Ozonation of Emergent Contaminants

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Certifican:

Que el presente trabajo de investigación titulado "Ozonation of Emergent Contaminants", constituye la memoria que presenta el licenciado en farmacia Renato Falcão Dantas para aspirar al grado de **Doctor por la Universidad de Barcelona** en el Departamento de Ingeniería Química de la Universidad de Barcelona bajo nuestra dirección.

Y para que así conste, firmamos el presente certificado, a quince de mayo de 2007.

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É necessário muita coragem para ter
tentado e fracassado, assim
como para ter tentado e conseguido.

"Anne Morrow Lindbergh"

Summary

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Abstract

In this work, the ozonation of emergent contaminants represented by pharmaceuticals (Sulfamethoxazole and Bezafibrate) and surfactants (Quaternary Ammonium Compounds) was studied. Results in terms of target compound degradation and mineralization along with the biodegradability and toxicity assessment of formed intermediates are presented. Moreover, a previous study about the suitability of the combination ozonation-Sequencing Batch Biofilm Reactor (SBBR), using the model compound 4-chlorophenol, is shown.

The first part of this work deals with the removal and mineralization of the compound 4-chlorophenol. The 4-CP is not included among the “new” or emerging contaminants. However this preliminary study allowed setting up our ozonation system as well as analytical methods. In addition, the coupling ozonation with SBBR constitute an innovative experimental procedure.

The preliminary runs aimed to assess the mineralization of 100 and 200 mg L^{-1} 4-chlorophenol (4-CP) solutions by ozonation and ozonation-biological treatment (SBBR). The experimental results showed that with an ozone flow rate of 5.44 and 7.57 g h^{-1}, 4-CP was completely removed from the solution in 15 and 30 minutes of ozonation, respectively. By the other hand, at the 4-CP abatement time, on average only 26 % of total organic carbon (TOC) removal was achieved. Quinone and hydroquinone were found as intermediates of reaction and a kinetic constant around $9 \cdot 10^{-2}$ min^{-1} was calculated for the ozone direct attack. The biodegradability (BOD_5/COD) of the pre-ozonated solutions increased from 0 until a range between 0.2-0.37. The combination of ozonation and aerobic biological treatment in an aerobic sequencing batch biofilm reactor (SBBR) gave an abatement of more than 90 % of the initial TOC. Moreover, the biofilter reactor showed fast recuperation after being submitted to absence of oxygen and feed.

The Quaternary Ammonium Compounds (QACs) ozonation was carried out in order to assess the mineralization potential of ozonation processes for this class of compounds. To perform this study, the QACs 16-BAC (Benzyl-dimethyl-hexadecylammonium-chloride) and 18-BAC (Benzyl-dimethyl-stearylammonium-chloride) were treated by ozonation at different O_3 dosage. The TOC (Total Organic Carbon) removal was monitored in order to follow the mineralization of the surfactants along the runs. According to experimental results, from an initial TOC concentration of 50 mg L^{-1}, 90 minutes of ozonation reached at most 50% of mineralization at the used conditions (ozone flow rate 7.57 g h^{-1}). Due to the experimental problems observed during the ozonation of QACs, an alternative advanced oxidation process (photo-Fenton) was applied. In order to observe the mineralization of QACs by means of photo-Fenton, the runs were carried out with the same QAC concentration used in ozonation runs. Besides, two different lamps were used (UV and Xe). According to experimental results, after 90 minutes of treatment, the photo-Fenton process achieved up to 80% of mineralization when the UV lamp was used. The efficiency of the photo-Fenton with Xe lamp was lower. An overall view of the two used oxidation process allows to state that the photo-Fenton process seems to be the most suitable process to treat waters containing QACs.

To carry out the study of the sulfamethoxazole (SMX) ozonation, 200 mg L^{-1} SMX solutions were treated by ozonation at different pH. Results showed that ozonation was proved to be an efficient method to degrade sulfamethoxazole. After 15 minutes of ozonation (corresponding dose = 0.4 g of ozone L^{-1}), the complete antibiotic abatement was almost achieved with just 10 % of mineralization. The biodegradability and toxicity of the ozonation intermediates were also studied. A biodegradability enhancement (increment of BOD_5/COD ratio) from 0 to 0.28 was observed after 60 min of ozonation. The acute toxicity of the intermediates was followed by the Microtox® test and the toxicity profile showed a slight acute toxicity increment in the first stage of ozonation. The pH variation had an important role in the TOC and COD removal, promoting their growth with the increment of alkalinity. The second order kinetic constants for the ozonation of the SMX in an order of magnitude of 10^5 L mol^{-1} s^{-1} were also determined for pH 5 and 7.

Concerning the Bezafibrate (BZF) ozonation, the results showed that ozonation is an efficient method to degrade BZF: after 10 minutes of treatment (corresponding to a dose of 0.73 mmoles L^{-1} of ozone), the complete BZF abatement is achieved, starting from an initial concentration of 0.5 mmoles L^{-1}. However, only a small part of the substrate is mineralized. Two different experimental approaches (absolute and competition method) are adopted to estimate the second order kinetic constants for the ozone attack at pH=6.0, 7.0 and 8.0. A good agreement was observed between the two kinetic methods adopted. The identification of main intermediates, attempted by HPLC-MS technique, indicates that the oxidation of BZF develops through both the hydroxylation of the aromatic ring and the attack of ozone on the unchlorinated aromatic one. The assessment of by-products biodegradability and acute toxicity demonstrates that ozonation is a suitable technique to improve the biodegradability and reduce the toxicity of waters containing BZF.

1 Introduction

1.1 The problem of water scarcity in the world

According to the Word Health Organization (WHO, 2003), 1.2 billion people do not have access to water for their domestic use. Besides, 2.18 million people die per year due to the lack of access to safe drink water, sanitation deficiency and poor personal hygiene. The majority of these people are younger than five years old and other 82 million people suffer diseases related with inappropriate water supply (Prüss et. al. 2002). Nowadays, there are great discussions if the water is truly scarce in the physical sense (a supply problem) or whether it is available but should be used better (a demand problem) (Rijsberman, 2006). An important example of that discussion refers to Asia, where a large part of its territory suffers from severe water scarcity while the average water availability appears to be plentiful. Moreover, other regions suffer from the presence of polluted water, being considered as water scarce areas without considering the available water after treatment.

The most used water scarcity indicator, the “Falkenmark water stress indicator”, represents scarcity as a relationship between water availability and human population, i. e. water availability per capta per year. Figure 1-1 presents, according to the falkenmark indicator, an overall view of the most affected countries by the water scarcity. However, the falkenmark indicator has some limitation because it does not consider important factors such as: presence of infrastructures, climate, life style, etc. The “water resources vulnerability index” focuses on a more accurate assessment of the demand for water. It relates the annual renewable water supply and the annual demand for water. This indicator presents water scarcity as a total annual water withdrawals as a percent of available water resources. It suggests that a country is water scarce if annual withdrawals are between 20 and 40 % of annual supply. In Figure 1-2, the water stress indicator (withdraw-availability) is presented.

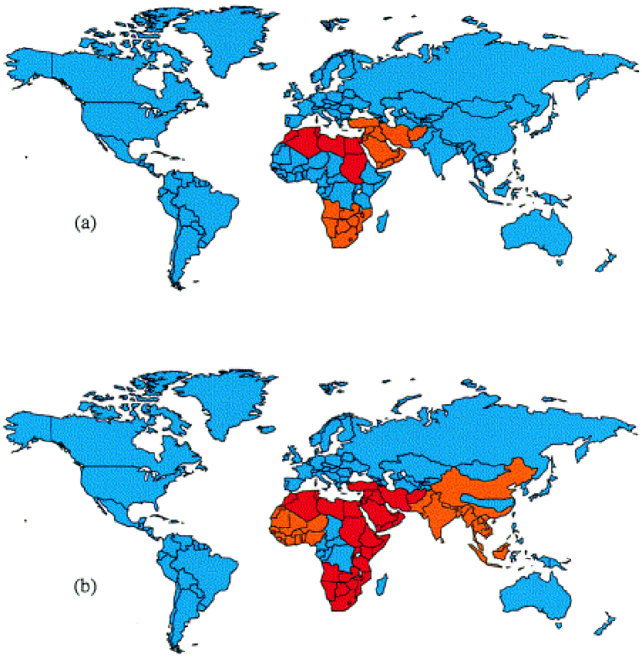

Figure 1-1 - Global water scarcity (a) now and (b) in 2050. Regions are coded according to their per capita annual renewable freshwater resource. Red-less than 1000 m^3 per person per year, orange-between 1000 and 2000 m^3 per person per year and blue-greater than 2000 m^3 per person per year (Source: Wallace, 2000).

An overview of Figure 1-1 supposes that only some countries of Africa and south Asia suffers water scarcity. Nevertheless, a simple analysis of Figure 1-2 leads to the conclusion that even European countries, USA and Canada have regions with important water stress. In addition, a great part of the world suffers of very high water stress.

The international water management institute (IWMI) attempts to overcome the discrepancies taking into account the share of the renewable water resource available for human needs. It proposes to classify countries that were not able to meet the estimated water demands in 2005 in physically water scarce, while countries that had sufficient renewable resources, but would have to make significant investment in water infrastructure to make these resources available to people are defined economically water scarce. Other indexes using factors like poverty and environmental aspects have been proposed (Sullivan et al., 2003).

Regarding the fact that many countries are affected by water stress, the need to treat and reuse water appear as a common priority and challenge for several governments around the world.

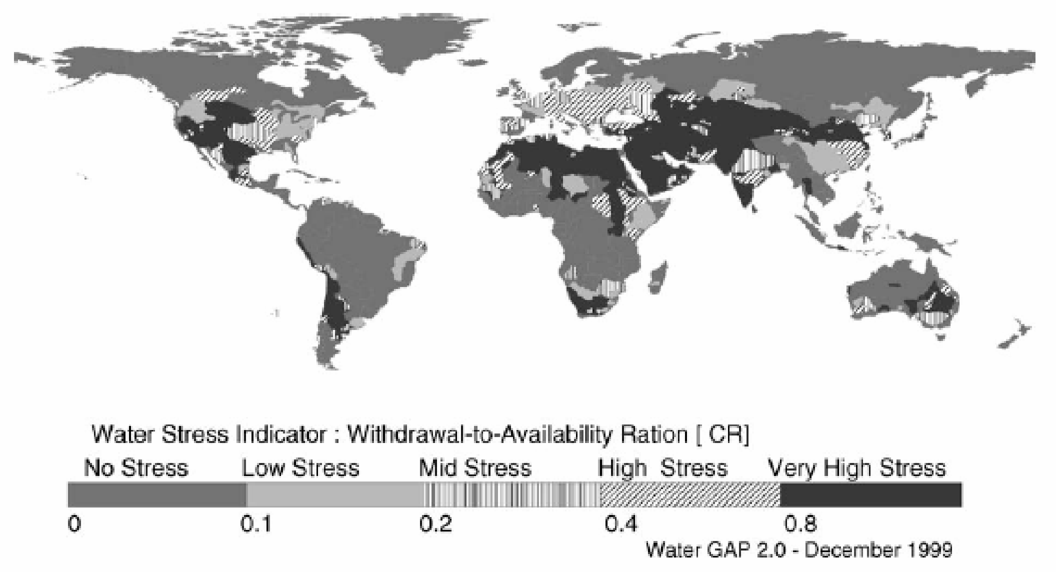

Figure 1-2 - Water stress analysis based on the criticality ratio. (Source: Alcamo et al., 2000).

The increasing population densities and increasing industrialization lead to a state where the freshwater resources, on which civilization relies, become strained (Pickering and Owen, 1997). Additionally, along with overconsumption and resulting water shortages, the introduction of hazardous substances to human health into terrestrial water bodies (or pollution) is the most serious threat to the world´s freshwater supplies.

Pollution can be defined as "*the introduction by man in the environment of substances or energy liable to cause hazards to human health, harm for living resources and ecological system, damages to structures or amenity, or interference with legitimate uses of the environment*" (Holdgate, 1979). Nowadays, a great part of the different water pollution sources are identified and the most difficult task is to carry out reductions of the amount released in environment by means of convenient treatments methods.

Table 1-1 - Major types of pollutant and their impacts in terrestrial water bodies (Jackson and Jackson, 1996).

Pollutant	Major anthropogenic sources	Environmental impacts
Oxygen-consuming wastes	Sewage effluent, agricultural run-off, some industrial effluents	Depletion of dissolved oxygen in waters bodies through decomposition by aerobic bacteria, leading to death of flora and fauna. Decomposition by aerobic bacteria produces toxic gases such as hydrogen sulfide
Nutrients	Sewage effluent, agricultural run-off	Algal Blooms and subsequent death of submerged vegetation. Large quantities of rotting organic material produced causes oxygen depletion
Hydrocarbons	Drilling operation, accidental spillage, water disposal	Various biological impacts, including death of organisms by ingestion or smothering
Other organic pollutants (e.g. organochlorines, organic solvents)	Agricultural run-off, sewage effluent, waste incineration, landfill sites, industrial effluents	Some components are carcinogenic and may bioaccumulate. Biological impacts include depression of immune system and reduced reproductive success in organisms
Acids	Acid rain, acid mine drainage	Acidification of natural waters and subsequent increase in toxic metal concentration. Decline in species richness, death of fish
Heavy metals	Ore mining and associated industries, various technological processes	Various toxic effects depending on metal present. May bioaccumulate through the food chain
Radionuclides	Nuclear weapons testing, deliberate and accidental release from nuclear facilities	Depending on exposure, may cause cell damage, genetics defects, and cancers
Heat	Coolant waters from industry	Changes in species composition, suffocation of fish, disruption of reproductive cycle in fish and other aquatic organisms

Although in underdeveloped countries sewage and agricultural pollution have a great importance in terms of water pollution, sewage wastes appears as the major source of contamination. Industrials effluents may also contain a variety of hazardous components, such as radioactive materials, hydrocarbons, heavy metals and toxic organic compounds (Cundy, 2004). Table 1-1 presents the main types of water pollutants and their impacts on environment.

Many compounds classified as contaminants are naturally present in the environment, even being tolerated by the organism or actively required. However, the accumulation of these substances beyond safe levels or additives effects of a series of contaminants may lead to detrimental impacts on the environment (e.g. Nitrate contamination). On the other side, many organic pollutants, such as pesticides and industrial chemicals, are entirely artificial and so have no natural background concentration in the environment. Thus, pollutants may build up over time, providing a long term contamination problem. They can be adsorbed and removed onto sediments and suffer uptake and breakdown by organisms, e.g. microbial oxidation and decomposition of sewage sludge.

Water treatment technologies are important tools to ensure a reasonable use of water supplies and protect the environment from the pollution caused by human activities. Among these technologies, the sewage treatments by activated sludge stand out as the most used. A sewage treatment plant (STP) attempts to reduce water pollution eliminating wastes, oils, fates and sands; eliminating dacantable organic and inorganic matter; eliminating ammoniacal compounds, etc (Ortiz et al., 2007). However, in order to reuse the treated water it is necessary to apply tertiary treatments. For this purpose, several types of physico-chemical treatments such as ammonium stripping, chemical precipitation, coagulation-flocculation, ultrafiltration, nanofiltration and reverse osmosis have been employed worldwide. Recently, the application of membrane technologies, specifically membrane bioreactor seems to be offering some advantages versus conventional processes commonly used (Cicek et a., 1998). On the other side, the

presence of biorecalcitrant and/or toxic compounds supposes an important problem for biological treatments. Consequently, to achieve a satisfactory removal of refractory compounds, a preliminary treatment is necessary. Moreover, in the last decades, the “emerging contaminants” supposes an additional concern due to the lack of information about its effects on the environment as well as its interference in biological treatments.

Due to its capability of transforming contaminants into innocuous substances within a short period of time, ozone has been identified as a potentially effective means to treat wastewaters containing new and potentially hazardous compounds. Depending of its operational procedure (i.e. pH of the medium), ozonation can be included in the group of the advanced oxidation technologies.

1.2 Advanced oxidation processes

Advanced oxidation processes (AOPs) are defined as processes that can generate radicals in a sufficient quantity to be able to oxidize majority of the complex chemicals present in the effluent water. Among these processes are included Cavitation (Gonze et al., 1999; Moholkar et al., 1999; Senthilkumar and Pandit, 1999; Adewuyi, 2001; Gogate and Pandit, 2001; Gogate, 2002;), photocatalytic oxidation (Blake, 1997; Herrmann, 1999; Yawalkar et al., 2001; Bhatkhande et al., 2002), wet oxidation (Garcia-Molina, 2007; Poulopoulos et al., 2007), electrochemical oxidation (Brillas et al., 2004; Xie and Li, 2006) and Fenton Chemistry (Venkatadri and Peters, 1993; Bigda, 1995, 1996; Nesheiwat and Swanson, 2000).

Table 1-2 - Oxidation-Reduction potential of species used in water treatment (Hunsberger, 1977)

Oxidation-Reduction Potential (ORP)	
Chemical specie	**E^o(V)**
Fluorine	3.0
Hydroxyl radical	2.8
Ozone	2.1
Hydrogen peroxide	1.8
Potassium permanganate	1.7
Hypochlorite acid	1.5
Chlorine dioxide	1.5
Chlorine	1.4
Oxygen	1.2

Hydroxyl Radicals OH· are powerful oxidizing reagents with an oxidation potential of 2.8 V. In addition, they react with most organic and many inorganic compounds, exhibiting faster rates of oxidation reactions as compared to that conventional oxidants (Gogate et al., 2002). Table 1-2 lists the oxidation reduction potential (ORP) of the most used oxidant species in water treatment. Afterwards, a short explanation of the most important advanced oxidation processes is given along with a detailed description of the ozonation process.

1.2.1 Cavitation

Cavitation is a phenomena of formation, growth and collapse of microbubbles within a liquid that promotes the formation of OH· radicals. Acoustic cavitation (Ultrasonication) occurs by means of high frequency sound waves, while hydrodynamic cavitation take place due to pressure variations in the flowing liquid promoted by a change in the geometry of the flowing system. The mean advantage of the cavitation use is the non-introduction of chemicals in the medium. Moreover, no toxic byproduct is formed as in the case with chemical treatment using chlorine. The suitability of this process could be real if the raw water supply is available with a considerable high pressure and its pressure needs to be reduced using pressure reducer (Jyoti and Pandit, 2001).

1.2.2 Photocatalysis

These processes entail a photochemical degradation of a lot of compounds present in wastewater, capable of achieving total mineralization at mild conditions of temperature and pressure (Hoffmann et al., 1995). In this process, the chemical reactions are characterized by a free radical mechanism as well. Radicals can be produced by the homogeneous radiations degradation of oxidizing compounds like hydrogen peroxide and ozone. Another way to achieve and at the same time enhance the production of free radicals is the photocatalytic oxidation mechanism occurring at the surface of semiconductors e.g. TiO_2 (Mazzarino et al., 1999). The photocatalytic oxidation enables the utilization of sunlight and near UV for irradiation, thus, resulting in a considerable saving especially for large-scale operations (Yawalkar et al., 2001).

1.2.3 Fenton and photo-Fenton process

The Fenton Chemical Process is an oxidation based on the Fenton´s Reagent (hydrogen peroxide in the presence of ferrous salt) (Fenton, 1894). This process consists on the formation of reactive oxidizing species able to degrade pollutants of the wastewater. It has been used for the treatment of both organic and inorganic substances under laboratory conditions as well as real effluents (Bigda, 1996). Such as in other AOPs, the rate of the oxidizing should be strongly dependent on the presence of radical scavengers such as t-butanol or Cl^- (Rahhal and Richter, 1988). When a Fenton process is irradiated with light in order to improve the OH· formation, the process is called photo-Fenton.

In this work, the photo-Fenton process is used as an alternative method to treat waters contaminated with quaternary ammonium compounds. Thus, a short explanation about the photo-Fenton reactions is given.

As cited above, the Fenton treatment method is based on the reaction between ferrous ion and hydrogen peroxide. The products of this reaction are hydroxyl radicals and hydroxide ions.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\cdot}$$ **equation 1-1**

$$Fe^{3+} + H_2O_2 \leftrightarrow H^+ + Fe - OOH^{2+}$$ **equation 1-2**

$$Fe - OOH^{2+} \rightarrow HO_2^{\cdot} + Fe^{2+}$$ **equation 1-3**

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\cdot}$$ **equation 1-4**

This group of reaction describes how the Fenton reaction mechanism works and explains the iron regeneration. When the system is irradiated and the photo-Fenton process takes place, one more series of reactions can be added to the mechanism.

$$H_2O_2 \xrightarrow{hv} 2OH^{\cdot}$$ **equation 1-5**

$$H_2O_2 \leftrightarrow HO_2^- + H^+$$ **equation 1-6**

$$HO_2^- \xrightarrow{hv} OH^{\cdot} + O^-$$ **equation 1-7**

During the photo-Fenton, both H_2O_2 and HO_2^- can absorb UV radiation at the wavelength of 254 nm for further formation of radicals, which are useful to destruct organic contaminants. After formation of $OH^{\cdot}$ radicals, it reacts promptly with organic compounds, where a radical chain takes place (Trapido et al., 1997). First, a radical is formed from the chain, which becomes an alcohol or an acid depending on whether it is hydrogen peroxide or oxygen it reacts with.

$$RH + OH^{\cdot} \rightarrow H_2O + R^{\cdot}$$ **equation 1-8**

$$2OH^{\cdot} \rightarrow H_2O_2$$ **equation 1-9**

$$R^{\cdot} + H_2O_2 \rightarrow ROH + OH^{\cdot}$$ **equation 1-10**

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$$ **equation 1-11**

$$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$$ **equation 1-12**

1.2.4 Electrochemical oxidation

The electrochemical purification of waters contaminated by pollutants generally dissolves simple and harmless molecules in a fluid (gas or more often liquid) through electrochemical reactions, which often occur in parallel with oxygen evolution, or Fenton's reactions and/or cathodic production of hydrogen peroxide. At the moment, several electrochemical methods are under study for wastewater purification, such as the electro-Fenton's treatment, oxidative processes, electrodeposition and direct reductions (Francesco and Costamagna, 2004).

Some techniques such as electro-Fenton and photoelectron-Fenton are included among the most used electrochemical oxidation. In these techniques, hydrogen peroxide is continuously generated in an acidic contaminated solution from the two-electron reduction of O_2 (Brillas et al., 2004; Xie and Li, 2006). In the electro-Fenton method, the oxidizing power of H_2O_2 is enhanced by adding small amounts of Fe^{2+} as catalyst to the acidic solution. Thus, hydroxyl radical $\cdot OH$ and Fe^{3+} are then generated from the classical Fenton reaction between Fe^{2+} and H_2O_2. In the photoelectro-Fenton process, the solution is irradiated with UVA light to promote the photodecomposition of Fe^{3+} complexes and to regenerate Fe^{2+} from additional photoreduction of $Fe(OH)^{2+}$ (Sun and Pignatello, 1993).

1.2.5 Wet oxidation

Wet oxidation processes include several technologies, such as Supercritical Water Oxidation (SCWO), Subcritical Oxidation or Wet Oxidation (WO), Catalytic Wet Oxidation (CWO) and Wet Peroxide Oxidation (WPO). These processes differ from the rest of the advanced oxidation processes not only in terms of operating conditions but also in the concentration of the pollutants present in the wastewater. They are mainly used for concentrated wastewaters in order to allow auto-thermal operation, and thus a reduction in the operating costs (Catrinescu et al., 2003). SCWO takes place above the critical point of water (T≥ 375 ºC and P ≥ 22.1 MPa) (Ding et al., 1996) and WO engages with oxidation at a temperature range of 125-300 ºC and pressures of 0.5-20 MPa. The use of oxygen as oxidizing agent is common to WO and SCWO processes. There is also one more process which involves oxidation with hydrogen peroxide and which uses temperatures and pressures both below the critical point of water, i.e., WPO (Debellefontaine et al, 1996).

1.3 Ozonation

Although ozonation constitutes a chemical oxidation, it exhibits lower rate of degradation when compared to the processes based on free radicals (Arslan and Balcioglu, 2001; Gogate et al., 2002). However, free radicals are generated when ozone is used in combination with hydrogen peroxide, UV/sun light or ultrasound (Weavers et al., 2000; Fung et al., 2000; Gogate et al., 2002). Another fact that must be taken into account is the decomposition of ozone in water, which induces the formation of hydroxyl radicals ($OH^{\cdot}$). This decomposition is catalysed by OH^- species, making the pH of the medium an important variable in the determination of kinetics and reaction pathways. The two agents involved in the process, play different parts in the process of ozonation. While disinfection is made by the molecular ozone, both agents are responsible for the oxidation process. The ozone is a selective oxidant, while the $OH^{\cdot}$ radical is not selective and it is very important for the oxidation of compounds that have resistance to ozone. The pH of the medium affects the double action of ozone on the organic matter, that may be a direct or an indirect (free radical) ozonation pathway. As commented before, these different reaction pathways lead to different oxidation products and are controlled by different kinetic models. At low pH, ozone mainly reacts with compounds with specific functional groups through selective reactions, such as electrophilic, nucleophilic or dipolar addition reactions (i.e. direct pathway). On the other hand, at basic conditions, ozone decomposes yielding hydroxyl radicals, which are high oxidizing species that react in a non-selectively way with a wide range of organic and inorganic compounds in water (i.e. indirect ozonation). Normally, under acidic conditions (pH <4) the direct ozonation dominates. In the range of pH 4–9 both are present, and above (pH >9) the indirect pathway prevails (Staehelin and Hoigné, 1982).

The radical pathway, during an ozonation process, can be prevented with the use of $OH^{\cdot}$ scavenger species. Usually, at laboratory scales, in order to determine kinetic constants as well as to propose reaction pathways of the direct ozone attack, a suitable quantity of radical scavenger is added into the solution before ozone contact. Among the OH· scavengers, the 2-methyl-2-propanol (t-butanol) stands as one of the most used to avoid the radical interference. The t-butanol is a strong hydroxyl radical scavenger with a reaction rate constant of $6 \times 10^{8}\ M^{-1}\ s^{-1}$ with OH· (Buxton et al., 1988) and $3 \times 10^{-3}\ M^{-1}\ s^{-1}$ with ozone (Hoigné and Bader, 1983). Thus, it is assumed that t-butanol greatly shuts down the chain reaction of OH· radical with ozone and increases the lifetime of molecular ozone (Song, 1997).

The water treatment by means of ozonation is a technique used since the beginning of the 20th century (Gottschalk, 2000). Among the characteristics that make the ozonation an attractive option for water treatment, the non introduction of new chemical species in the medium and its strong oxidant nature stand out as important advantages when compared with conventional techniques. Its high reduction potential enables oxidizing numerous chemical species (odour and flavour control and elimination of micro pollutants), and it can be useful as pre-treatment to improve the effectiveness of later treatments (Contreras, 2003). Moreover, others oxidant agents like chorine and potassium permanganate may release hazardous byproducts in the medium that could be even more toxic than their parent compounds. The mean product of the ozone decomposition in water is oxygen, which is a non toxic compound and necessary for aerobic biologic activities (Manahan, 2005).

1.3.1 Chemical characteristics and physical properties of ozone

Ozone is, at ambient pressure and temperature, an irritating pale blue gas, heavier than air, very reactive and unstable. Moreover, at some conditions the ozone can be explosive and toxic. It can be neither stored nor transported, so it has to be generated in situ. The structure of molecular ozone is presented in Figure 1-3, where its two extreme forms of resonance are presented. Besides, the physical and chemical properties of the ozone are presented in Table 1-3.

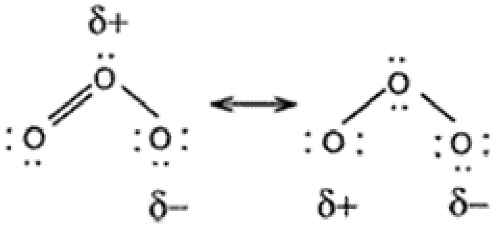

Figure 1-3 - Molecular structure of ozone

The molecular structure of ozone allows its reaction as a dipole, electrophilic and a nucleophilic pathway. In general, the degradation reactions of organic compounds by ozone occur preferably with unsaturated compounds like those with aromatic rings, alkenes, alkynes, etc (Langlais et al., 1991). The direct ozonation of organic compounds is a selective reaction with kinetic constants lower that those calculated for the OH· radical. In the past few years, many authors attempted to determine kinetic constants for reaction of organic and inorganic compounds with ozone. As a result, a large amount of data is now available (Hoigné and Bader, 1983; Hoigné and Bader, 1985; Yao and Haag, 1991).

Although ozonation presents many advantages when compared with other water treatment technologies, the reaction of some compounds with ozone and/or OH· radicals can produce undesired byproducts that may increase the toxicity of the medium (Miltner, 1992). In addition, the only regulated ozonation byproduct is Bromate, that could be formed by ozone reaction with bromide-containing waters (EU, 1998). Therefore, the toxicity and biodegradability assessment of byproducts from ozonation of new contaminants appears as important information for environment protection.

Table 1-3 - Properties of the ozone (Ullmann ´s, 1995)

Properties	Value
Molar mass	47.998 g mol^{-1}
Density (1 atm and 0 °C)	2.144 g L^{-1}
Solubility in water	0.105 g 100 mL^{-1} 0 °C
Melting point	-192.5 °C
Boiling point	-111.9 °C
Standard enthalpy of formation	+142.3 kJ mol^{-1}
Standard molar entropy	237.7 JK^{-1} mol^{-1}

1.3.2 Ozone decomposition in water

During ozonation, if the ozone is responsible for the substrate oxidation, disinfection and oxidation can be achieved simultaneously. However, if some compounds resistant to ozone are present in the medium, ozone has to be converted into OH· radicals in order to achieve accepted levels of substrate removal. When the ozonation is carried out by means of the radical pathway, a reduction of disinfection power occurs (Gunten, 2003). Thus, a careful evaluation of the overall process is essential to optimise the system. With regard to better control of the ozonation process, the understanding of the diverse reactions that have influence on the ozonation mechanism constitute an important tool for a proper operation.

In aqueous medium, the anion OH^- promotes the decomposition of ozone with subsequent reaction chains that lead to the formation of the OH· radicals. The reactions involved in the ozone decomposition pathway are complex and can suffer influence of several experimental factors and concentration of present species (Sehested et a., 1984; Staehelin and Hoigné, 1985; Elloit and McCracken, 1989). An explanation, step by step, of the ozonation reactions (decomposition in water) is attempted as follows:

The reaction between ozone and the hydroxide ion produces the ion superoxyde radical and the hydroperoxyde radical.

$$O_3 + OH^- \rightarrow O_2^{\cdot -} + HO_2^{\cdot} \qquad k = 70\ M^{-1}s^{-1} \qquad \textbf{equation 1-13}$$

The ozone reacts with the hydroperoxyde radical producing hydroxyl radicals. In addition, the anion $O_3^{\cdot-}$ formed by the reaction between the ozone and the anion superoxide radical decomposes quickly in hydroxyl radicals.

$O_3 + HO_2^{\cdot} \rightarrow OH^{\cdot} + O_2^{\cdot-} + O_2$ k = $2.8 \cdot 10^6$ $M^{-1}s^{-1}$ **equation 1-14**

$O_3 + O_2^{\cdot-} \rightarrow O_3^{\cdot-} + O_2$ k = $1.6 \cdot 10^9$ $M^{-1}s^{-1}$ **equation 1-15**

For a pH ≤ 8

$O_3^{\cdot-} + H^+ \Leftrightarrow HO_3^{\cdot}$ $K^+ = 5 \cdot 10^{10}$ $M^{-1}s^{-1}$ **equation 1-16**
$K^- = 3.3 \cdot 10^2$ s^{-1}

$HO_3^{\cdot} \rightarrow OH^{\cdot} + O_2$ k = $1.4 \cdot 10^5$ s^{-1} **equation 1-17**

For a pH ≥ 8

$O_3^{\cdot-} \Leftrightarrow O^{\cdot-} + O_2$ $K^+ = 2.1 \cdot 10^3$ $s^{-1}s^{-1}$ **equation 1-18**
$K^- = 3.3 \cdot 10^9$ s^{-1}

$O^{\cdot-} + H_2O \rightarrow OH^{\cdot} + OH^-$ k = 10^5 s^{-1} **equation 1-19**

Additionally, the ozone can react with hydroxyl radicals.

$O_3 + OH^{\cdot} \rightarrow OH_2^{\cdot} + O_2$ k = 10^5 s^{-1} **equation 1-20**

Some compounds can act as promoters or inhibitors of the ozone reaction chain (decomposition). If the molecule reacts with $OH^{\cdot}$ radicals releasing in the medium radicals superoxydes or hydroperoxyde, they promote the reaction chain.

$H_2R + OH^{\cdot} + O_2 \rightarrow R + HO_2^{\cdot} + H_2O$ **equation 1-21**

When the products of the reaction are radicals that produce neither superoxide nor hydroperoxide, they promote the termination of the reaction chain.

$OH^{\cdot} + CO_3^{-2} \rightarrow OH^{-} + CO_3^{\cdot-}$ **equation 1-22**

$OH^{\cdot} + HCO_3^{-2} \rightarrow OH^{-} + HCO_3^{\cdot-}$ **equation 1-23**

Additionally, two radicals could react among themselves.

$OH^{\cdot} + HO_2^{\cdot} \rightarrow O_2 + H_2O$ **equation 1-24**

Transition metals could be added in the medium in order to improve the degradation of organic compounds (Pines and Reckhow, 2002). The reaction pathway of the homogeneous catalytic ozonation was not completely elucidated. However, among the proposed theories, the decomposition of the ozone followed by the OH$^{\cdot}$ formation could be directly improved by the presence of some transition metals (Hill, 1949).

$M^{n+} + O_3 + H_2O \rightarrow MOH^{n+} + O_2 + OH^{\cdot}$ **equation 1-25**

1.3.3 Kinetics

The kinetic study of an ozonation process along with the determination of kinetic constants represents important information to carry out modelling and optimization of the attack of potential molecules by ozone. In general, the reaction of ozone and an organic compound can be described according to the reaction:

$Compound + nO_3 \xrightarrow{k} \mathrm{Pr}\,oducts$ **equation 1-26**

where n is the stoichiometric coefficient that relates the moles of ozone consumed per moles of compounds removed and k the kinetic constant of the reaction. When the reaction rate is based in a second order, the degradation rate can be expressed as follows:

$$-\frac{d[C]}{dt}=k[C]\cdot[O_3]$$ **equation 1-27**

$$-\frac{1}{n}\frac{d[O_3]}{dt}=k_{oz}[C]\cdot[O_3]$$ **equation 1-28**

where, [C] = compound concentration.

In this work, the determination of kinetic constants was carried out by means of three different methods. For each compound under study, the choice of a suitable method was made according to the experimental condition used (i.e. initial concentration of the reactants, experimental device, time of reaction, etc).

1.3.3.1 Pseudo first order kinetics

It is important to point out that the ozone mass transfer from the gas phase to the aqueous solution may control the ozonation process (Beltran, 2004). Nevertheless, in the most of the cases, pseudo first order kinetics fitted with the experimental results.

Sometimes, the calculus of the second order constants could be difficult because of the concentration of the two reactants (ozone and substrate) must be properly and simultaneously followed during the reaction. A common solution for this problem is the use of the pseudo first order approximation. Thus, the determination of the second order kinetic constant could be performed if it is considered that one of the reagents is in excess during the ozonation. This method enables to calculate easily the second order kinetic constant of a reaction monitoring the consumption of only one reactant.

Considering the following overall reaction to describe the ozonation of an organic compound:

$$v=k[OC]\cdot[O_3]$$ **equation 1-29**

where [OC] is the concentration of an organic compound and $[O_3]$ is the ozone concentration. If it is considered that the $[O_3]$ is much higher than [OC] in the course of the ozonation, the concentration of $[O_3]$ will not change during the course of the reaction. It means that the $[O_3]$ remains constant. Thus, the rate dependence based on [OC] can be written:

$$v = -\frac{d[OC]}{dt} = k'[OC]$$ **equation 1-30**

Where,

$$k' = k[O_3]$$ **equation 1-31**

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

$$\ln\left[\frac{[OC]}{[OC]_0}\right] = k'\cdot t$$ **equation 1-32**

Plotting the neperian logarithm of the normalised organic compound concentration against time, the slope of the resulting straight line represents the k´.

1.3.3.2 Absolute method

In the absolute method, the variables that can affect the ozonation process such as stirring, temperature, ozone and target compound concentration, mass transfer coefficient, etc should be know and properly controlled during experimentation. Thus, the data recorded along the ozonation is used to build a mathematical model that can represent the overall ozonation. In this case, 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 developed in a quasi-diffusional regime of absorption with reaction, a set of differential mass balance equations for ozone in the two phases (bubble, $[O_3]_B$ and freeboard, $[O_3]_F$), each considered as a well-mixed stirred reactor and the substrate, can be written:

$$\frac{d[O_3]_B}{dt} = \frac{Q}{V_B}\cdot\left([O_3]_{in} - [O_3]_B\right) - \frac{k_L^o a\cdot[O_3]_B\cdot\alpha\cdot E}{V_B}\cdot V_L$$ **equation 1-33**

$$\frac{d[O_3]_F}{dt} = \frac{Q}{V_F} \cdot \left([O_3]_B - [O_3]_F\right)$$ **equation 1-34**

$$\frac{d[OC]}{dt} = -\frac{k_L^o a \cdot [O_3]_B \cdot \alpha \cdot E}{z}$$ **equation 1-35**

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 1-36**

where Ha is the dimensionless Hatta's number:

$$Ha = \sqrt{\frac{D_{O3} \cdot z \cdot k_{OC} \cdot [OC]_o}{\left(k_L^o\right)^2}}$$ **equation 1-37**

being known for the adopted experimental conditions the mass transfer coefficient k_L°, the overall volumetric physical mass-transfer coefficient k_L°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:

$$OC + zO_3 \xrightarrow{k_{OC}} \mathrm{Pr}\,oducts$$ **equation 1-38**

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

This model allows the estimation of 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 1-39**

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.

1.3.3.3 Competition method

The competition method is based on the comparison between the degradation rate of the organic compound and that of a reference compound (RC). The choice of a reference compound is based on the similarity of its kinetic constant found in literature and that expected for the OC.

If it is considered that the following equations can be written to describe the degradation of the two species:

$$\frac{d[OC]}{dt} = -k_{OC} \cdot [O_3] \cdot [OC]$$ **equation 1-40**

$$\frac{d[RC]}{dt} = -k_{RC} \cdot [O_3] \cdot [RC]$$ **equation 1-41**

dividing equation 1-41 by equation 1-40 and integrating between t=0 and t_R the following relationship is obtained:

$$\ln \frac{[RC]}{[RC]_0} = -\frac{k_{RC}}{k_{OC}} \cdot \ln \frac{[OC]}{[OC]_0}$$ **equation 1-42**

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

1.4 Coupling Ozonation-Biological treatment

When oxidation treatments do not achieve a total pollutant mineralization or long reaction times are necessary to mineralize, a subsequent biological treatment would be convenient in order to achieve concentration of these compounds below the accepted values. In the last decades, numerous studies integrating chemical and biological oxidation processes for water treatment were carried out (Wang et al., 1989; Stowell et al., 1992; Scott and Ollis, 1995, 1997; Amat et al., 2003; Contreras et al., 2003), obtaining satisfactory biodegradable improvements after pretreatment.

Biological treatment of wastewater is often the most economical alternative when compared with other treatments options. Characteristics of the wastewater, like pH and presence of inhibitor compounds in the matrix, can be very important for a biological treatment. Moreover, biological degradation can be affected by brusque changes of treatment conditions, for example, the shock load appears when the toxic concentration in the influent increases. A toxic shock can increase the reaction time, diminish the efficiency and may poison the biomass (Buitrón et. al., 2005). Another important factor is that although many organic molecules can be degraded by biological treatment, many other are biorecalcitrants, i.e. resistant to biodegradation. In the same way, chemical treatments can destroy various synthetic organic compounds, but the capital and chemicals cost associated with the chemical oxidation can often be a limiting factor for wastewater treatment. A potentially viable solution is the combination of chemical and biological treatment processes as an economical option to treat biorecalcitrant organic chemicals in wastewater (Adams et al., 1997).

1.5 Ozone installation

Basically, ozonation devices in both water treatment plant and laboratory consist of an oxygen source, an ozone generator, a contact reactor and an ozone destructor. The operational understanding of the different installation parts as well as the control of factors that influence the overall process efficiency can considerably contribute to a proper operation of an ozonation device.

1.5.1 Ozone generation

Nowadays, numerous methods to produce ozone are known and a large amount of patents have been published. Nevertheless, three categories of ozone production stand out as the most important. Electrochemical, UV and discharge methods are those most used. Among them, the last one appears as the most common in water treatment.

In the discharge method, a continuous flow of oxygen or oxygen containing-gas (usually air) passes through the space between two electrodes separated by a dielectric material which is habitually glass made. When a voltage is supplied to the electrodes, a corona discharge is formed between the two electrodes, and the oxygen in the discharge gap is converted to ozone. So, oxygen molecules (O_2) are split into oxygen atoms (O) and then oxygen atoms combine with remaining oxygen molecules to form ozone. The ozone production by electrical discharges can be described by the following reaction:

$$3O_2 \xrightarrow{Discharges} 2O_3 + heat$$

This type of ozone generation is based on a reversible reaction. As a result, the inverse reaction increases when temperature rises. Consequently, more oxygen molecules are formed.

In the electrochemical method, an electrical current is applied between an anode and cathode in an electrolytic water solution containing high electronegative anions. Thus, a mixture of oxygen and ozone is produced at the anode.

When oxygen is bombarded with ultraviolet radiation (UV), the oxygen molecules are divided in oxygen atoms that combine with oxygen molecules to form ozone. The electrochemical and the UV methods are used when low quantities of ozone are needed (e. g. at laboratory scale).

1.5.2 Reactor and mass transfer

After ozone production, the gas stream is bubbled into a reactor containing the water to be treated. In order to have high transfer of ozone into water, the reactor should promote the maximal interfacial area. Usually, the reduction of the bubble size is achieved by using small size ozone diffusers. However, the use of ozone diffuser in the form of porous disc or rods can suffer the reduction of the ozone transfer by the presence of suspended solids or oxidized precipitates. Side streams injectors can be used to avoid plugging. Moreover this type of injector gives higher ratio of gas flow rate to liquid flow rate and higher mixing efficiency (Gogate and Pandit, 2004).

Ozone transfer efficiency from gas to liquid phase is mainly controlled by physical parameters such as temperature, gas flow rate, ozone partial pressure, and reactor geometry. Besides, chemical factors like pH, ionic strength and composition of aqueous solutions also affect ozone transfer (Sotelo et al., 1989; Tiware, 2007). The effect of physical parameters can be represented by partition coefficients and a mass transfer coefficient, while the effect of chemical parameters can be represented by a description of the ozone decomposition and consumption in the aqueous phase.

The developing of a valid model to describe the behaviour of an ozonation system needs a proper experimental determination of the mass transfer coefficient. Usually, the ozone physical solubility in water is described by the parameter:

$$m = \frac{[O_3]_L}{[O_3]_G}$$ **equation 1-43**

where m = ozone solubility parameter, $[O_3]_L$ = ozone concentration in the liquid and $[O_3]_G$ = ozone concentration in the gas.

This equation describes the equilibrium between the ozone concentration in the liquid and the ozone concentration in the gas.

The size of the bubbles during ozone contact along with the presence of most OH· scavengers also has an important role in the mass transfer. The control of all these parameters is essential to achieve good determination of reaction kinetics between ozone and organic compounds (Lopez-Lopez et al., 2007). The mass transfer inside a bubble plume reveals that the mass transfer process is affected by a number of factors. The contact area depends on the bubble diameter. Thus, at the same fraction, the contact area increases as the size of the bubbles decreases. In addition, the bubble diameter reduction increases the contact time. However, in practice, to reduce the bubble size may not be the most cost-effective solution for achieving good mass transfer efficiency (Gong et al., 2007). Other factors like the presence of salts in the solution and stirring have great importance on the ozone water solubility. Therefore, to achieve an optimal treatment condition, along with the evaluation of the wastewater to be treated, the assessment of parameters like mass transfer must be taken into account for an effective treatment.

1.5.3 Destruction of the residual ozone

In an ozonation process, not all the ozone present in the bubbles passes to the liquid phase, releasing in the air the residual ozone. The tropospheric ozone is a contaminant and depending the total dose, it can be toxic. The total dose of ozone is commonly expressed as a CT value, which is the product of the ozone concentration (C) and exposure time (T) (Coman et al., 2005). So, during an ozonation process, after the ozone contact with the wastewater, the residual ozone must be collected and destroyed. Generally, it is destroyed by three methods: thermo-decomposition, catalytic and chemical reaction. The destruction of the ozone as well as the control of the ozone concentration in air is essential for the safety of workers near the zones of ozone application.

The Catalytic destruction of ozone is the most used method to reduce ozone to oxygen due to its easy installation whether in a new or existent ozone equipments. Active carbon is also used to reduce ozone in oxygen. However, the carbon is consumed during ozone reduction and in that case its use is limited to applications with low ozone doses. Another alternative to reduce ozone to oxygen are performed by means of temperature increment up to values higher than 300 °C.

1.6 Contaminants in water

A common problem to perform the toxicity assessment of contaminated environmental samples resides in the fact that only a fraction of the amount of contaminants is responsible for toxic effects. This leads to a situation where the knowledge about the potential toxicity of some contaminants contributes to a proper evaluation of the hazardousness of wastewaters (Esplugas et al., 2002; Eljarrat and Barcelo, 2003; Pera-Titus et al., 2004).

Nowadays, the emission of the “emerging” or “new“ unregulated contaminants have become a great environmental problem. Among them, those that are used in large quantities in every day life, such as pharmaceuticals, surfactants, plasticizers and various industrial additives deserve a special attention (Petrovic et al., 2003). Concerned about the presence of emerging contaminant in environment, scientists from numerous countries started to investigate the suitability of different water treatment methods to remove them.

The Water Policy Report published in April 16th 2007 by the US Environmental Protection Agency (EPA) via “InsideEPA.com” reported a study concerning the surveillance of emerging contaminants in sewage sludge. In this study, EPA has added pharmaceuticals and personal care products (PCPs) to the list of contaminants being studied. This research should give significant new occurrence data about unregulated contaminants.

The survey comes as EPA is increasingly looking towards contaminants of emerging concern (CECs) in the wake of findings that some fish and other aquatic organisms may be adversely affected by high levels of pharmaceuticals and pharmaceutical byproducts found in waterbodies. The study also found that the concentration of emerging contaminants is much higher in biosolids than it is in effluent from wastewater treatment plants. However, it remains unclear whether the higher concentration is harmful to humans and the environment, because it is not yet known whether the contaminants may leach out of the biosolids into surface water or groundwater supplies. Besides, the sheer number of emerging contaminants in biosolids, which some EPA and industry sources estimate to be in the thousands, poses a daunting research challenge.

Although the concentration of pharmaceuticals and surfactants found in WWTP effluents and drink water are much lower than those used in this work (Ternes, 1998), it is assumed that the experimental data found could be useful for effluents with higher concentration of these compounds such as hospital effluents, wastewater from pharmaceutical industry or concentrate from membrane processes.

This work deals with the treatment of compounds representing the class of pharmaceuticals (Sulfamethoxazole and Bezafibrate) and surfactants (quaternary ammonium compounds). These compounds are used in a large scale and recently are the aim of diverse environmental studies in order to assess their hazard potential for environment. Besides, as a previous study, the 4-chlorophenol abatement by means of coupling ozonation-biological treatment was carried out.

1.6.1 4- Chlorophenol

Chlorinated phenols (CPs) are synthetic organic compounds, obtained mainly at commercial scales by chlorinating phenols and hydrolyzing chlorobenzenes. They are also produced as intermediates during the wood pulp bleaching. CPs can also be formed during water disinfection by chlorination, cooking process or distillation of wood. Another source of chlorophenols is natural processes that can produce chlorinated organic compounds in soils by chemical reactions, fungus or biological decomposition of pesticides and fungicides. It has been shown the presence of CPs in a large number of ecosystems, like surface and ground water, bottom sediments, atmospheric air and soils. Analysis of the surface water from Canada (1986), Greece (1999) and Poland (2001), showed that the CPs could be found from 2 to 2000 ng/L (Czaplicka, 2004).

CPs usually present a resistance to chemical and biological treatments in environmental conditions. The toxicity of these substances to man and animals is comparable to that of phenol and therefore great care is required to achieve a complete abatement of chlorophenols in water and wastewater (Keith et al., 1979, Deanna and Shieh, 1986). The intermediates of 4-chlorophenol obtained by means of treatment with ozone have been detected and its reaction mechanism has also been proposed (Andreozzi and Marotta, 1999).

1.6.2 Quaternary Ammonium Compounds

Quaternary ammonium compounds (QACs) are an important class of industrial chemicals widely used in the cosmetic industry, detergents, pesticide formulations, etc. The following properties are the basis for their widespread use: surface activity, adsorption onto negatively charged solids, biocidal activity and their reactions with anionic surfactants. Thus, they are used in large amounts in a number of applications such as fabric softeners, disinfectants, demulsifiers, emulsifiers, wetting agents and processing aids (Garcia et al., 1999). Surfactants are toxic in the mg L^{-1} range and lower to a wide variety of aquatic organisms, and may also cause serious effects to human beings. Those compounds require extensive treatment before delivery to environment. Nevertheless, various domestic and industrial surfactants are disposed of in rivers and lakes without prior treatment (Boethling, 1984, Basar et al., 2004).

Some procedures have been considered as potentially applicable for the mineralization of surfactants, in particular and organic pollutants in general: bacterial biodegradation, synthesis of destructible surfactants, photolysis and photocatalytic degradation. Each of those processes has particular advantages and disadvantages. For example: the production of degradable surfactants generally involves high costs (Hidaka et al., 1995). Moreover, biodegradation processes using activated sludge are generally considered to be the most economical way of treating biodegradable surfactants. However, some kinds of surfactants are biorecalcitrant due to enzymatic deficiencies or to their toxicological properties. Cationic surfactants containing a quaternary ammonium ($R4N^+$; where R=alkyl chain and N=quaternary nitrogen), often have a strong biocidal nature. The biodegradability in these compounds usually decreases with the number of non-methyl alkyl groups (i.e. $R_4N^+ < R_3MeN^+ < R_2Me_2N^+ < RMe_3N^+ < Me_4N^+$). Besides, a replacement of a methyl group in a quaternary amine with a benzyl group can decrease biodegradability (i.e. $RBzMe_2N^+ < R_2MeN^+$) (Adamns and Kurzhikannil, 2000).

Many studies have been performed for recalcitrant surfactants by means of chemical and photochemical degradation, like O_3/UV, H_2O_2/UV and TiO_2/UV (Hidaka et al., 1990; Schroder et al., 1999; Sanz et al., 2003; Amat et al, 2004). However, works dealing with the treatment of quaternary ammonium compounds are scarce in the literature.

1.6.3 Sulfamethoxazole

Among the pollutants presents in the lists of emerging contaminants, various pharmaceuticals can be found (Eljarrat and Barcelo, 2003; Smital et. al., 2004). Some classes of antibiotics and hormones have been found in surface water and sewage wastewater treatment plants (WWTP) effluents (Ternes, 1998; Hirsch et al., 1999; Kolpin et al, 2002). Antibiotics deserve a special concern due to their widely use and even for the specific effect caused by human contamination via environmental exposure such as bacterial resistance (Gilliver et al., 1999). Their presence in the environment is directly related to the resistance to antibiotic shown by bacteria in natural media (Pretovic et al., 2003) and some pharmaceuticals are only partially removed by biological treatment. The presence of a pharmaceutical in the WWTP supposes an introduction of compound completely different from the majority of compounds, having a different chemical behaviour when compared with the rest of organic matter present. The lack of appropriate detection methods of pharmaceuticals and their metabolites is also a problem for a suitable treatment (Heberer, 2002).

Sulfamethoxazole (SMX) in combination with trimethoprim is largely used to treat respiratory diseases like pneumonia. Coccidiosis, diarrhea, gastroenteritis are well known illnesses that can be treated with sulfamethoxazole. Large number of animals are also treated by a combination of drugs containing sulfamethoxazole, generating residues by excreting of unmetabolized or active metabolites (Tolls, 2002; Jones et. al., 2002). Concerning this, many countries have established 1mg L^{-1} the maximum residue levels for this compound in food (Nevado et al., 2001).

1.6.4 Bezafibrate

Bezafibrate (2-[4-[2-[(4-chlorobenzoyl)amino]ethyl]phenoxy]-2-methyl-propanoic acid) belongs to the group of fibrate drugs, which is an important class of pharmaceuticals largely used for the treatment of hyperlipidaemia, when high cholesterol levels are associated with increased levels of triglycerides. Recently, bezafibrate was included in the list of the most used pharmaceuticals in the world (Cermola et al., 2005). Bezafibrate concentrations up to 27 ng L^{-1} and 4.6 μg L^{-1} have been found in drinking waters and in Sewage Treatment Plant effluents (STP) in Germany (Stumpf et al., 1996; Ternes, 1998) and up to 57.15 ng L^{-1} in Italian rivers (Calamari et al., 2003). A recent work demonstrates that, at the concentration detected in environment, BZF does not induce acute or chronic toxic effects in non-target organisms. Nevertheless, its harmfulness to the environment can not be excluded due to the possible mixture toxicity, synergistic and additives effects, bioaccumulation and biomagnification (Isidori et al., 2007). Concerning BZF ozonation, no work dealing with the toxicity assessment of BZF ozonation byproducts was found in the literature.