Due to its large use in the treatment of diverse infections in both humans and animals, the sulfamethoxazole is one of the most used drugs. Recently, its presence in environment produced a great concern about its identification and treatment. This part of the work presents results of the degradation and mineralization of water contaminated with sulfamethoxazole as well as the biodegradability and toxicity assessment of the formed products.

4.3.1 Detailed experimental procedure

The ozonation of sulfamethoxazole (SMX) was carried out in a 1.2-L reactor with a continuous supply of O_3 (2.04 g h^{-1}). SMX solutions containing 200 mg L^{-1} were charged into the reactor. For experiments carried out at fixed pH, SMX solutions were buffered by the addition of adequate quantities of Na_2HPO_4, H_3PO4 and KH_2PO_4. To avoid the interference of the radical pathway on the SMX ozonation, some runs were performed in presence of t-butanol. Ozonation experiments lasted one hour, and during this period of time samples were withdrawn from the reactor and quickly analyzed. Total Organic Carbon (TOC) was analyzed by means of a Shimadzu 5055 TOC analyzer. The concentration of the SMX was quantified by means of a high performance liquid chromatography (HPLC) supplied by Waters Corporation (Massachusetts, USA). The column used was a TR-016059 supplied by Tecknokroma S. Coop. C. Ltd (Barcelona, Spain) with a length of 250 mm and an inner diameter of 4.6 mm. The mobile phase used was a mixture of acetonitrile and millipore water at a 40:60 volume ratio, acidified at pH 3 by the addition of phosphoric acid. The wavelength used in the UV detector was 270 nm. To determine the mass of intermediates during ozonation, an Agilent 6890 HPLC coupled with a Delta Plus Finnigan MAT Mass Spectrophotometer was used. To follow the biodegradability of the samples, the biological oxygen demand (BOD_5) (by means of an Oxitop system, Standard method, 5210 D) and the chemical oxygen demand (COD) (Standard method, 5220 D) analysis were carried out. The ratio BOD_5/COD has been chosen as biodegradability indicator. The acute toxicity test was carried out in the

Microtox® M500 toxicity analyzer according to the standard procedure for the basic test (Azur Environmental, Delaware, USA). Where the samples were diluted and put in contact with a diluent solution containing the bioluminescent bacteria *Vibrio Fischeri* . Subsequently, the inhibition of the light emission was measured and the data recorded was used to calculate the EC_{50}. The contact time used was 15 minutes.

4.3.2 Sulfamethoxazole abatement and TOC removal

Figure 4-20 shows the ozonation profile of a 200 mg L^{-1} SMX solution at free pH during one hour of reaction. According to the degradation profile, an ozone dosage of 0.4 g L^{-1} (15 minutes of reaction) was enough to achieve almost a complete SMX abatement (up to 98.6 %). After this period of time, the antibiotic removal rate becomes lower due to the low SMX concentration available in the medium to react with the ozone. From 20 minutes of ozonation (0.5 g L^{-1} of ozone dose), the SMX concentration was lower than 1 mg L^{-1}. Taking into account the moles of ozone needed to remove 95.5 % of the SMX present in the solution (10 minutes of ozonation = 0.26 g L^{-1} of O_3 dose), a stoichiometric coefficient of approximately 2 moles O_3 / mol SMX was calculated. At the end of the ozonation time (60 minutes) only an 18 % of TOC was removed, indicating that a high ozone dosage should be used for achieving a complete mineralization in a reasonable reaction time. This fact supposes that ozonation presents a high efficiency to remove SMX but not to mineralize the by-products produced along the reaction.

4.3.3 Biodegradability and toxicity of intermediates

One viable alternative to reduce the ozonation cost would be the combination with biological treatment. Thus, to verify the biodegradability of intermediates in the course of ozonation, the BOD_5 was measured along the ozonation time. In the Figure 4-21, the data recorded from the BOD test during the reaction is presented along with COD measurements. Thus, the ratio BOD_5/COD at different ozonation times was calculated. The analysis carried out all along the run showed that after 60 minutes of ozonation (1.5 g L^{-1} of ozone dose) the biodegradability increases up to values near 0.3 indicating a good conversion of the antibiotic to biodegradable products (Figure 4-20).

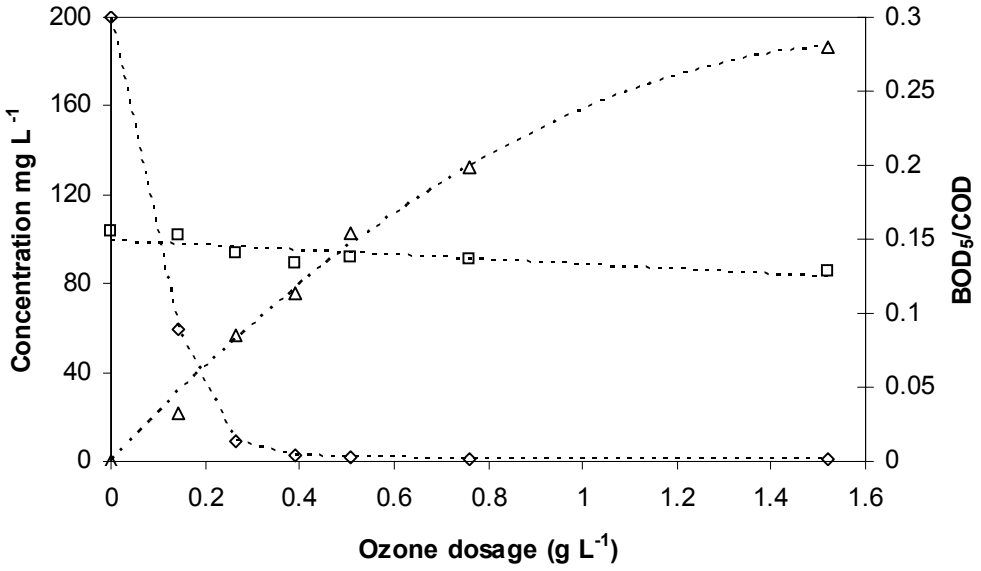


Figure 4-20 - Ozonation of sulfamethoxazole. ◊ = SMX concentration; □ = TOC concentration; Δ = ratio BOD_5/COD. 20 °C and pH no adjusted.

In order to assess the acute toxicity in natural media caused by intermediates produced during the SMX ozonation, Microtox® test was carried out. The obtained data was used to calculate the EC_{50}, which is the percentage of sample dilution (v/v) that causes a 50 % reduction in bacteria bioluminescence (Chen and Que-Hee, 1995; Guzzella et al., 1996). In Figure 4-22, the variation of the EC_{50} with time for the ozonation of a SMX solution is presented and compared with the biodegradability profile. Since lower EC_{50} value implies more inhibition to the bacteria (Neng-Chou et al., 2006), the toxicity profile showed that in the first 30 minutes of reaction the ozonation of SMX induces the formation of intermediates with higher acute toxicity than the SMX untreated solution. After this point, the formation of secondary intermediates promotes an EC_{50} increment to values near the initial value. However, the biodegradability indicator increases constantly along the ozonation time. Thus, it could be stated that the ozonation of SMX produces more biodegradable byproducts that will facilitate the organic matter biodegradation in a wastewater treatment plant. Nevertheless, short ozonation times could induce an increment of the acute toxicity for some organisms. The discrepancy between the biodegradability indicator and the acute toxicity profile could reside in the

sensibility of the microorganisms used in the cited tests. While the bacteria used in the microtox basic test (Vibrio fischeri) are sensitive marine bacteria, the seed used to carry out the BOD tests are a community of microorganisms, which are supposed to be much more adaptable and resistant to different substrates. This fact along with the difference in the contact time used in these tests, 15 minutes for microtox and 5 days for the BOD could let to different bacteria responses in terms of inhibition.

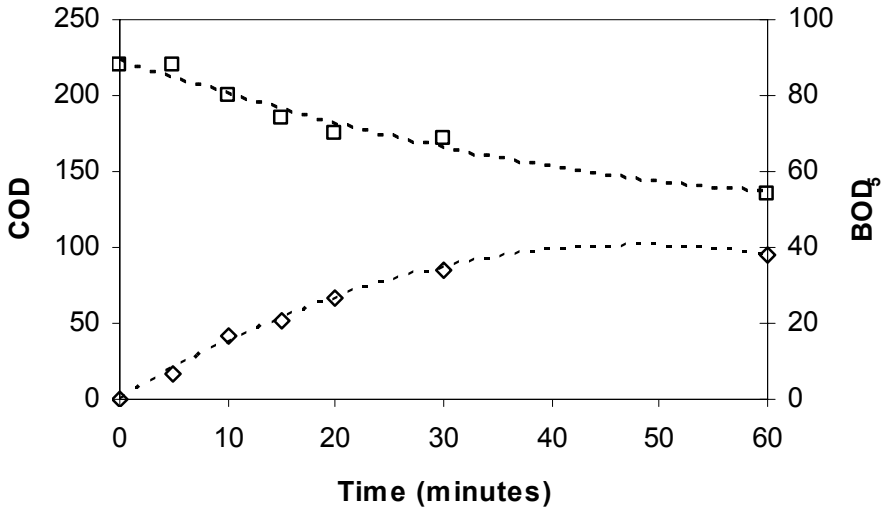


Figure 4-21 - Ozonation of sulfamethoxazole. ◊ = BOD_5 (mg O_2 L^{-1}); □ = COD (mg O_2 L^{-1}). 20 °C and pH no adjusted.

4.3.4 Understanding the ozone reaction with sulfamethoxazole

It is well known that compounds presenting in their structures double bonds and aromatic rings readily react with ozone (Bailey, 1978). In Figure 4-23, the molecular structure of sulfamethoxazole is presented with its dissociation pathway (pKa1 = 1.8; pKa2 = 5.57) (Ching-Erh et al., 1997). Observing the structure of the SMX, the possible reaction centers that are more susceptible to ozone electrophilic attack can be deduced. The amino group seems to be the primary site where ozone attack can be expected. However, the pH of the medium has an important role on the mechanism of reaction. At pH lower than the pKa1 value (1.8) the nitrogen of the amino group is in a protonated

form, which is less susceptible to ozone attack. On the other hand, at pH > 3.8 the non protonated amine is the predominant species. When the pH reaches values higher than the second pKa, the dissociation of the hydrogen present in the sulfonamide group promotes a slight increment of the SMX reactivity.

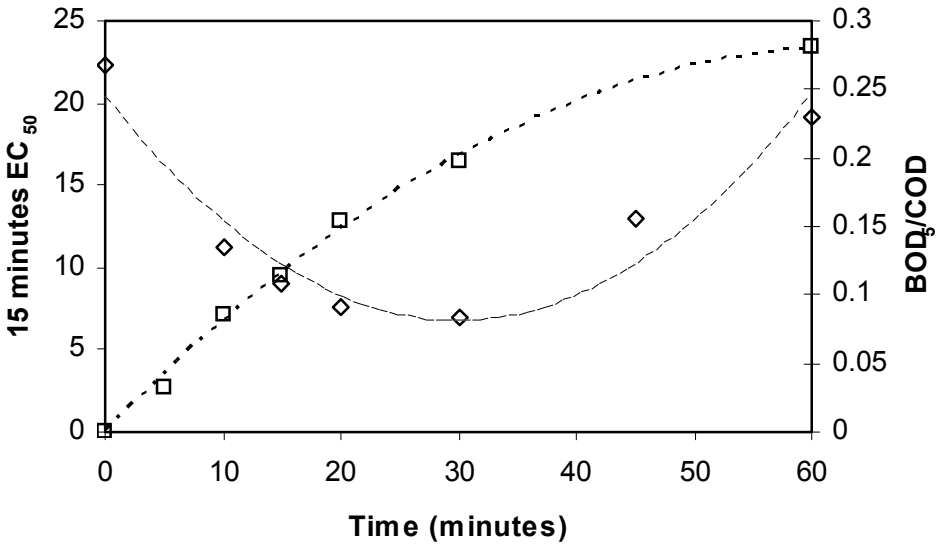


Figure 4-22 - Biodegradability and toxicity evolution for the SMX ozonation. □ = Ratio BOD_5/COD; ◊ = 15 minutes EC_{50}. 20 °C and pH no adjusted.

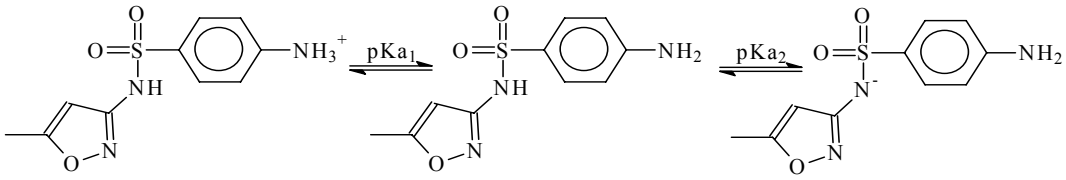


Figure 4-23 - Structure of Sulfamethoxazole and its dissociation pathway.

In order to better understand the reaction mechanism of the SMX ozonation, the by-products identification by means of a HPLC-MS was attempted. From the obtained chromatograms, four mass peaks were detected (I = 283, II = 271, III = 227 and IV = 196

m/z). The mass peaks 271 (+18) and the 283 (+30) could indicate a possible hydroxylation of the aromatic amino group and/or aromatic ring. The structure of the product ions with a mass of 227 (-26) and 196 (-57) m/z could not be identified with only the use of HPLC-MS. However, it is possible that these fragments are originated by the cleavage of the aromatic ring. The final products of SMX ozonation that are supposed to be compounds like organic acids, aldehydes and ketones with low molecular weight could not be identified by the used method.

The oxidation degree of the formed intermediates was also determined by means of the average oxidation state (AOS), which is a very useful parameter for estimating the oxidation degree of mixed solutions and gives indirect information on its probability of biodegradation. This value was calculated using COD and TOC measurements through the following equation (Scott and Ollis, 1995):

$$AOS = \frac{4(TOC - COD)}{TOC}$$ **equation 4-5**

where TOC and COD are expressed in mmol of C L^{-1} and mmol of O_2 L^{-1}, respectively. AOS takes values between 4 for CO_2, the most oxidized state of carbon, and −4 for CH_4, the most reduced state of carbon.

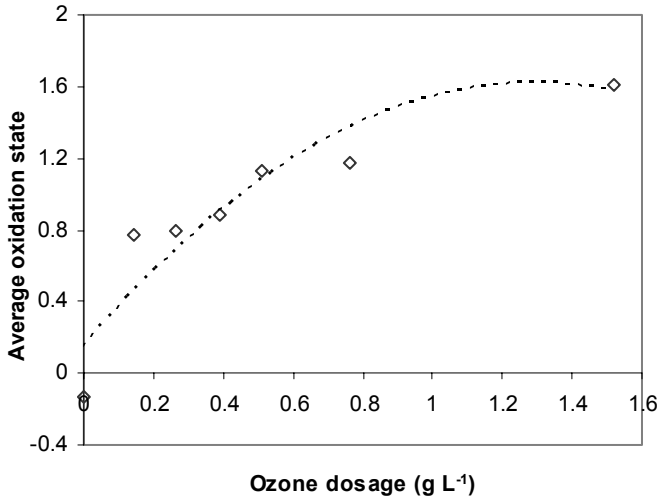


Figure 4-24 – Average oxidation state measurements during the ozonation of a 200 mg L^{-1} SMX solution. 20 ^{0}C and pH no adjusted.

From the AOS profile showed in Figure 4-24, it can be stated that in the early stage of ozonation the SMX undergo a fast oxidation. An increment of the AOS from -0.1 of the raw solution up to 0.8 was promptly achieved with an ozone dose of 0.15 g L^{-1} (5 minutes of ozonation). In the remaining reaction time, the ozonation was able to reach values in the vicinity of 1.6, indicating that all the aromatic and unsaturated intermediates were converted to saturated compounds such as short chains acids (Contretas et al, 2003). Since hydroxylation and cleavage of aromatic rings are associated with biodegradability increment showed by waters contaminated with organic compounds, the increase of AOS is in agreement with those results related to SMX removal and biodegradability improvement previously shown.

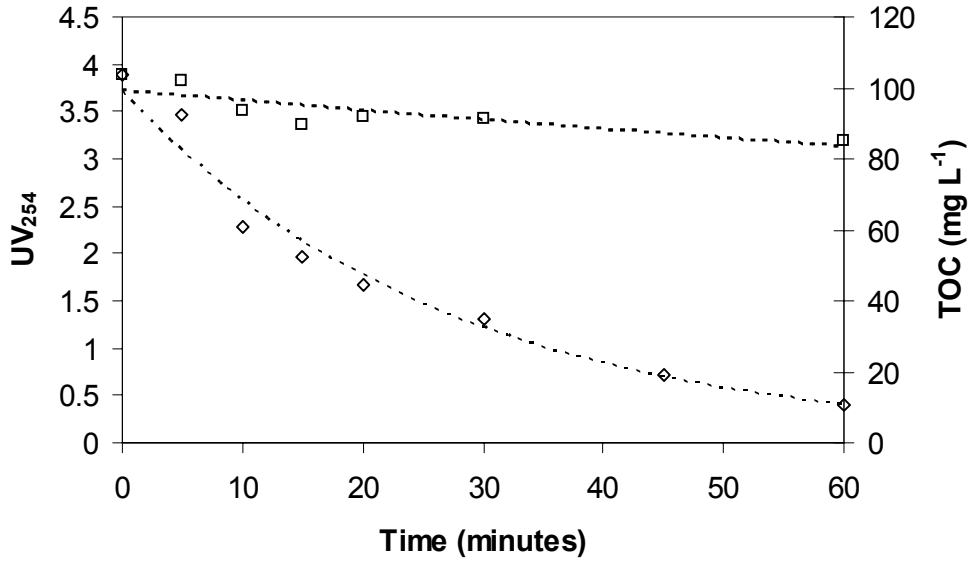


Figure 4-25 - UV_{254} absorbance (◊) and TOC (□) vs. time for the ozonation of SMX. 20 °C and pH no adjusted

In order to follow qualitatively the content of aromatic intermediates along the reaction, the UV_{254} absorbance, representing the aromatic content of wastewater (Ravikumar and Gurol, 1994) was determined. In Figure 4-25 the UV_{254} absorbance is plotted against time along with the TOC for a run carried out with a 200 mg L^{-1} SMX solution without pH adjustment. The decrease of absorbance with time indicates that ozonation reduces considerable the quantity of aromatic intermediates in the medium, achieving values higher than 80 % of UV_{254} absorbance removal. However, it is evident

that only a low percentage of TOC was removed at the end of 60 minutes of reaction (18 %). These results show that at the end of ozonation time a high quantity of organic compounds was still present. Nevertheless, those compounds have a small aromatic character. An important fact to remark is that since the aromatic content is directly related to the presence of toxic and/or non-biodegradable compounds, its reduction is in agreement with the increment of biodegradability previously shown.

4.3.5 pH and temperature influence on the mechanism of ozonation

To study the pH influence on the ozonation of SMX, runs with 1 L of 200 mg L^{-1} SMX solution buffered with adequate quantities of Na_2HPO_4 and K_2HPO_4 in presence and absence of hydroxyl radical scavenger t-butanol were carried out. Table 4-3 presents the data recorded during the runs performed. TOC, COD and UV_{254} absorbance removals are the values at the end of 60 min of ozonation (1.5 g h^{-1} of O_3 flow rate).

Table 4-3 - Data recorded after 60 minutes of SMX ozonation at different pH.

pH	t-butanol	TOC removal (%)	COD removal (%)	UV_{254} removal (%)
3	-	10	48	78
7	-	25	63	86
11	-	31	79	84
3	+	-	-	79
7	+	-	-	79
11	+	-	-	82
free	-	18	40	81

The runs carried out in absence of t-butanol showed similar trend of TOC and COD removals, increasing with the pH. This fact can be explained by the formation of hydroxyl radicals, which are more powerful than ozone to oxidize a wide range of organic and inorganic compounds and besides react in a non-selectively way (Staehelin and

Hoigné, 1982). Experiments in presence of t-butanol had TOC and COD measurements disturbed by the presence of carbons proceeding from the t-butanol. Both experiments in absence and in presence of t-butanol achieved a high UV_{254} removal, although no major changes with the increment of the pH were observed.

Ozonation at different temperatures (10, 20 and 30 ^{o}C) in absence of t-butanol and without pH adjustment were also carried out. Nevertheless, the temperature variation did not show any changes in the degradation behaviour (results not shown).

4.3.6 Determination of the kinetic constant

To calculate the kinetic constant of the SMX ozonation, buffered solutions containing both Fumaric Acid (FA) and SMX in concentration of 0.5 mmoles L^{-1} were ozonated and their concentrations were followed with time. In Figure 4-26, an example of a run is presented. The runs were carried out at pH 5 and 7 in presence of t-butanol and each run was performed three times to ensure reproducibility. The method applied is based on the comparison between the degradation rate of SMX and that of a reference compound, which in this case was the fumaric acid.

Considering that the kinetic of both SMX and FA follow the equations:

$$\frac{d[SMX]}{dt} = -k_{SMX} \cdot [O_3] \cdot [SMX] \qquad \textbf{equation 4-6}$$

$$\frac{d[FA]}{dt} = -k_{FA} \cdot [O_3] \cdot [FA] \qquad \textbf{equation 4-7}$$

Dividing equation 4-7 by equation 4-6 and solving the resulting integration, the equation 4-8 is obtained.

$$\ln \frac{[FA]}{[FA]_0} = -\frac{k_{FA}}{k_{SMX}} . \ln \frac{[SMX]}{[SMX]_0} \qquad \textbf{equation 4-8}$$

To calculate the ratio k_{FA}/k_{SMX} the neperian logarithm of the normalized concentration of both compounds was plotted thus obtaining a straight line (Figure 4-27). As the k_{FA} for the studied pH values are known from the literature (Hoigné and Bader, 1983; Bembelkacem et al., 2004), the kSMX can be calculated.

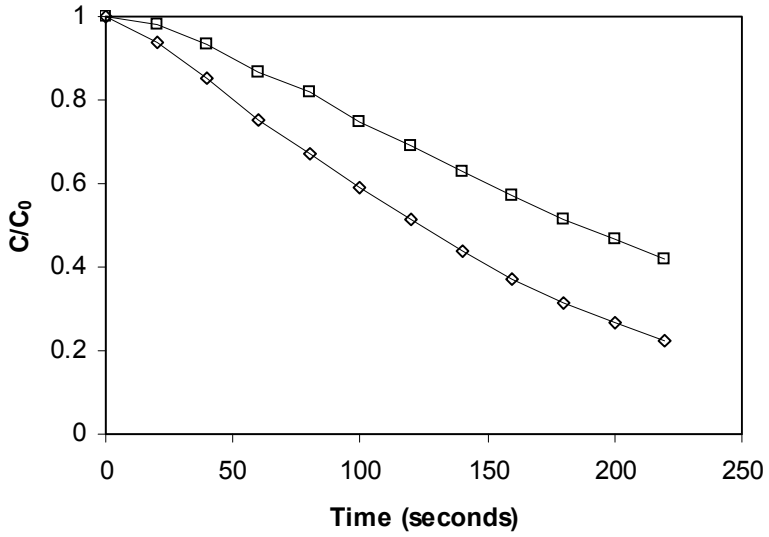


Figure 4-26 - Ozonation of SMX 0.5 mmol L^{-1} + FA 0.5 mmol L^{-1}. 20 ^{o}C, I = 0.1 M, pH = 5. □ = FA; ◊ = SMX.

In the Table 4-4, calculated values of k_{SMX} are presented along with the values of the ratio k_{FA}/k_{SMX} recorded from the experimental data and the k_{FA} found in literature.

A slight increase of the kinetic constants values was observed when the pH passes from 5.0 to 7.0, which can be attributed to the dissociation degree of the SMX molecule. At pH 5 the sulfonamide group is in a protonated form which consequently may reduces the reactivity of the molecule. At pH values higher about two unites than the pKa2 (5.57) practically all the SMX molecules are present in a complete dissociated form, what gives higher reactivity to the structure.

Table 4-4 - Calculated values of k_{SMX} (L mol^{-1} s^{-1}). T = 25 ^{0}C, I = 0.1 M.

pH	Ratio K_{FA}/k_{SMX}	K_{FA} - Hoignè and Bader, 1983	K_{FA} - Benbelkacem et al., 2004	k_{SMX}
5.0	0.57(±0.005)	$1 \cdot 10^5$	-	$1.8 \cdot 10^5$
7.0	0.34(±0.005)	-	$1.5 \cdot 10^5$	$4.4 \cdot 10^5$

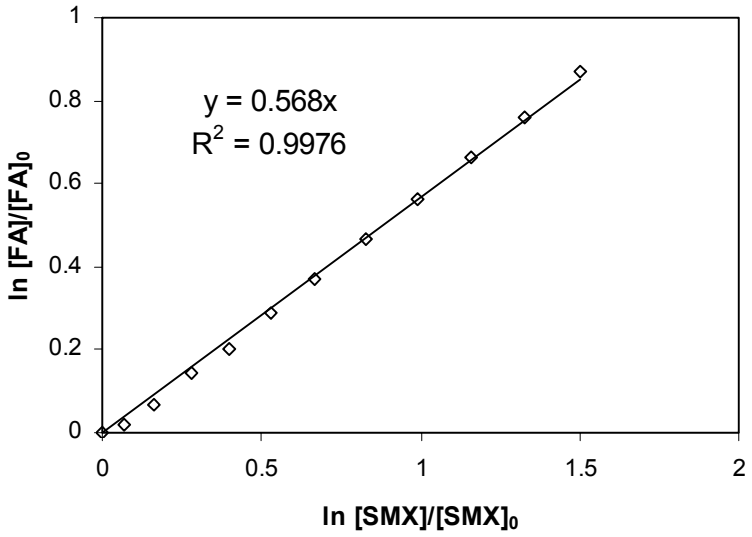


Figure 4-27 - Neperian logarithm of the normalized concentration of FA and SMX. 20 oC, I = 0.1 M, pH = 5.

4.4 Ozonation of Bezafibrate

The last section of this thesis deals with the ozonation of bezafibrate, which is a lipid regulator largely used for cholesterol and triglycerides control. An extended discussion about the degradation and mineralization of bezafibrate solutions is given along with an explanation about its ozonation pathway. In addition, the structures of the intermediates formed in the first stage of ozonation are also proposed.

4.4.1 Detailed experimental procedure

Ozonation experiments were carried out in a 0.8 L reactor with a continuous supply of ozone gas stream (Andreozzi et al., 1992). Ozone was generated by means of a Fischer 502 Ozonator using oxygen as a feeding gas. The gaseous outlet from the reactor is led to an ozone decomposer, for destroying the residual ozone on a proper decomposition catalyst. The aqueous solutions contaminated with an initial BZF concentration ranging from 0.2 to 0.5 mmoles L^{-1} were charged into the reactor, where an ozonized gaseous mixture with an ozone concentration of 1 mmoles L^{-1} was bubbled in. The gas flow rate was kept at 0.38 L min^{-1}. Samples were withdrawn at fixed reaction times and quickly analyzed. For the experiments carried out at fixed pH, BZF solutions were buffered by the addition of adequate quantities of Na_2HPO_4, Na_3PO_4 and KH_2PO_4. For kinetic runs, the ionic strength (I) of the solutions was adjusted at 0.1 moles L^{-1} by addition of phosphate salts. The pH range chosen to perform the runs was from 6.0 to 8.0 (measured by an Orion 960 pH meter with a glass pH electrode). No runs at pH lower than 6.0 could be carried out because of the low solubility of BZF at acidic conditions (21 mmol L^{-1} for pH 6.0; 0.27 mmol L^{-1} for pH 4.0 at 25 °C). The data used to calculate the kinetic constants came from samples withdrawn during the initial stages of reaction.

To prevent the intervention of radical mechanisms, some experiments using t-butanol as scavenger were performed. All the chemicals used were supplied by Aldrich (Italy). Total organic carbon (TOC) measurements were performed by means of a Shimadzu 5000 A TOC analyzer. The concentration of the BZF was quantified by means of a high performance liquid chromatograph (HPLC) from Hewlett Packard (mod. 1090 II) equipped with a Synergy Polar 4RP column and a UV–VIS detector (λ = 200 nm). The eluent was a 60:40 buffered solution (H_2O:CH_3OH:H_3PO_4 500:25:2):CH_3CN with a flow rate of 1.5 mL min^{-1}. The LC-MS analyses were performed by means of an HPLC-MS Agilent 1100 equipped with a Synergi Polar 4RP column. Chromatographic conditions: a

mixture of 75% formic acid (0.1% by volume) and 25% acetonitrile, flow rate 0.7 ml min^{-1}. The mass-spectrometric detection was performed on MSD Quad VL (Agilent Mass Spectrometer) equipped with electrospray ionization. MS data were acquired in ESI mode (capillary temperature 350 °C; source voltage 3.5 kV, drying N_2 gas flow 11 l/min). The collision energy to produce the desired quantity of [M+H]+ (positive mode) or [M-H]- (negative mode) molecular ion was individually optimized.

The biodegradability and acute toxicity of raw and ozonated BZF solutions was tested. To follow the biodegradability of the samples, the Biological Oxygen Demand (BOD_5) (Standard method, 5210 D) and the Chemical Oxygen Demand (COD) (Standard method, 5220 D) were carried out. The bacteria used to perform the BOD test came from BOD-seed capsules supplied by Cole-Parmer Instrument Company (USA) and the ratio BOD_5/COD has been used as a biodegradability indicator.

The acute toxicity test was carried out with a Microtox® M500 toxicity analyser, using Vibrio fischeri strains, according to the manufacturer procedure (Azur Environmental, Delaware, USA). The basic Microtox® test is based on measuring light emission from the bacteria when exposed to a sample dilutions series of 45.00, 22.5, 11.25 and 5.62 %. The diluting solution was supplied by Azur Environmental and the dilutions were performed to a total volume of 1 mL. Results are expressed as $EC_{50,15min.}$, which represents the percentage of initial solution dilution (% v/v) that causes 50% reduction of bacteria bioluminescence in 15 minutes. The Microtox® test was operated in duplicate.

4.4.2 Bezafibrate removal

A simple analysis of the structure of bezafibrate molecule indicates the presence of different possible centers of reaction represented by the two aromatic rings (Figure 4-28) (Bailey, 1982).

At a first sight the chlorine-containing ring can be supposed to be characterised by a lower reactivity with respect to the unchlorinated one due to the electron withdrawing effect of chlorine itself. Figure 4-29 shows the data collected during an experiment in which a solution containing a 0.5 mmoles L^{-1} of BZF was submitted to ozonation at pH=6.0. For a reaction time of about 10 minutes a complete disappearance of the substrate was recorded, with a degree of mineralization of only 20% and about 73% of initial chlorine content released into the solution as chloride ions. The continuous ozone feeding to the reactor for reaction times longer than 10 minutes up to 105 minutes

allowed achieving mineralization degrees not higher than 30%. On the other hand, an increase of the concentration of chloride ions in the solution was observed for reaction times longer than 10 minutes with a final value of about 0.5 mmoles l^{-1}, corresponding to 100% of initial chlorine content in the molecule.

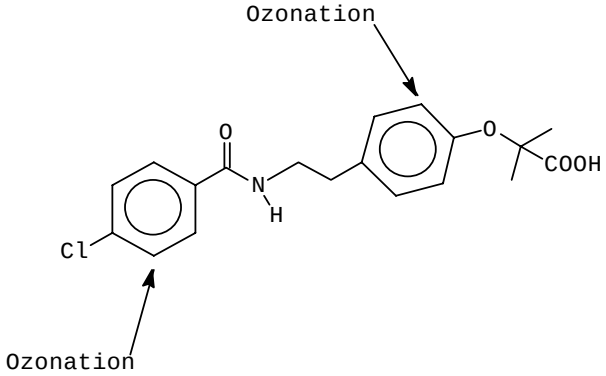


Figure 4-28 - Possible centers of reaction for ozone attacks

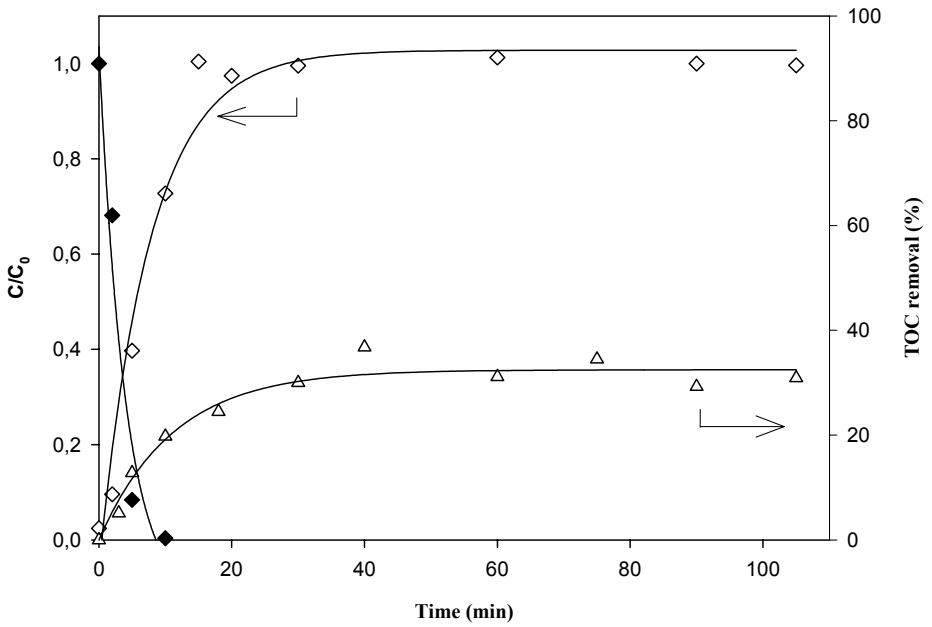


Figure 4-29 Ozonation of bezafibrate, T = 25 °C pH=6.0; ◆ = BZF concentration; ◇ = Chloride release; △ = TOC removal.

4.4.3 Identification of chemical intermediates

To throw light on the reaction mechanism through which ozone attacks BZF, HPLC-MS analyses were carried out on the reaction samples collected at different reaction times.

In Figure 4-30 the chromatogram recorded during the HPLC-MS analysis on the sample collected at 5 minutes of ozonation is reported. Unfortunately the sole HPLC-MS technique does not allow the identification of all the peaks recorded. The peaks for which the identification procedure was successful are indicated with capital letters in the chromatogram and their main fragmentations along with the proposed structures are shown in Table 4-5.

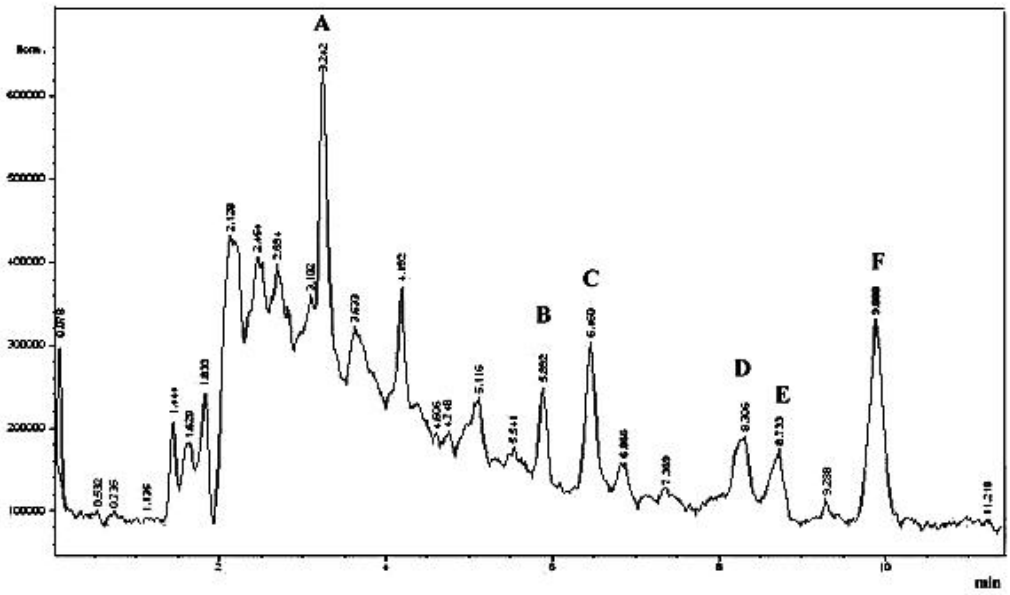
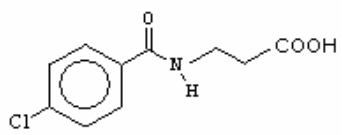
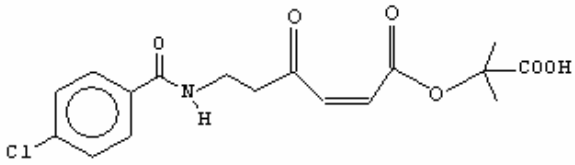
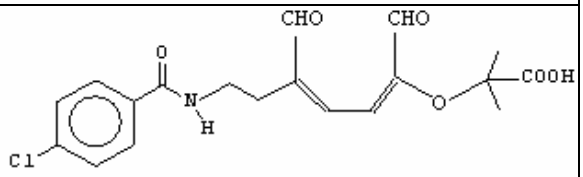
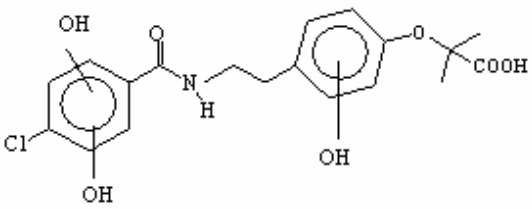
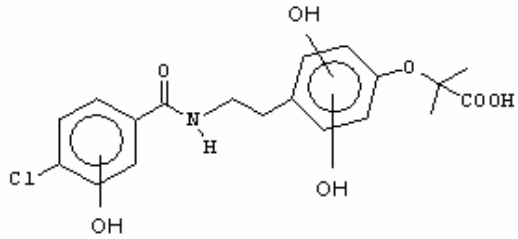


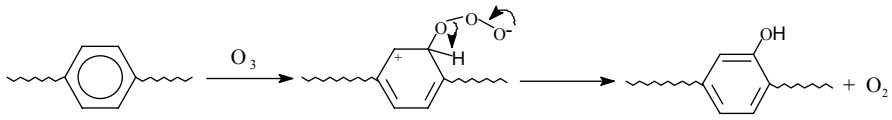
Figure 4-30 - Chromatogram recorded during LC-MS analysis of the sample collected at 5 minutes of ozonation.

The formation of the species whose structures are proposed in Table 4-5 may be justified on the basis of the well-known ozone chemistry. In particular, the formation of all the compounds identified can be explained on the basis of a direct mechanism of ozonation and an anomalous one (Yamamoto et al., 1979).

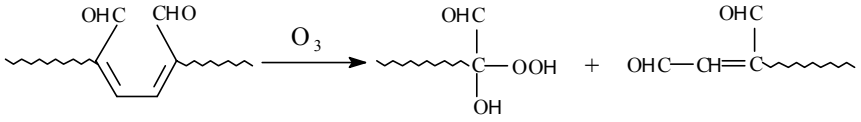
Table 4-5 - Proposed structure for the peaks highlighted in Figure 4-30.

Peak	Tr (min)	m/z	Ionization mode	Proposed Structure (M)
A	3.2	228(M+1), 183, 169, 139, 111.	Positive	
B	5.9	366(M-1), 280, 264, 154.	Negative	
C	6.4	392(M-1), 306,154	Negative	
D	8.3	408(M-1), 322	Negative	
E	8.7	408(M-1), 322	Negative	
F	9.8	360(M-1), 274, 154	Negative	Bezafibrate

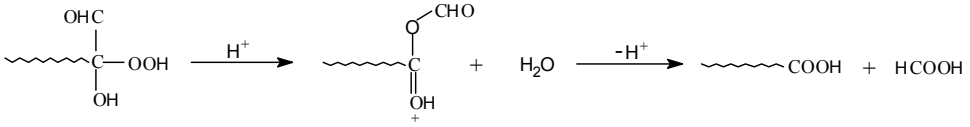
For example, it has been reported (Bailey, 1982) that an ozone attack on the aromatic ring (Figure 4-31, step 1) may result also in a hydroxylation reaction (species d).



(step 1)



(step 2a)



(step 2b)

Figure 4-31 - Direct and anomalous mechanisms of ozonation

The formation of the species “A” may be explained through an anomalous ozonolysis mechanism (Figure 4-31, steps 2a and 2b) of the species “c”.

The presence of the species B and C may be explained on the basis of a direct ozone attack to the unchlorinated aromatic ring. For the species D and E the signals in the mass spectra indicate that these structures differ from that of BZF for three oxygen atoms ([M-1] = 408 m/z for D and E and [M-1] = 360 m/z for BZF). On the basis of the known ozone chemistry it can be put forward that the three oxygen atoms are introduced in the molecules as hydroxyl groups. No conclusive indications have been collected to fix the exact position of these groups. The unavailability of the chemical standards prevented the determination of the concentrations of all the identified species.

4.4.4 Biodegradability and toxicity of intermediates

Since it is well-known that oxidative processes can generate intermediates which are more toxic than the starting species, mainly in the early stage of oxidation, the biodegradability and toxicity of the ozonation intermediates of BZF have been

investigated. Thus BOD_5 and COD were measured during an ozonation run up to 105 minutes. First of all, BOD_5 measurements indicated that a 0.5 mmoles L^{-1} aqueous solution of BZF is not readily biodegradable (BOD_5 = 0). In Figure 4-32 the results obtained on the samples collected during the course of the ozonation are reported along with the ratio BOD_5/COD which continuously increases from 0 up to 0.26 with increasing ozone dose. An increase in the BOD_5/COD ratio indicates an improvement in the biodegradability of the pollutant due to the formation of biochemically more degradable reaction products. A biodegradability ratio over 0.2 indicates a partially biodegradable effluent being 0.4 (Sarria et al., 2002) a threshold value above which the stream can be considered as easily biodegradable. When all BZF was eliminated from the solution (after having dosed 0.73 mmol of ozone), the biodegradability ratio was only 0.15, suggesting the presence in the reacting solution of some not biodegradable intermediates. Therefore it can be stated that longer ozonation times are requested to increase the biodegradability of BZF-containing aqueous solutions.

To assess the acute toxicity of the samples collected during the ozonation runs, the inhibition of the light emission of Vibrio fischeri bacteria caused by the presence of toxic compounds was measured by Microtox® test. In Figure 4-33, the values of $1/EC_{50,15\ min}$ calculated for different preozonated samples are presented. From this figure it can be observed that the acute toxicity of BZF starting solution is relatively low (EC_{50} near 80 %). Acute toxicity response from Microtox® considerably changes when analysing the ozonation products. Since a higher value of $1/EC_{50}$ implies a higher inhibition to the bacteria, a significant increase in toxicity was observed in the early stage of BZF ozonation. Nevertheless, the subsequent intermediates degradation promotes a toxicity reduction which after 105 minutes of ozonation was lower than that of the initial BZF solution.

The Microtox® toxicity trend of preozonated samples is in agreement with the BOD_5/COD results calculated for the same ozonation time. It can be thus concluded that ozonation is a suitable technique to improve the biodegradability and reduce the toxicity of waters containing BZF, although optimal ozone dose needs to be determined according to the effluent composition.

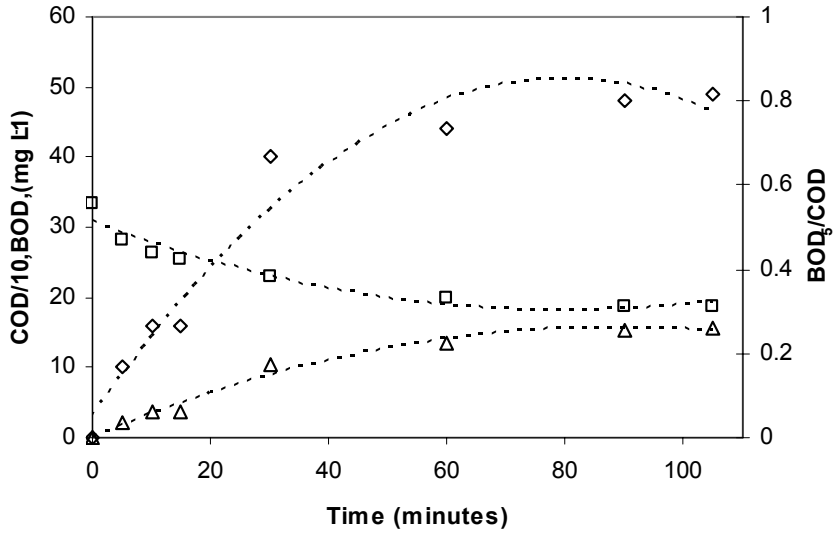


Figure 4-32 - Biodegradability increment during the ozonation of BZF. ◊: BOD_5; □: COD; Δ: BOD_5/COD.

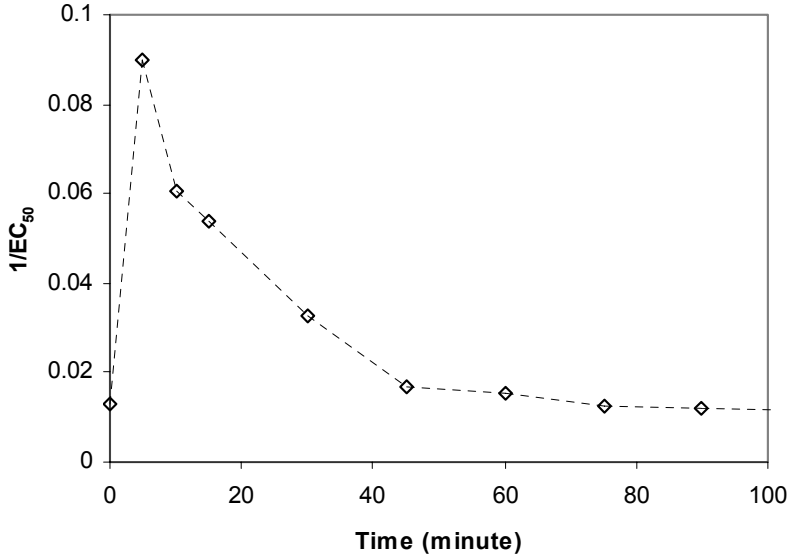


Figure 4-33 - $1/EC_{50,15\ min}$ from Microtox® test vs. time for the BZF ozonation.

4.4.5 Kinetic study

4.4.5.1 Determination of kinetic constants: Absolute method

The ozonation runs were carried out by adding 0.1 mL of a radical scavenger (t-butanol) to the solution (V_L = 800 mL) in order to avoid the influence of radical mechanism (Hoigné and Bader, 1983). BZF solutions were buffered at pH 6.0, 7.0 and 8.0 and the ionic strength adjusted to 0.1 moles L^{-1}. BZF solutions with initial concentrations ranging from 0.2 to 0.5 mmoles L^{-1} were ozonated following the BZF abatement and ozone concentration in the freeboard of the reactor.

To determine the second order kinetic constants for the ozonation of BZF, two methods were carried out. In the first one (absolute method) the data were analyzed by a proper model, which had been developed by coupling fluid-dynamic and chemical sub-models.

By assuming that the ozonation of BZF developed in a quasi-diffusional regime of absorption with reaction, a set of differential mass balance equations for ozone in the two phases (bubble, $[O3]_B$ and freeboard, $[O3]_F$), each considered as a well-mixed stirred reactor and the substrate can be written:

$$\frac{d[O_3]_B}{dt} = \frac{Q}{V_B} \cdot \left([O_3]_{in} - [O_3]_B\right) - \frac{k_L^o a \cdot [O_3]_B \cdot \alpha \cdot E}{V_B} \cdot V_L \qquad \textbf{equation 4-9}$$

$$\frac{d[O_3]_F}{dt} = \frac{Q}{V_F} \cdot \left([O_3]_B - [O_3]_F\right) \qquad \textbf{equation 4-10}$$

$$\frac{d[BZF]}{dt} = -\frac{k_L^o a \cdot [O_3]_B \cdot \alpha \cdot E}{z} \qquad \textbf{equation 4-11}$$

where V_B, V_F are bubble and freeboard volumes respectively and Q the volumetric gas flow rate

The Enhancement factor E was calculated through the following formulas:

$$E \approx \sqrt{1 + Ha^2}$$ **equation 4-12**

where Ha is the dimensionless Hatta's number:

$$Ha = \sqrt{\frac{D_{O3} \cdot z \cdot k_{BZF} \cdot [BZF]_o}{\left(k_L^o\right)^2}}$$ **equation 4-13**

being known for the adopted experimental conditions the mass transfer coefficient kL°, the overall volumetric physical mass-transfer coefficient kL°a in absence of chemical reaction (Andreozzi et al., 2003), the ozone diffusivity D_{O3} (Reid et al., 1983) and Ostwald coefficient α (Andreozzi et al., 1996a).

As previously reported (Andreozzi et al., 1996b, 1999), an overall reaction has been used to describe the oxidation of the substrate which in the present case is:

$$BZF + z\,O_3 \xrightarrow{k_{BZF}} \text{Products}$$ **equation 4-14**

Where z is the stoichiometric coefficient represented as a linear function of the reaction time (z = a + bt).

This model allowed to estimate the best values of kinetic constant k_{O3} and the stoichiometric coefficients "a" and "b" by means of a suitable optimizing procedure in which the minimum of the objective function is found

$$\Phi = \sum_{m=1}^{N_m} \sum_{j=1}^{N_j} \left(Y_{m,j} - C_{m,j}\right)^2$$ **equation 4-15**

where Nm and Nj represent the set of measured species and experimental reaction times respectively, Ym,j, Cm,j indicate calculated and measured m-th component concentrations at the j-th reaction time.

In the Table 4-6 the values calculated for these parameters are shown. The values of kinetic constants show a small increase by raising the pH, although all are of the same order of magnitude.

Table 4-6 - BZF kinetic parameters obtained from experimental runs at different pH values. T = 25 ^{0}C, I = 0.1 M.

pH	6.0	7.0	8.0
$\mathbf{k_{BZF}}$ (L mol^{-1} s^{-1})	$2.66 \cdot 10^3 \pm 0.29 \cdot 10^3$	$4.24 \cdot 10^3 \pm 0.66 \cdot 10^3$	$1.0 \cdot 10^4 \pm 1.07 \cdot 10^3$
a	$1.96 \pm 1.6 \cdot 10^{-2}$	$2.40 \pm 33 \cdot 10^{-2}$	$2.02 \pm 19 \cdot 10^{-2}$
b	0.96 ± 0.20	0.53 ± 0.36	1.53 ± 0.24
σ_S (%)	6.08	7.60	5.81
σ_{O3} (%)	3.76	8.98	8.67

σ_S = Percentage standard deviation for the substrate (BZF).
σ_{O3} = Percentage standard deviation for the ozone in freeboard.

With the aim of validating the results reported above, a second method was used for estimating the kinetic constants of the ozonation of BZF at the three investigated pH values:

4.4.5.2 Determination of kinetic constants: competition method

The competition method is based on the comparison between the degradation rate of BZF and that of a reference compound. Maleic acid (MAL) was chosen as a reference compound since during a literature survey it has been found that it shows kinetic constant values for the ozonation which are very close to those calculated for the BZF by means of the absolute method. From the literature review, four different kinetic constants for maleic acid ozonation were found (Hoigné and Bader, 1983; Prior et al., 1984; Caprio et al., 1987; Benbelkacem et al., 2003).

For each experiment a solution containing both MAL and BZF in concentration of 0.4 mmoles L^{-1} was ozonized and their concentrations were followed with the time. In Figure 4-34 the results of one of these runs are shown.

If one considers that the following equations can be written to describe the degradation of the two species:

$$\frac{d[BZF]}{dt} = -k_{BZF} \cdot [O_3] \cdot [BZF] \qquad \textbf{equation 4-16}$$

$$\frac{d[MAL]}{dt} = -k_{MAL} \cdot [O_3] \cdot [MAL] \qquad \textbf{equation 4-17}$$

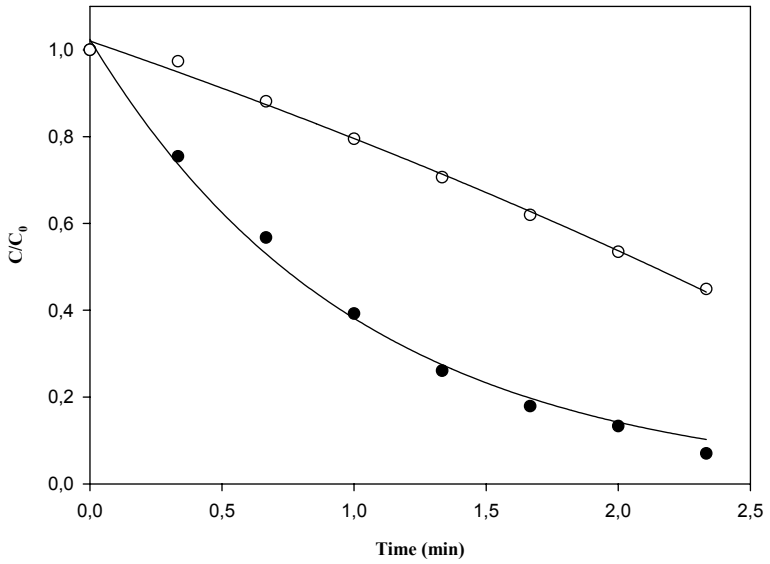


Figure 4-34 - Normalized concentration of BZF (○) and MAL (●) versus time. Buffered at pH = 6.0. T = 25°C, Ionic strength = 0.1 mol L^{-1}.

Dividing equation 4-17 by equation 4-16 and integrating between t=0 and t_R the following relationship is obtained:

$$\ln\frac{[MAL]}{[MAL]_0} = -\frac{k_{MAL}}{k_{BZF}} \cdot \ln\frac{[BZF]}{[BZF]_0} \qquad \textbf{equation 4-18}$$

It is possible to calculate the ratio k_{MAL}/k_{BZF} by plotting the neperian logarithm of the normalized concentration of both compounds one against the other thus obtaining a straight line. As the k_{MAL} is known from the literature, the k_{BZF} can be easily calculated.

Since as previously stated different values can be adopted for the kinetic constant kMAL according the literature (Table 4-7), calculated second order kinetic constants for BZF ozonation are plotted versus pH (Figure 4-35). All the values for kBZF calculated according to literature data reported for MAL are inserted in Figure 8 and connected by dotted lines. It is interesting to note that the values calculated at each pH (Deborde et al., 2005) employing the data for MAL given by Caprio et al., are about 2-3 times higher then those obtained by other researchers. The values obtained by means of the absolute method (full circles) are within the area delimited by dotted lines thus showing a good agreement between the two methods, although it was not possible to carry out a careful

statistical analysis, no uncertanties on the kinetic constant values being given in the original quoted papers.

Table 4-7 - Value adopted for k_{MAL} (L mol^{-1} s^{-1}) according to literature to evaluate k_{BZF}

pH	Ratio k_{MAL}/k_{BZF}	Caprio et al., 1987	Hoignè and Bader, 1983	Benbelkacem et al., 2003	Pryor et al., 1984
6.0	3.4	$1.60 \cdot 10^4$	$5.00 \cdot 10^3$	-	-
7.0	4.2	$2.82 \cdot 10^4$	-	$1.20 \cdot 10^4$	-
8.0	2.3	$3.12 \cdot 10^4$	-	-	$2.40 \cdot 10^4$

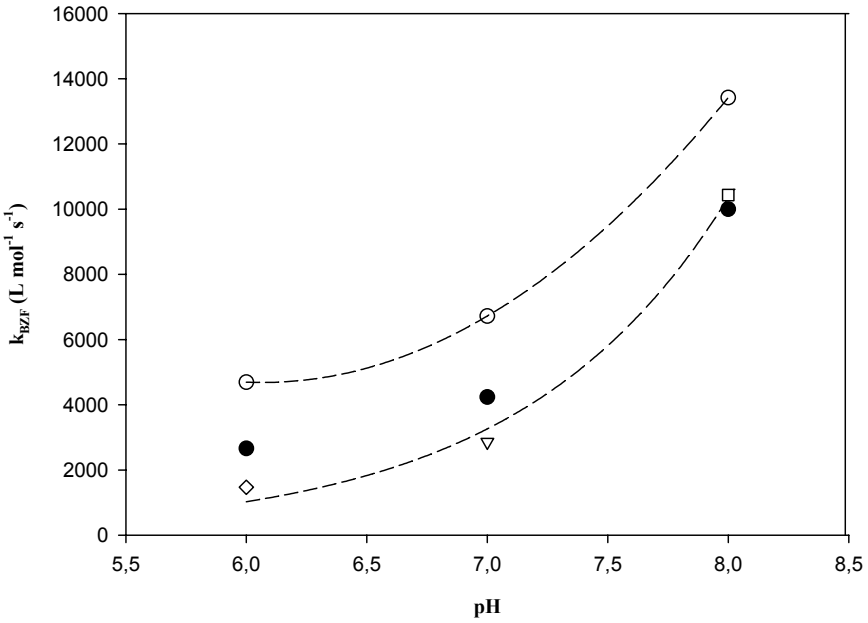


Figure 4-35 - Kinetic constant values for the BZF ozonation versus pH obtained by means of absolute method (●) and calculated using the literature data for maleic acid reported in table 3 (○: Caprio et al., 1987; ◇:Hoignè and Bader, 1983; ▽: Benkelkacem et al., 2003; □: Pryor et al., 2004).

A slight increase of the kinetic constants values presented for both methods when the pH passes from to 6.0 to 8.0 is evident from the diagrams of the Figure 4-35.

Considering that in the studied range of pH all the bezafibrate molecules are dissociated (pKa = 3.29, ACD Software, 2006), the observed increase in the reactivity cannot be ascribed to a change in the dissociation degree when the pH varied from 6.0 to 8.0. A possible explanation may be found in the intervention of the radical mechanism whose occurrence could not be completely prevented by the scavenger addition at increasing the pH.

5 Conclusions

5.1 Coupled ozonation-SBBR to treat 4-chlorophenol

- Ozonation has been proved to be a suitable method to remove 4-CP from water. However, the results showed that a long time of ozonation should be applied to reach high mineralization of byproducts.

- At the used condition, the biodegradability (BOD_5/COD) of the 4-CP solution was increased from 0 to values up to 0.37 by the ozonation. However, the ozone dose is an important factor to determine the level of biodegradability increment of water containing 4-CP.

- Quinone and hydroquinone have been found among intermediates of the 4-CP ozonation. Moreover, their oxidation contributes to the biodegradability increment in the course of the ozonation.

- A kinetic constant of $9.7 \cdot 10^{-2}$ min^{-1} was calculated for the direct attack of the ozone.

- The average of the volatile suspended solids (VSS) in the course of the SBBR cycles was 0.110 g L^{-1}. This low value indicates that the majority of bacteria were attached on the volcanic stones.

- A combination of ozonation-SBBR has proved to be a suitable option to mineralize water containing 4-CP. The method achieved values up to 97 % of TOC removal with the use of 60 minutes of ozonation combined with a subsequent HRT of one day in the SBBR. In addition, the SBBR reactor showed a good recuperation of the bacteria activity after the air and feed absence.

5.2 Quaternary ammonium compounds mineralization in aqueous phase by ozonation and photo-Fenton

- Both ozonation and photo-Fenton were proved to be alternative methods to mineralize quaternary ammonium compounds.

- At the applied conditions, a mineralization of maximum 50% could be achieved with ozonation, compared to about 80% reached by photo-Fenton treatment. In addition, the foam formation during the gas bubbling in ozonation process represents a serious problem for experimentation in ozonation runs.

- The efficiency of the photo-Fenton decreased with the use of a Xe lamp. However, if the objective is to apply the solar radiation, economics aspects must be taken into account.

- The 16-BAC presented higher mineralization when treated by photo-Fenton, while the compound 18-BAC seemed to be more reactive with the ozone. The ozone influence on the QACs solubility play an important role on the mineralization of water containing QACs.

- The critical micellar concentration is an important factor that must be taken into account on the interpretation of mineralization profiles.

5.3 Ozonation of sulfamethoxazole

- Ozonation was proved to be a suitable method to remove sulfamethoxazole antibiotic in water. However, it is stated that a high ozone dosage would be necessary to achieve the complete mineralization of the intermediates.

- From an initial concentration of 200 mg L^{-1}, an increment of the biodegradability indicator (BOD_5/COD) from 0 up to 0.28 with an ozone dose of 2.04 g L^{-1} was observed.

- Regarding the acute toxicity, the trend of the EC_{50} values along the ozonation indicates that the SMX ozonation favor, in the early stages of ozonation (first 30 minutes), the formation of intermediates with higher acute toxicity than the SMX untreated solution. However, at longer ozonation times the acute toxicity increases to a vicinity of the initial value.

- From the biodegradability results shown by the pre-treatment with ozonation, it could be stated that the combination of ozonation with conventional biological treatment would be a suitable option to mineralize water contaminated with sulfamethoxazole, although ozonation pretreatment would not decrease its acute toxicity to natural media with the use of short ozonation time.

- The ozone attack on the SMX molecule probably occurs first on the amino group and aromatic ring, giving byproducts with mass equals to 283, 271, 227 and 196 m/z. However, their structures could not be determined only with the use of the HPLC-MS.

- In absence of t- butanol, TOC and COD removals increased with the pH. However, the aromaticity of the samples did not undergo important variation with pH increment.

- Temperature variation in the range between 10 and 30 ºC had no significant effect on SMX degradation.

- The kinetic constants calculated for the SMX are in an order of magnitude of 10^5 L mol^{-1} s^{-1}. Furthermore, a slight increment of the constant is observed when the pH passes from 5 to 7. This increment could be attributed to the dissociation of the SMX, which became slightly more reactive.

5.4 Ozonation of bezafibrate

- Ozonation has been proven to be an effective method to remove BZF from aqueous solution. Nevertheless, low mineralization degrees have been achieved during the ozonation runs performed. Besides, a chloride release corresponding to the 100% of initial chlorine content in BZF molecule was observed.

- The LC-MS analyses indicated that ozone react mainly with the unchlorinated ring, with respect to chlorinated one, leading to aldehydic and ketonic intermediates. Moreover the presence of some species with three additional

oxygen atoms suggests that hydroxylation mechanisms of both the aromatic rings may also occur.

- A good agreement was observed between the absolute and the competition kinetic method, adopted for the kinetic investigations.

- Second order kinetic constants for the ozone attack to the substrate were found in the range between $2.7 \cdot 10^3$ and $1.0 \cdot 10^4$ L mol^{-1} s^{-1} with absolute method and $1.5 \cdot 10^3$ and $1.3 \cdot 10^4$ L mol^{-1} s^{-1} with competition one.

- The ozonation of BZF-containing aqueous solutions showed a continuous increase of the ratio BOD_5/COD up to a value of 0.26 thus indicating an enhancement of the biodegradability of the pre-ozonated samples.

- The toxicity of these treated solutions determined by means of the Microtox® test changed in a more complex way with an initial increase (in the early ozonation stages) and a successive reduction to values lower than that measured for the starting solution.

6 Recommendations for future works

1. From the set of data obtained in this work, to carry out the coupling ozonation with conventional biological treatments to mineralize the studied pharmaceuticals.

2. To perform the combination ozonation-Biological treatment using the Sequencing Batch Biofilter Reactor (SBBR).

3. To carry out the complete investigation of the quaternary ammonium compounds ozonation in terms of kinetic study and degradation pathway.

4. To apply other toxicity methods in order to better understand the toxicity evolution of byproducts produced along the ozonation of the target pharmaceuticals.

5. To perform the scale up for the ozonation of the target pharmaceuticals.

6. To test the ozonation on the treatment of real samples containing the target compounds.

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DANTAS, Renato Falcão; SANS, Carmen; CONTRERAS, Sandra; ESPLUGAS, Santiago. **Sufamethoxazole abatement by means of ozonation**. Journal of Hazardous Materials, Accepted, 2007.

DANTAS, Renato Falcão; CANTERINO, Marisa; MAROTTA, Raffaele; SANS, Carme; ESPLUGAS, Santiago; ANDREOZZI, Roberto. **Abatement of Bezafibrate by ozonation: primary intermediates, kinetics and toxicity assessment**. Water research (41) 2525-2532.

DANTAS, Renato Falcão; BACARDIT, Jordi; GONZÁLES, Oscar; GARCIAMOLINA, Verónica; CONTRERAS, Sandra; CHAMARO, Esther; SANS, Carme; ESPLUGAS, Santiago. **Comparison of ozonation vs wet peroxide oxidation for the removal of 4-chlorophenol**. in: Ollis, David f.; Al-ekabi, Hussain. (org.).photocatalytic and advanced oxidation processes for the treatment of air, water soil and surfaces. Londres, 2005, p. 294-299.

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9 Resumen en Castellano

9.1 Introducción

De acuerdo con la organización mundial de salud (WHO, 2003), 1,2 mil millones de personas no tienen acceso a agua para sus necesidades domésticas. Además, 2,18 millones de personas mueren por año debido a la ausencia de agua potable, deficiencia sanitaria e inadecuada higiene personal. La mayoría de estas personas son menores de cinco años de edad y otras 82 millones sufren enfermedades relacionadas con un uso inapropiado del agua (Prüss et. al. 2002). Actualmente, hay una gran discusión referente a si el agua es verdaderamente escasa en un sentido físico (un problema de disponibilidad) o si hay disponibilidad pero los recursos deberían ser utilizados de una manera mas conveniente (un problema de demanda) (Rijsberman, 2006).

El aumento de la densidad de las poblaciones juntamente con el aumento de la industrialización produce un estado donde las fuentes de agua dulce, en las cuales las poblaciones confían, se vuelven en situación de estrés (Pickering and Owen, 1997). Al mismo tiempo, juntamente con el exceso de consumo y sequías, la introducción de compuestos peligrosos para la salud humana en acuíferos (polución) es la más seria amenaza para las fuentes de aguas dulces del mundo.

Muchos compuestos clasificados como contaminantes están naturalmente presentes en el medio ambiente, incluso siendo tolerados por organismos. Sin embargo, la acumulación de estos compuestos en una cantidad superior a los límites seguros o efectos aditivos de una serie de contaminantes pueden conllevar impactos ambientales (ejemplo: Contaminación por Nitratos). Por otra parte, muchos contaminantes orgánicos como los pesticidas y los residuos de la industria química son completamente artificiales y no biodegradables. Estos contaminantes pueden acumularse con el tiempo, produciendo problemas de contaminación a largo plazo. Ellos pueden ser absorbidos o removidos por sedimentos y sufrir biodegradación (ej. degradación biológica de las aguas residuales).

Debido a su capacidad de transformar los contaminantes en sustancias inertes en un corto periodo, el ozono ha sido considerado como un agente potencialmente efectivo para tratar aguas residuales contaminadas con nuevos contaminantes. De una manera general, trabajando a pH alcalino la ozonización puede ser incluida dentro del grupo de las tecnologías de oxidaciones avanzadas.

Los procesos de oxidación avanzada (POAs) son definidos como procesos que pueden generar radicales en cantidades capaces de oxidar la mayoría de los compuestos químicos presentes en efluentes acuosos. Entre estos procesos están

incluidos la cavitación (Gonze et al., 1999; Moholkar et al., 1999a; Senthilkumar and Pandit, 1999; Adewuyi, 2001; Gogate and Pandit, 2001; Gogate, 2002), oxidación catalítica (Blake, 1997; Herrmann, 1999; Yawalkar et al., 2001; Bhatkhande et al., 2002), oxidación húmeda (Garcia-Molina, 2007; Poulopoulos et al., 2007) y Fenton (Venkatadri and Peters, 1993; Bigda, 1995, 1996; Nesheiwat and Swanson, 2000; Rodríguez et al., 2002). Los radicales hidroxilo OH· son fuertes agentes oxidantes con un potencial de oxidación de 2.8 V, y además, reaccionan con muchos compuestos orgánicos y inorgánicos exhibiendo velocidades de oxidación mas rápidas que los agentes oxidantes convencionales (Gogate et al., 2002a).

Aunque la ozonización es considerada como una oxidación química, tiene velocidad de oxidación mas baja que los procesos que usan el radical hidroxilo como agente oxidante (Arslan and Balcioglu, 2001a; Gogate et al., 2002a). Sin embargo, los radicales libres son generados cuando el ozono es combinado con peroxido de hidrogeno, UV/Luz solar o ultrasonidos (Weavers et al., 2000; Fung et al., 2000a; Gogate et al., 2002a). Otro factor que debe ser considerado es la descomposición del ozono en agua, que promueve la formación de radicales hidroxilo (OH·). Esta descomposición es catalizada por especies OH^-, siendo el pH del medio una importante variable en la determinación de las constantes cinéticas y en los mecanismos de reacción. Estos dos agentes actúan en el proceso, teniendo distintas relevancias en el mismo. Mientras la desinfección es llevada a cabo únicamente por el ozono molecular, la oxidación se lleva a cabo por ambos agentes (O_3 y HO·).

El ozono es un oxidante selectivo, mientras que el radical OH· es importante para la oxidación de compuestos que presentan resistencia a la oxidación por ozono (Hautaniemi, 2001). Por otro lado, el pH del medio afecta la doble acción del ozono en la materia orgánica. El ozono puede actuar de una forma directa o indirecta (vía radicales libres). Como ya se ha comentado, estos diferentes mecanismos de reacción conllevan a la formación de diferentes intermedios de reacción y son controlados por diferentes modelos cinéticos. A bajo pH, el ozono reacciona principalmente con compuestos que presentan grupos funcionales mediante reacciones selectivas, como adicciones eletrofilicas, nucleofilias o bipolares (ataque directo). Por otra parte, en condiciones alcalinas, el ozono se descompone produciendo radicales hidroxilos, que son fuertes especies oxidantes que reaccionan de una manera no selectiva con un alto número de compuestos orgánicos y inorgánicos (ataque indirecto). Normalmente, bajo condiciones ácidas (pH <4) la reacción directa es la dominante, mientras que en rangos de pH entre 4

y 9 las dos están presentes, y a pH mas altos (pH >9) la reacción indirecta prevalece (Staehelin and Hoigné, 1982).

Cuando la mineralización total de un compuesto no es conseguida, o un largo tiempo de reacción es necesario para la mineralización total, un tratamiento biológico posterior seria conveniente para alcanzar concentraciones de estos compuestos por debajo de los límites aceptables. Numerosos estudios que utilizan la integración de los procesos químicos y biológicos han sido desarrollados para el tratamiento de aguas (Wang et al., 1989; Stowell et al., 1992; Scott and Ollis, 1995, 1997; Amat at al., 2003; Contreras et al., 2003), llegando a obtener mejoras satisfactorias en la biodegradabilidad.

El tratamiento biológico de aguas residuales es generalmente la alternativa más económica comparada con otras opciones de tratamiento. Las características de las aguas residuales, como el pH y la presencia de inhibidores en la matriz pueden ser muy importantes durante un tratamiento biológico. Además, la degradación biológica puede ser afectada por cambios bruscos en las condiciones de tratamiento, por ejemplo, los choques tóxicos que ocurren cuando la concentración toxica en un afluente aumenta. Un choque toxico puede producir un aumento en el tiempo de reacción, disminución de la eficiencia y puede envenenar la biomasa (Buitrón et. al., 2005). Otro factor importante es que aunque muchas moléculas orgánicas pueden ser degradadas mediante los tratamientos biológicos, muchas otras pueden ser recalcitrantes, o sea, resistentes a la biodegradación. De la misma manera, hay distintos tratamientos químicos capaces de destruir una gran variedad de contaminantes orgánicos sintéticos, pero el coste del proceso de oxidación puede generalmente ser el factor limitante para un tratamiento de aguas residuales. Es por eso que una solución viable es la combinación de tratamientos químicos y biológicos como una opción para tratar productos químicos biorecalcitrantes en aguas residuales (Adams at al., 1997).

Hoy en día, la emisión de los “nuevos” o “emergentes” (no regulados) contaminantes se ha vuelto un gran problema ambiental. Entre ellos, aquellos que son usados en largas cantidades a diario, como son los productos farmacéuticos, tensioactivos u otros aditivos industriales (Petrovic et al., 2003).

En este trabajo se estudia el tratamiento de compuestos representativos del género farmacéutico (Sulfametoxazol y Bezafibrato) y de los tensioactivos (compuestos de amonio cuaternario). Ambos tipos de compuestos son usados a gran escala y actualmente son el objetivo de varios estudios ambientales que tienen como finalidad evaluar sus potenciales de peligrosidad para el medioambiente. Además, se ha realizado

un estudio previo sobre la degradación del compuesto 4-clorofenol mediante la combinación ozonización-tratamiento biológico.

9.2 Objetivos

- Estudiar la combinación del proceso de ozonización-SBBR para tratar contaminantes en aguas, utilizando el compuesto 4-clorofenol como modelo;

- Evaluar la aplicación de la ozonización en el tratamiento de los contaminantes emergentes, que son representados en este trabajo por los fármacos y los tensioactivos;

- Examinar la naturaleza de los intermedios de las reacciones de ozonización, así como su biodegradabilidad y toxicidad;

- Usando como base los resultados de ozonización, crear un protocolo que permitan una posterior puesta en marcha de una instalación que combine los procesos de ozonización y tratamiento biológico para tratar aguas contaminadas que contengan QACs, SMX y BZF.

9.3 Procedimiento experimental

Las reacciones de ozonización fueron realizadas en tres instalaciones: un reactor de vidrio cilíndrico con un volumen de 1,2 L, un segundo reactor semejante con un volumen de 0.8 L y una planta piloto con 21 L de capacidad. Los tres sistemas tienen características semejantes en cuanto a funcionamiento.

Para realizar las reacciones de ozonización para tratar los contaminantes estudiados, se ha cargado un volumen adecuado de la solución a tratar en los tres reactores, donde las soluciones han sido agitadas constantemente. Posteriormente, se borboteó una mezcla de ozono y oxígeno continuamente en el reactor. El ozono ha sido producido por medio de un generador de ozono, que en todos los casos utilizaba oxígeno puro como gas de alimentación. Con la finalidad de calcular la cantidad de ozono que ha reaccionado, se ha medido el ozono en la salida del reactor mediante un

medidor de ozono en fase gas. Después de la medición del ozono en la salida, el ozono residual ha sido destruido mediante técnicas adecuadas.

El reactor biológico fue un reactor aerobio "SBBR" ("Sequencing Batch Biofilm Reactor"), donde la biomasa se encontraba adherida a la superficie de las piedras volcánicas contenidas en el reactor. Durante los ciclos, se ha alimentado el reactor con un flujo continuo de oxígeno de 10 L h^{-1}. Los fangos activos del reactor eran los mismos que se usaron en un estudio previo sobre la degradación de soluciones de 4-clorofenol mediante la combinación del proceso foto-Fenton con tratamiento biológico (Bacardit et al., 2005). Las soluciones pretratadas se neutralizaron con soluciones de NaOH y H_3PO_4 y se les añadieron NH_4Cl, $CaCl_2$, $FeCl_3$, y $MgSO_4$ como nutrientes. La temperatura del reactor ha sido mantenida a 25 ^oC mediante un baño termostático. Para cargar el reactor con las soluciones pretratadas durante los ciclos, los flujos de aire y recirculación fueron apagados y el sobrenadante fue extraído del reactor. Seguidamente, el reactor fue alimentado con 1L de la solución pretratada, y a continuación tanto la recirculación como el flujo de aire fueron puestos nuevamente en marcha.

Se ha usado una combinación HPLC-MS con la finalidad de seguir la concentración de los compuestos durante los experimentos e intentar determinar la estructura química de los productos de la ozonización del Sulfametoxazol y del Bezafibrato. Las mediciones del carbono orgánico total y la demanda química de oxigeno han sido realizados con la finalidad de seguir la degradación de la materia orgánica durante la ozonización.

Para seguir la evolución de la biodegradabilidad durante las reacciones de ozonización, la demanda biológica de oxígeno fue analizada en las muestras. El método utilizado ha sido el método respirométrico Oxitop (Standards Methods, 5210 D). La toxicidad de las muestras ha sido medida mediante un Microtox® M500 toxicity analyzer (Azur Environmental, Delaware, USA), y los resultados se han expresado en $EC50_{15\ minutos}$. Para ayudar en la caracterización de los intermedios, se ha medido la absorbancia UV_{245} de las muestras y en algunos casos el estado de oxidación medio.

9.4 Resultados y discusiones

En este trabajo, se ha estudiado la ozonización de compuestos emergentes, representados por fármacos y tensioactivos. Los resultados son presentados primeramente en término de degradación y mineralización de los intermedios. Además,

se han seguido la biodegradabilidad y la toxicidad aguda de los intermedios durante todo el tiempo de ozonización. Como estudio preliminar, fue testada la combinación de la ozonización-SBBR para la eliminación del compuesto modelo 4-clorofenol.

La primera parte de este trabajo tenía la finalidad de evaluar la mineralización de soluciones de 4-CP en concentraciones de 100 y 200 mg L^{-1} mediante el acoplamiento de la ozonización y el tratamiento aerobio mediante un reactor SBBR. Los primeros resultados experimentales demuestran que las dosis de ozono de 5.44 y 7.57 g h^{-1} han sido suficientes para eliminar completamente el 4-CP de la solución. Por otra parte, en el punto donde ocurre la desaparición del 4-CP**,** solamente se produjo un 26 % de eliminación del carbono orgánico total (TOC). Los compuestos Quinona e Hidroquinona fueron identificados como intermedios formados en los primeros minutos de la ozonización. Durante el pretratamiento con ozono se observó un aumento del indicador de biodegradabilidad (BOD_5/COD) de las soluciones desde 0 hasta un rango entre 0.2-0.37 (Figura 1). En el estudio cinético, realizado mediante la aproximación de pseudos-primer orden se ha hallado una constante cinética de $9 \cdot 10^{-2}$ min^{-1} para la reacción directa del ozono con el 4-CP.

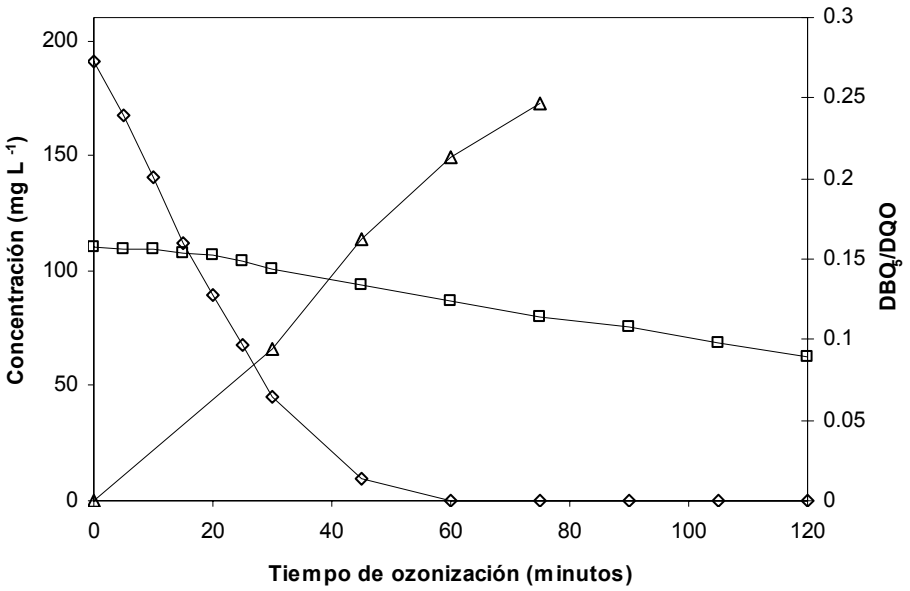

Figura 1 - Ozonización de una solución de 4-CP a 200 mg L^{-1} utilizando una dosis de ozono de 7.57 g h^{-1}.

Después de una evaluación de las diferentes condiciones de ozonización probadas, se ha elegido 60 minutos de ozonización en una solución de 200 mg L^{-1} utilizando una dosis de ozono de 7.57 g h^{-1} como la condición inicial para el proceso de combinación. La combinación de los procesos de ozonización y del tratamiento biológico aerobio mediante un "Sequencing Batch Biofilm Reactor" (SBBR) ha conseguido una eliminación del carbono orgánico total de más de 90 % (Figura 2). Además, el reactor ha demostrado una rápida recuperación después de ser sometido a la ausencia de aire y alimento.

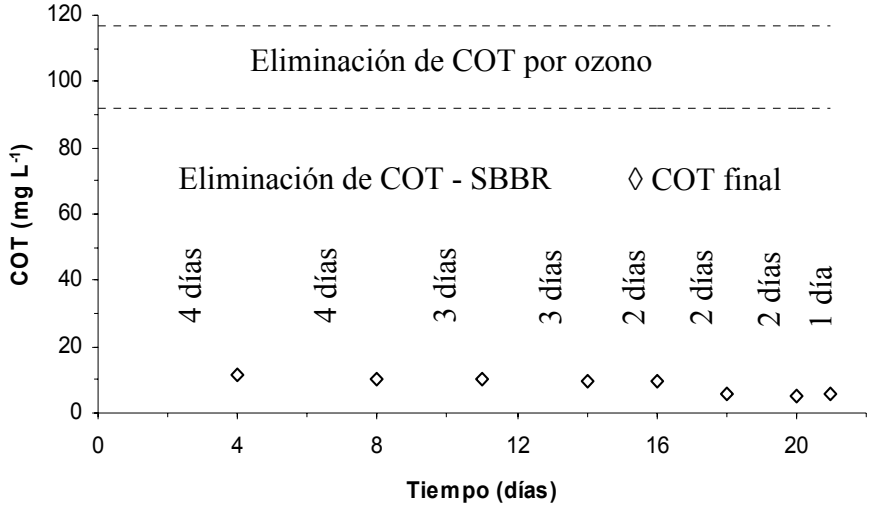

Figura 2 – Eliminación de COT mediante la combinación ozonización-SBBR.

El estudio de la ozonización de los compuestos de amonio cuaternario (tensioactivos) ha sido realizado con el objetivo de evaluar el potencial del proceso de ozonización para mineralizar estos compuestos. Para realizar este estudio, los tensioactivos: 16-BAC (Benzyl-dimethyl-hexadecylammonium-chloride) y 18-BAC (Benzyl-dimethyl-stearylammonium-chloride) fueron ozonizados con distintas dosis de ozono. La eliminación del carbono orgánico total ha sido medida para seguir la mineralización de los intermedios producidos en la ozonización. De acuerdo con los resultados experimentales, después de 90 minutos de ozonización, con una dosis de ozono de 7.57 g h^{-1} el tratamiento de los tensioactivos ha conseguido un valor máximo de 50 % de mineralización (Figura 3).

De acuerdo con la figura 3, el compuesto 18-BAC ha sido el más reactivo con el ozono. Sin embargo, es importante subrayar que de acuerdo con la literatura, el ozono puede afectar a la disolución de los tensioactivos (Brambilla et al., 1997). En estos estudios se observó que por un lado el ozono reacciona con los intermedios de reacción promoviendo su mineralización, mientras que por otra parte, las moléculas no disueltas que se encuentran en la superficie de la solución pueden disolverse en presencia de ozono. Así, la presencia del ozono en el medio puede hacer aumentar la solubilidad del compuesto 18-BAC y entonces promover el aumento de la velocidad de reacción. Debido a la acción del ozono en la solubilidad de los tensioactivos en agua, las medidas de carbono orgánico total han sido afectadas por la variación de la solubilidad de estos compuestos durante el tiempo de reacción. Debido a la gran oscilación de las medidas de COT y para hacer los resultados más comprensibles, solamente la medida final de COT ha sido presentada y no las curvas de mineralización.

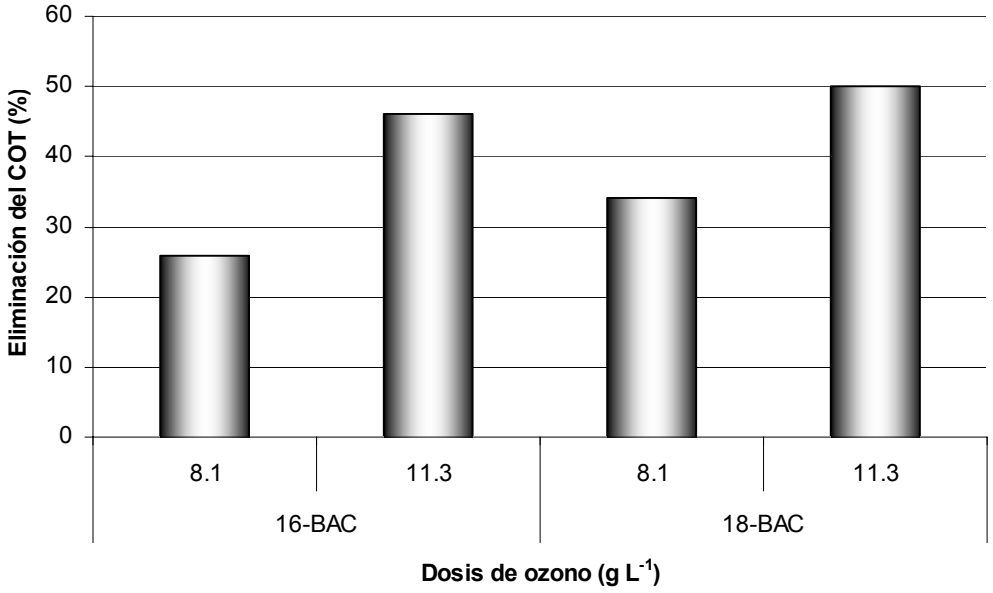

Figura 3 – Eliminación del COT de los compuestos 16 y 18-BAC después de 90 minutos de ozonización.

Con la finalidad de estudiar y comparar la mineralización de los compuestos de amonio cuaternario conseguida por el proceso de ozonización con otro método de oxidación avanzada, se han realizado experimentos de foto-Fenton. De acuerdo con los

resultados experimentales, después de 90 minutos de tratamiento, el proceso foto-Fenton ha obtenido hasta un 80 % de mineralización con el uso de una lámpara UV y con la cantidad estequiométrica de peróxido de hidrógeno. Para verificar la posible utilización de la radiación solar en el proceso de foto-Fenton, algunos experimentos han sido realizados utilizando una lámpara de Xenon. Sin embargo, la eficiencia del proceso en términos de mineralización ha disminuido (Figura 4).

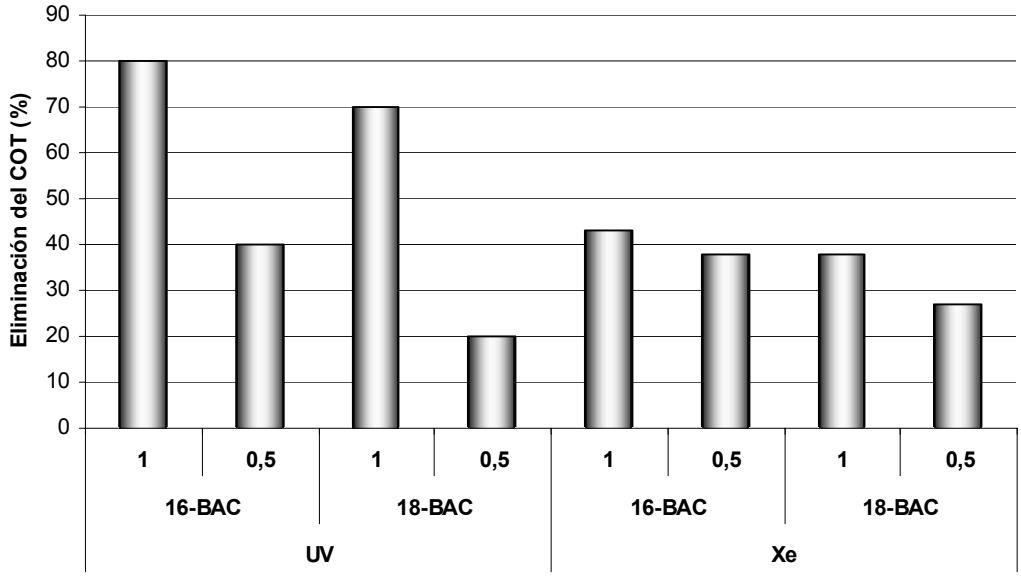

Figura 4 – Eliminación de COT después de 90 minutos de tratamiento con foto-Fenton con diferentes proporciones de H_2O_2/tensioactivo.

El tratamiento de soluciones contaminadas con sulfametoxazol ha sido llevado a cabo con concentraciones de 200 mg L^{-1}. Los resultados han comprobado que la ozonización ha sido un método efectivo para tratar aguas contaminadas con SMX. De acuerdo con la Figura 5, después de 15 minutos de tratamiento (0.4 g de dosis de ozono L^{-1}), la completa eliminación del antibiótico ha sido conseguida, y por otra parte, solamente un 10 % de mineralización ha sido observado en este mismo punto de tratamiento.

Se ha observado un aumento de la biodegradabilidad (aumento del ratio BOD_5/COD) de 0 a 0.28 tras 60 minutos de ozonización. El "Microtox® test" ha sido usado con la finalidad de evaluar la toxicidad aguda en el medio natural de los intermedios de la ozonización de SMX durante el tiempo de reacción. Los resultados de

las pruebas de toxicidad demuestran que en las primeras etapas de ozonización se observa un ligero aumento de la toxicidad aguda. Sin embargo, después de 30 minutos de ozonización, los valores de toxicidad tienden a aumentar hasta un valor cercano al de la solución de SMX sin tratamiento (Figura 6).

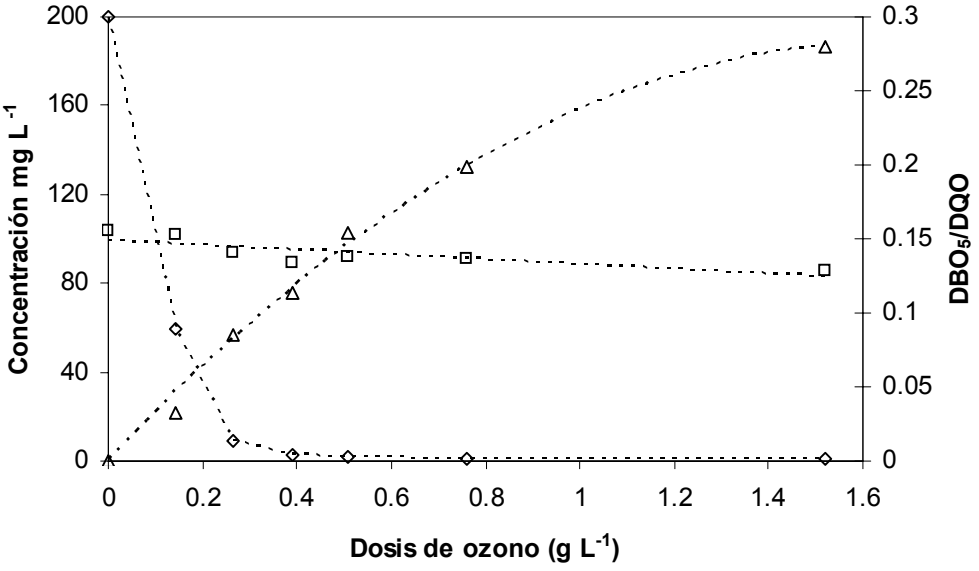

Figure 5 – Ozonización del sulfametoxazol. ◊ = concentración del SMX; □ = COT; Δ = BOD_5/COD. 20 °C y pH no ajustado.

La variación del pH durante la ozonización de SMX ha tenido una gran influencia en la eliminación del COT y de la DQO, promoviendo su incremento con el aumento del carácter alcalino de la solución. El estudio cinético de la degradación de sulfametoxazol se ha llevado a cabo mediante el método comparativo. En este método, la velocidad de degradación del sulfametoxazol ha sido comparada con la del ácido fumárico. Se han determinado constantes cinéticas en el orden de magnitud de 10^5 L mol^{-1} s^{-1} para la ozonización a pH 5 y 7.

La última parte de este trabajo ha consistido en el tratamiento de soluciones contaminadas con el fármaco bezafibrato. De acuerdo con los resultados experimentales obtenidos, como en el caso del SMX, la ozonización ha demostrado ser una opción adecuada para tratar aguas contaminadas con este fármaco. Durante la reacción de ozonización de BZF, se ha observado que 10 minutos de ozonización (0.73 mmoles

L^{-1} de ozono) han sido suficientes para eliminar todo el BZF de la solución. Sin embargo, solamente una pequeña parte del los intermedios ha sido mineralizada (Figura 7).

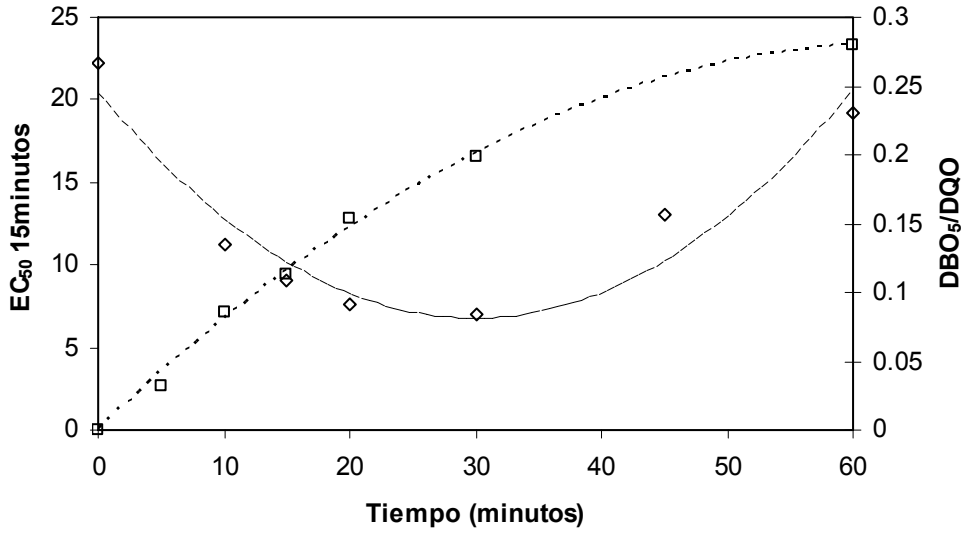

Figura 6 – Evolución de la Biodegradabilidad y de la toxicidad durante la ozonización del SMX. □ = Ratio DBO_5/DQO; ◊ = EC_{50} en 15 minutos. 20 ^oC y pH no ajustado.

El estudio cinético ha sido realizado tanto por método absoluto como por competición, que han sido utilizados con el objetivo de determinar las constantes cinéticas de segundo orden para el ataque directo del ozono en la molécula del Bezafibrato. Los pH estudiados han sido 6, 7 y 8. De acuerdo con los valores obtenidos en los cálculos, las constantes cinéticas determinadas por el método absoluto concuerdan con las obtenidas por el método de competición, siendo los valores calculados del orden de 10^3 y 10^4 L mol^{-1} s^{-1} (Figura 8).

La identificación de los intermedios de la reacción ha sido llevada a cabo mediante la técnica HPLC-MS. De acuerdo con los cromatogramas obtenidos a raiz de esta técnica, se puede afirmar que la oxidación del bezafibrato se desarrolla mediante la hidroxilación de los anillos aromáticos. Con relación a la biodegradabilidad y a la toxicidad de las muestras de diversos tiempos de ozonización, se demuestra que la ozonización es una técnica adecuada para aumentar la biodegradabilidad y reducir la toxicidad de aguas contaminadas con BZF.

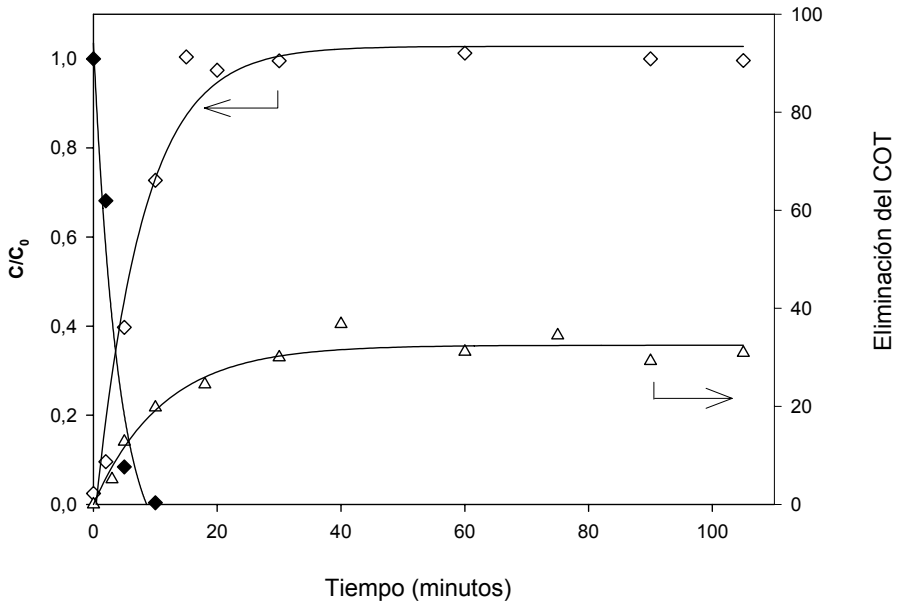

Figura 7 – Ozonización del bezafibrato, T = 25 °C pH=6.0; ◆ = concentración del BZF; ◇ = liberación de Cloruros; △ = eliminación del COT.

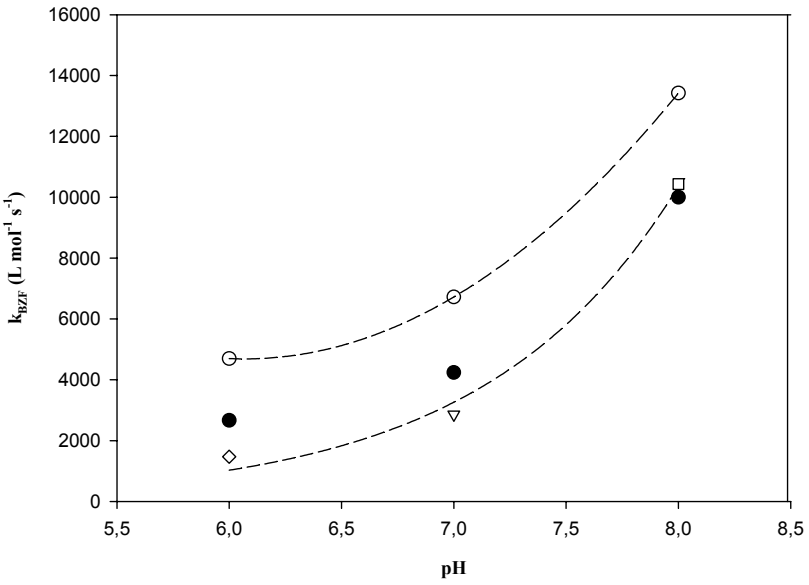

Figure 8 – Valores de las constantes cinéticas para la ozonización de BZF versus el pH obtenidos mediante el metodo obsoluto (●) y por el método de la competición usando los

datos de la bibliografía para el acido maleico (○: Caprio et al., 1987; ◇:Hoignè and Bader, 1983; ▽: Benkelkacem et al., 2003; □: Pryor et al., 2004).

9.5 Conclusiones

- La combinación de la ozonización con el tratamiento biológico usando un reactor "SBBR" ha conseguido en un día de tratamiento más de 95 % de mineralización de aguas contaminadas con 4-clorofenol.

- La mineralización de los compuestos de amonio cuaternario mediante el proceso de ozonización ha alcanzado un valor máximo de 50 % después de 90 minutos de tratamiento.

- Factores como la formación de espumas durante los experimentos juntamente con la fluctuación de los valores medidos de carbono orgánico total suponen un gran inconveniente para el tratamiento de QACs mediante ozonización.

- En las condiciones testadas, el proceso foto-Fenton ha conseguido valores finales de mineralización para soluciones contaminadas con los QACs de hasta un 85 % utilizando UV como fuente de irradiación. El uso de la lámpara de Xe ha disminuido la velocidad de mineralización. Sin embargo, los costes de tratamiento podían ser considerablemente disminuidos con la utilización de energía solar.

- El tratamiento de aguas contaminadas con los fármacos en estudio, han tenidos resultados semejantes, siendo el compuesto rápidamente degradado en un tiempo corto de ozonización, mientras que la mineralización de los intermedios ha sido más lenta.

- Mediante ozonización, se observó un importante aumento de la biodegradabilidad de las soluciones contaminadas con los fármacos hasta valores cercanos a 0.3.

- La toxicidad de las muestras en distintos tiempos de ozonización se ha comportado de una manera más compleja, aumentando en los primeros periodos de ozonización y luego alcanzando valores cercanos a los iniciales en el tiempo final de ozonización.

- Las constantes cinéticas calculadas para la reacción directa del ozono con los dos fármacos en estudio están de acuerdo con sus estructuras químicas.