Ozonation of Emergent Contaminants

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2 Objectives

2.1 General objectives

- To assess the suitability of ozonation to treat waters containing emerging contaminants, which are represented in this work by pharmaceuticals and surfactants;

- To evaluate the nature of intermediates forming during the ozonation as well as the biodegradability and toxicity evolution of ozonated solution;

- To create a set of data about the degradation and mineralization of the target compounds as well as useful information about the biodegradability and toxicity of the formed byproducts. Thus, this data could be useful for a future combination ozonation-biological treatment.

2.2 Specific objectives

2.2.1 4-Chlorophenol (4-CP)

In the last years, the group of chlorophenols and specifically 4-chlorophenol was widely studied from the point of view of removal from water by advanced oxidation processes and ozonation. Nevertheless, the ozonation of 4-CP represents in this work an important tool to set up the ozonation devices and analytical methods. Besides, a comparison between ozonation results obtained in this work and those of previous papers confirms the reliability of the methods. On the other hand, the coupling ozonation-SBBR (Sequencing Batch Biofilter Reactor) applied to treat waters contaminated with 4-chlorophenol is an innovative work. Therefore, the following objectives were proposed for this section:

- To study the abatement and mineralization of waters containing 4-clorophenol as well as to calculate the kinetic constant for the direct reaction between ozone and 4-chlorophenol. The data recorded would be compared with the available data in literature in order to confirm the reliability of the used methods.

- To follow the biodegradability evolution during the runs in order to determine the optimal ozone dosage to start up a subsequent biological treatment;

- To carry out the combination ozonation-SBBR to mineralize the intermediates from the ozonation of 4-chlorophenol. From experimental results, to evaluate the SBBR efficiency.

2.2.2 Quaternary ammonium compounds (QACs)

- To assess the mineralization of QACs solution by ozonation at different conditions;

- From experimental results, to propose the most important variables that must be carefully controlled to perform the QACs mineralization during an ozonation process.

- To compare these results with those carried out by means of photo-Fenton process;

- To examine the possibility of using solar light in the photo-Fenton process with the use of a Xe lamp.

2.2.3 Pharmaceuticals: sulfamethoxazole and bezafibrate

- To assess the removal profile of the target pharmaceuticals by means of ozonation as well as the mineralization of intermediates;

- To calculate the kinetic constants of the direct ozone attack and understand the mechanism of ozonation;

- With the use of proper methods, to attempt the identification of byproducts formed in the course of the reaction;

- To study the biodegradability and toxicity profile of the formed intermediates along the ozonation time;

- Based in the overall degradation results, to create a set of data, which could be used to start up the combination ozonation-biological treatment (SBBR) for the treatment of waters containing the studied pharmaceuticals.

3 Experimental

3.1 Chemicals

To carry out this work, the following list of reactants was necessary:

Target compounds:

- 4-chlorophenol (4-CP), Panreac Quimica, S.A. (Spain);
- Benzyl-dimethyl-hexadecylammonium-chloride (16-BAC), Aldrich (Spain);
- Benzyl-dimethyl-stearylammonium-chloride (18-BAC), Aldrich (Spain);
- Sulfamethoxazole, Panreac Quimica, S.A. (Spain);
- Bezafibrate, Aldrich (Italy).

Radical scavenger:

- 2-Methyl-2-propanol (t-butanol), Panreac Quimica, S.A. (Spain).

Antifoam:

- Antifoam A concentrate A5633, Aldrich (Spain).

Buffer solutions:

- Na_2HPO_4, H_3PO_4 and KH_2PO_4, Panreac Quimica, S.A. (Spain);
- Na_2HPO_4, Na_3PO_4 and KH_2PO_4, Aldrich (Italy).

Reference compounds for kinetic runs:

- Maleic acid, Aldrich (Italy).
- Fumaric Acid, Panreac Quimica, S.A. (Spain).

Note: The chemicals used for analytical instrumentation are not listed.

3.2 Ozonation devices

3.2.1 1.2-L reactor

The reactor was a 1.2 L cylindrical glass vessel provided with a thermostatic jacket. In order to improve the gas contact with the aqueous phase, solutions were continuously stirred while the mixture oxygen/ozone was bubbled into the reactor. Thus, volumes of 1 L of the target compound solutions containing different concentration were

charged into the reactor. Ozone was generated by means of a Sander Labor Ozonizator (Germany) using oxygen as a feeding gas, The ozonator has a maximum ozone production equal to 30 g O_3 h^{-1}. However, the operation condition was in the range from 2.04 to 7.57 g O_3 h^{-1}. The ozone in the outlet was measured by a QuantOzon "1" ozone measurer (detection range = 0-20 g O_3/m^3) (Germany). The gaseous outlet from the reactor was led to a killer, where the remaining ozone was destroyed by means of the reaction with KI saturate solution. A scheme of this device is depicted in Figure 3-1. This device is located in the photochemistry laboratory at the University of Barcelona and it was used to perform experiments with 4-chlorophenol, sulfamethoxazole and quaternary ammonium compounds.

3.2.2 Pilot plant

A second installation used in this work was a 21-L gas-liquid contact reactor, made of PVC, where a venture diffuser was used to make contact with the oxygen-ozone mixture and water. The liquid was re-circulated through a centrifugal stainless steel pump (model 63/2 EMG-Italy) at a flow rate of 200 L h^{-1}. The ozone generation as well as freeboard measurements were performed by the same equipments previously described for the 1.2 L reactor. The complete pilot plant installation is shown in Figure 3-2. This experimental system is in the photochemical laboratory of the University of Barcelona. The investigation of the ozone effect on the biodegradability of waters contaminated with 4-CP was carried out in this device. The advantage of this installation is the possibility of having large sample volumes to perform simultaneously BOD, COD, TOC and HPLC analysis.

3.2.3 0.8-L reactor

In order to study the bezafibrate ozonation, a 0.8 L stirred reactor was used. This investigation was carried out at the "Università Federico II" (Italy). In this system, a continuous supply of O3 was fed into the reactor, where 0.8 L of the solution was continuously stirred. Ozone was generated by means of a Fischer 502 Ozonizator (0-10 g O_3 h-1) using oxygen as a feeding gas. The ozone concentration in the outlet gaseous stream was evaluated by continuous UV monitoring at a wavelength of 253 nm by means of a Varian UV spectrophotometer equipped with a quartz cell (optical length = $3.0 \cdot 10^{-2}$

dm). The gaseous outlet from the reactor was led to an ozone decomposer, where the remaining ozone was destroyed by means of a proper decomposition catalyst. Thus, contaminated solutions were charged into the reactor, where an ozonized gaseous mixture was bubbled in. The gas flow rate was kept at 22.8 L h^{-1}. Figure 3-3 shows a scheme of the 0.8 L reactor.

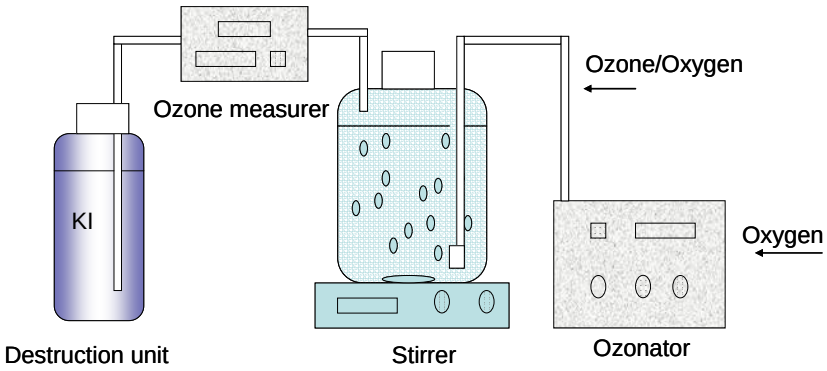

Figure 3-1 - 1.2 L reactor

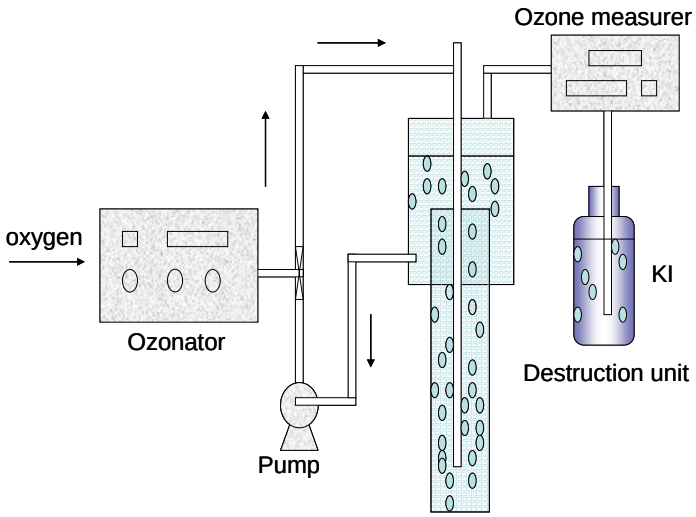

Figure 3-2 - Pilot plant

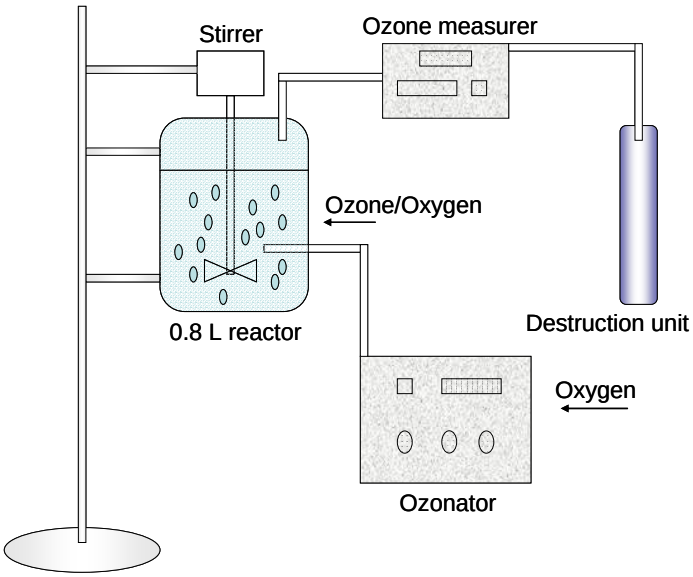

Figure 3-3 - 0.8 L reactor

3.3 Biological assay

The bioassay was carried out with pre-ozonated solutions. After the pre-treatment, to be certain that there was not remaining ozone dissolved in the solution, pre-ozonated solutions were left about 24 hour before feeding the reactor. The biological reactor (Figure 3-4) was an aerobic Sequence Batch Biofilm Reactor (SBBR) and the biomass was supported on 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 degrading pre-treated 4-CP solution from photo-Fenton experiment (Bacardit et al., 2005). The pH of the pre-ozonated samples were neutralized before feeding the reactor with a NaOH solution and NH_4Cl, $CaCl_2$, $FeCl_3$, and $MgSO_4$ solutions were added as nutrients. The pH of the reactor was kept near 7 and adjusted with diluted solutions of NaOH and H_3PO_4. The temperature of the reactor was kept at 25 ^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 of 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.

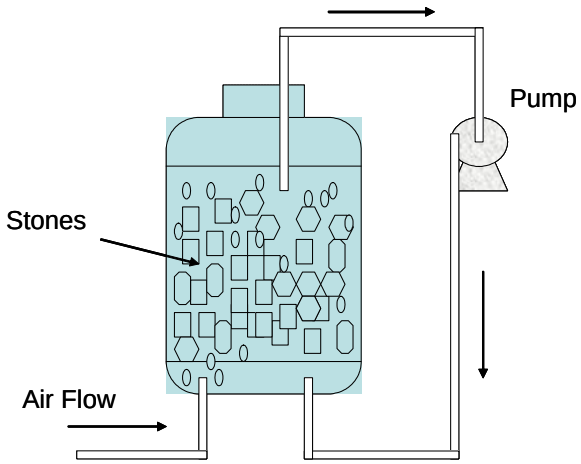

Figure 3-4 - Bioassay device

3.4 Analytical methods

3.4.1 High performance liquid chromatography (HPLC) and mass spectrometry (MS)

In order to follow the concentration of the target compounds during the runs and determine the structure of intermediates from the ozonation of sulfamethoxazole and bezafibrate, a combination of HPLC-MS was used. To identify the intermediates during the ozonation of the sulfamethoxazole, an Agilent 6890 HPLC coupled with a Delta Plus Finnigan MAT Mass Spectrophotometer was applied. In the case of the Bezafibrate, The LC-MS analyses were performed by means of an HPLC-MS Agilent 1100 equipped with a Synergi Polar 4RP column. 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 4-CP concentration was followed by means of a 996 high performance liquid chromatography (HPLC) supplied by Waters Corporation (Massachusetts, USA). The detailed chromatographic condition for each compound is given separately in the results and discussions section.

3.4.2 Total organic carbon (TOC)

To measure the total carbon (TC) of the samples, a Shimadzu 5055 TOC analyzer was used. In this system, TC determination is based on the catalytic combustion oxidation (680 ^oC) using a non-dispersive infrared (NDIR) detection method (Shimadzu). Thus, the TC of the sample is burned in the combustion tube to form carbon dioxide. After that, the carrier gas containing the carbon dioxide and other combustion products are collected and detected by the NDIR.

In order to eliminate the interferences of the inorganic carbon (IC) in the solution, represented for the presence of dissolved CO_2, samples were acidified before TC measurement. Besides, in some cases an oxygen stream was bubbled in the solution. With this procedure, it was stated that TC values were equal to total organic carbon (TOC). The calibrate curves were prepared from standards solutions of potassium biftalate ($C_8H_5KO_4$) and the results were expressed in mg L^{-1}.

3.4.3 Chemical oxygen demand (COD)

In wastewater treatment, the COD is widely used to indirectly determine the organic matter content of the water (Baker et al., 1999). This measurement is carried out through the oxygen mass consumed for the oxidation of organic and oxidizable inorganic matter. The oxygen demand is usually calculated by a relationship between the phthalate oxidation reaction by dichromate and oxygen as described by the reactions:

$$41H_2SO_4 + 10K_2Cr_2O_7 + 2KC_8H_5O_4 \rightarrow 10Cr_2(SO_4)_3 + 11K_2SO_4 + 16CO_2 + 46H_2O$$

$$2KC_8H_5O_4 + 15O_2 + H_2SO_4 \rightarrow 10CO_2 + 6H_2O + K_2SO_4$$

Considering that 10 mol of potassium dichromate has the same oxidation power as 15 mol of oxygen, the theoretical COD of potassium acid phthalate is 1.175 g of oxygen per gram of potassium acid phthalate.

The COD analysis (standard method, 5220 D) consists in heating during two hours at 150 ^{o}C a sample volume with excess of potassium dichromate in presence of sulphuric acid in a closed vial. During this period, the organic matter is oxidized and the dichromate releases Cr^{+3} ions in the solution, which are measured by a colorimetric method. The following equation describes the reaction between an organic compound and the dichromate ion:

$$C_nH_aO_bN_c + dCr_2O_7^{-2} + (8d + c)H^+ \rightarrow nCO_2 + \frac{a + 8d - 3c}{2}H_2O + cNH_4^+ + dCr^{3+}$$

were: $d = \frac{2n}{3} + \frac{a}{6} - \frac{b}{3} - \frac{c}{2}$

Chloride is often the most serious source of interference. Thus, prior to the addition of other reagents, mercuric sulphate may also be added to eliminate the interference of chloride ions. The reaction of chloride and dichromate is described below. In addition, other inorganic molecules that can cause interference are nitrite, ferrous iron and sulfides.

$$6Cl^- + Cr_2O_7^{-2} + 14H^+ \rightarrow 3Cl_2 + 2Cr^{3+} + 7H_2O$$

To prepare vials for the digestion, 2.5 mL of the sample are mixed with 1.5 mL of 0.2 N dichromate solution and 3.5 mL of Ag_2SO_4/H_2SO_4 5.4:1000 g/g catalytic solution. After two hours of digestion, the samples are left to cool down at room temperature. To carry out the colorimetric measurement of the Cr^{+3} ions, the spectrophotometer (odyssey DR/2500) was calibrated with standards solution of potassium hydrogenophtalate ($C_8H_4O_4HK$, KHP) using a wavelength of 600 nm. The absorbance of the samples were measured and compared with a blank made with millipore water. From the COD values for each standard solution

absorbance, the COD values of the samples were easily calculated by means of a linear regression. The results are expressed in terms of mg O_2 L^{-1}.

3.4.4 Biological oxygen demand (BOD)

To follow the biodegradability variation of the samples in the course of the ozonation experiments, the biological oxygen demand was measured. The method used to carry out the analysis was a manometric system (oxitop®), which is described at Standard Method for the respirometric analysis (Standards Methods, 5210 D). The biological oxygen demand measures the consumed oxygen by the microorganisms per water volume unity during an established period of time at controlled temperature (i.e. mg O_2 L^{-1} during 5 days at 20 ^oC).

The analysis performed with the oxitop® method used a manometer (Tap of the bottle) which relates the oxygen consumption with the pressure changes at constant volume. During the microorganism respiration, CO_2 is produced and then it is eliminated by a strong alkaline agent (NaOH). Thus, a pressure reduction is achieved and measured by the manometer present in the tap of the bottle. The sample volume used to fill the bottle depends on the BOD range expected for the sample. In this case, 425 mL of the sample was filled into the bottle. With this volume, the highest BOD value that can be measured is 40 mg O_2 L^{-1}. Subsequently, the sample was buffered at pH 7.2 with 2.595 mL of NaH_2PO_4 1.5 N solution and 0.865 mL of each nutrients solution (NH_4Cl, $MgSO_4$, $FeCl_3$, $CaCl_2$ and KOH) was added. The bacteria used to perform the BOD test came from BOD-seed capsules supplied by Cole-Parmer Instrument Company (USA). The biomass was activated with 2 hours of air bubbling and 0.650 mL of the supernatant was used for each bottle. To avoid O_2 consumption by nitrification, nine drops of a nitrification inhibition solution were added. The bottles were left for a period of five days and the oxygen consumed in mg O_2 L^{-1} was measured directly from the caps of the bottles.

3.4.5 UV_{254} absorbance

In order to assess the ozonation byproducts nature, the samples absorbance of ultraviolet light at a wavelength of 254 nm (UV_{254}) was used as an aromaticity indicator. As UV_{254} measurements can provide inexpensive and meaningful prescriptive guidance of the aromatic content in the solution, during ozonation runs samples were withdrawn and its UV_{254} absorbance were properly analysed. The reduction of the UV_{254} values is directly related with the reduction of the aromatic content in the samples (Ravikumar and Gurol, 1994).

To perform the test, the solution was left two hours to ensure the absence of ozone in the medium and then 1 mL of the solution was transferred to a 1 cm quartz cell and placed in a spectrophotometer. The results were reported in cm^{-1}.

3.4.6 Microtox acute toxicity test

The acute toxicity test was carried out with a Microtox® M500 toxicity analyzer, according to the manufacturer procedure (Azur Environmental, Delaware, USA). In this test, luminescent organisms are 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. The increase or decrease of the light output is measured. Afterward, these values are compared with controls (reagent blank) that contains no samples. A difference of the light output between the sample and the control is attributed to the effect of the sample content on the organisms. The microtox acute toxicity reagent is a freeze-dried preparation of a specially selected strain of the marine bacterium *Vibrion Fischeri* (formally knows as *Photobacterium phosphoreum*, NRRL number B-11177). Taking into account that different chemicals affect living organisms at different rates, reflecting differences in the mechanism of action, the contact time need to complete the effect on light output may change. Usually, a contact time of 5 or 15 minutes

of contact is recommended. Nevertheless, in some cases a time of 30 minutes is suitable. In this work, after a careful analysis, a time of 15 minutes of contact was considered as reliable.

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 of contact. The Microtox® test was operated in duplicate.

3.4.7 Total and volatile suspended solids

During the cycles in the SBBR, in order to control the quantity of biomass attached on the volcanic stones, a daily sample was withdrawn from the reactor and the total and volatiles suspended solids were analysed. Solids analyses were used to control,

based on mass, the composition of the reactor aqueous phase. *Total solids* can be subdivided into *total suspended solids* and *total dissolved solids*. Each division can be further subdivided into fixed or volatile. *Total solids* is the term applied to the material residue left in a vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature (either 103 or 180 °C). *Total solids* includes total suspended solids, the portion of total solids retained by a filter, and total dissolved solids, the portion that passes through the filter. *Fixed* solids is the term applied to the residue of total, suspended, or dissolved solids remaining after combustion at 550 °C. The weight lost during combustion is referred to as *volatile solids*. Fixed and volatile may not be the best measure of inorganic or organic material. For example, the loss of mass during combustion is not confined to organic material, and may include the decomposition or volatilization of some mineral salts. However, this measure can helps to control the composition of a biological reactor because they give a rough approximation of the amount of organic matter present in the solid fraction of wastewater, activated sludge and industrial wastes.