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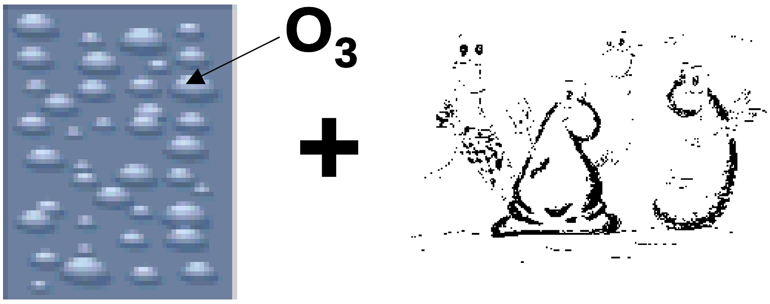
DEGRADATION AND BIODEGRADABILITY ENHANCEMENT OF NITROBENZENE AND 2,4-DICHLOROPHENOL BY MEANS OF ADVANCED OXIDATION PROCESSES BASED ON OZONE



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Dr. Santiago Esplugas Vidal

Barcelona, Noviembre de 2002

La perseverancia refleja siempre el estado de nuestra vida interior, de nuestra filosofía y de nuestra perspectiva

David Guterson

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NITROBENZENE

2,4-DICHLOROPHENOL

1. Introduction

Reflecting the new environmental conscience, already pointed out in the Spanish Water Act 29/1985, the Directive 2000/60/EC points out that "*water is not a commercial product like any other but, rather, a heritage which must be protected, defended and treated as such*". The domestic use and industrial activity, of especial impact among the developed countries, generate high amounts of residual waste water, whose direct disposal to the natural channels causes a considerable impact in the environment. This fact, together with the necessity of recycling this water for new uses, makes practically essential the purification of waste water to achieve the desired quality degree.

1.1. Definition of pollution of a watercourse.

The Directive 2000/60/EC defines the *pollution* as the "direct or indirect introduction, as a result of human activity, of substances or heat into the air, water or land which may be harmful to human health or the quality of aquatic ecosystems or terrestrial ecosystems directly depending on aquatic ecosystems, which result in damage to material property, or which impair or interfere with amenities and other legitimate uses of the environment".

A pollutant can be defined as the product that can cause a detrimental alteration of the physical, chemical or biological properties of a watercourse. Thus, they can be classified as physical, chemical or biological pollutants:

a) *Physical pollutants*: color, odor, solids, temperature (the solubility of oxygen changes from 14.6 $mg.L^{-1}$ at 0ºC to 7.6 $mg.L^{-1}$ at 30ºC in pure water; this fact affects the biological activity)

b) *Chemical pollutants*: They are classified into organic and inorganic:

   - Organic: domestic wastes (fats, oils, surfactants…), agricultural wastes (pesticides, herbicides,…) and industrial wastes (phenols, oils, hydrocarbons…)
   - Inorganic: metallic salts (chlorides, sulfates, nitrates,…), heavy metals (Cu, Cd, Cr, Hg, Pb, As, …) and dissolved gases (methane, hydrogen sulfide…)

   Some of them can be biodegraded by means of the microorganism present in the water. Some other have a extremely low biodegradability and are called *refractory contaminants.* They can remain in water for long periods in which its chemical action and/or toxicity may constitute a potential hazard.

c) *Biological pollutants*: the presence of determined microorganisms is necessary to complete the food chain. However, besides this group can be found pathogenic organisms, which can cause typhoid fever, dysentery, diarrhea and cholera.

The European Union made out a list of dangerous compounds, considered as contaminants, to which constantly new substances are added ("black list" of the E.U., see Table 1.1).

Table 1.1. Black list of chemicals substances selected by the E.U. (Harrison, 1992)

Group	Included substances
Chloride Hydrocarbons	Aldrin, dieldrin, chlorobenzene, dichlorobenzene, chloronaphthalene, chloroprene, chloropropene, chlorotoluene, endosulfane, endrin, hexachlorobenzene, hexachlorobutadiene, hexachlorocyclo-hexane, hexachloroethane, PCBs, tetrachlorobenzene, trichlorobenzene.
Chlorophenol	Monochlorophenol, 2,4-dichlorophenol, 2-amino-4-chlorophenol, pentachlorophenol, 4-chloro-3-methylphenol, trichlorophenol.
Chloroanilines and nitrobenzenes	Monochloroanilines, 1-chloro-2,4-dinitrobenzene, dichloroaniline, 4-chloro-2-nitrobenzene, chloronitrobenzene, chloronitrotoluene, dichloronitrobenzene.
Policyclic Aromatic Hydrocarbons	Antracene, biphenyl, naphthalene, PAHs
Inorganic substances	Arsenic and its compounds, Cadmium and its compounds, Mercury and its compounds
Solvents	Benzene, carbon tetrachloride, chloroform, dichloroethane, dichloroethylene, dichloromethane, dichloropropane, dichloropropanol, dichloropropene, ethylbenzene, toluene, tetrachloroethylene, trichloroethane, trichloroethylene.
Other	Benzidine, chloroacetic acid, chloroethanol, dibromomethane, dichlorobenzidine, dichloro-diisopropyl-ether, diethylamine, dimethylamine, epichlorhydrine, isopropylbenzene, tributylphosphate, trichlorotrifluoroethane, vinyl chloride, xilene.
Pesticides	Cyanide chloride, 2,4-dichlorophenoxyacetic acid and derivatives, 2,4,5-trichlorophenoxyacetic acid and derivatives, DDT, demeton, dichloroprope, dichlorvos, dimethoate, disulfoton, phenitrothion, phenthyon, linuron, malathion, MCPA, mecoprope, monolinuron, omethoate, parathion, phoxime, propanyl, pirazone, simacine, triazofos, trichlorofon, trifularin and derivatives.

More recently, the Directive 2000/60/EC defined *pollutant* as "any substance liable to cause pollution, in particular those listed below:

- Organohalogen compounds and substances which may form such compounds in the aquatic environment
- Organophosphorous compounds
- Organotin compounds
- Substances and preparations, or the breakdown products of such, which have been proved to possess carcinogenic or mutagenic properties or properties which may affect steroidogenic, thyroid, reproduction or other endocrine-related functions in or via the aquatic environment
- Persistent hydrocarbons and persistent and bioaccumulable organic toxic substances
- Cyanides
- Metals and their compounds
- Arsenic and its compounds
- Biocides and plant protection products
- Materials in suspension
- Substances which contribute to eutrophication (in particular, nitrates and phosphates)
- Substances which have an unfavorable influence on the oxygen balance (and can be measured using parameters such as BOD, COD, etc.)"

This Directive is to contribute to the progressive reduction of emissions of hazardous substances to water. In Article 16, it is pointed out that specific measures against pollution of water by individual pollutants or groups of pollutants presenting a significant risk to or via the aquatic environment have to be adopted. Those measures are aimed at the progressive reduction of that pollutants and, for priority hazardous substances, the cessation or phasing out of discharges, emissions and losses within 20 years after their adoption at Community level. The list of the first 33 priority pollutants has been presented in the Directive 2455/2001/EC.

1.2. Studied compounds: nitrobenzene and 2,4-dichlorophenol

Aromatic nitro compounds are commonly used in the manufacture of pesticides, dyes and explosives, and are often detected in industrial effluents, in ambient freshwater, in ambient environments and in the atmosphere (Lipczynska-Kochany, 1992). Moreover, nitroaromatic hydrocarbons are naturally generated, as a result of photochemical reactions produced in the atmosphere (in countries like Germany, Japan, Switzerland and USA nitrophenol and dinitrophenol have been detected in air and rain) (Alonso y del Pino, 1996 and references herein).

Chlorophenols constitute a group of organic substances that are introduced into the environment as a result of several man-made activities, such as waste incineration, uncontrolled use of wood preservatives, pesticides, fungicides and herbicides, etc, as well as by-products formed during bleaching of pulp with chlorine and in the disinfection by chlorination to get drinking water (Ahlborg and Thunberg, 1980).

As nitroaromatics and chlorophenols constitute a threat to human health and produce a public concern, several of them have been listed among the 130 priority pollutants given by the US EPA in the federal Clean Water Act (CWA), e.g. nitrobenzene and 2,4-dichlorophenol (EPA, 2002). Recently, the US EPA has also included them in a reduced list of drinking water contaminants to be investigated in the period 2001-2005 (Hayward, 1999).

1.2.1. Nitroaromatic compounds. Nitrobenzene.

Aromatic nitro compounds are commonly used in industrial processes (manufacture of pesticides, dyes and explosives) and as a consequence they appear as contaminants in every kind of water (especially in surface waters) and industrial wastewaters. This substances present a high toxicity, provoking serious health problems: blood dyscrasia, eyes and skin irritations, they affect the central nervous system, etc.

Several studies have shown the presence of these substances in surface waters (Howard, 1989) and ground waters (Duguet et al., 1990). One of the main ways of contamination of superficial wastewaters by nitroaromatic compounds are the residual industrial effluents. In Table 1.2, data related to the presence of these substances in different industrial effluents is presented.

Table 1.2. Concentration of nitroaromatic compounds in industrial effluents (Howard, 1989)

Industry	**Concentration of 2-nitrophenol (µg.L^{-1})**	**Concentration of 4-nitrophenol (µg.L^{-1})**
Iron and steel manufacture	<21	-
Foundries	20 - 40	-
Pharmaceuticals	<10	-
Organic chemical manufacturing/plastics	<130	<190
Rubber processing	<4,9	-
Textile mills	<4,1	<10
Coal mining	<17	-
Metal finishing	72 - 320	<10
Electrical/electronic components	75 - 320	22 - 35
Photographic equipment/supplies	19 - 32	<57
Oil refining	1400	<10

The presence of these compounds in water is determined by its solubility and stability. The solubilities of some of these compounds are presented in Table 1.3. As it can be observed, values are very different, being some of them very high. Some of these compounds are very stable in water, and consequently they can remain in her long periods of time, although the solar action, besides the presence of other substances (in general, humics) can lead to its partial elimination.

Table 1.3. Solubility of nitroaromatic compounds in water (Howard, 1989)

Compound	**Solubility (mg.L^{-1})**
1-Chloro-2-Nitrobenzene	440 (20ºC)
1-Chloro-4-Nitrobenzene	225 (20ºC)
2,4-Dinitrophenol	6000 (25ºC)
2,4-Dinitrotoluene	300 (22ºC)
Nitrobenzene	1900 (20ºC)
2-Nitrophenol	1060 (20ºC)
3-Nitrophenol	13500 (25ºC)
4-Nitrophenol	11300 (20ºC)
2-Nitrotoluene	652 (30ºC)
4-Nitrotoluene	442 (30ºC)
Propoxur	1750 (20ºC)
Carbaryl	32 (20ºC)
Diuron	37,3 (20ºC)

Nitrobenzene (NB)

Nitrobenzene ($C_6H_5NO_2$, molecular weight 123.1), is a pale yellow liquid with an odor that resembles bitter almonds. Depending on the purity, its color varies from pale yellow to yellowish brown. Nitrobenzene was first synthesized in 1834 by treating benzene with fuming nitric acid and was first produced commercially in England in 1856. The relative ease of aromatic nitration has contributed significantly to the large and varied industrial applications of nitrobenzene, other aromatic nitro compounds, and their derivatives (Mark et al., 1992).

Physical properties.

Nitrobenzene is readily soluble in most organic solvents and is completely miscible with diethyl ether and benzene. It is a good solvent for aluminum chloride and is therefore used as solvent in Friedel-Craft reactions. It is only slightly soluble in water (0,19% at 20ºC; 0,8% at 80ºC). Some other physical properties of nitrobenzene are as follows (see Table 1.4)

Table 1.4. Physical properties of nitrobenzene (Ullmann's, 1991)

Physical property	Value
Melting point	5.85ºC
Boiling point	
at 101 kPa	210.9ºC
at 13 kPa	139.9ºC
at 0,13 kPa	53.1ºC
Density	
$d_4^{1.5}$ (solid)	1.344
$d_4^{15.5}$ (tech. spec.)	1.208-1.211
d_4^{25}	1.199
Vapor pressure (20ºC)	0.15 mm Hg
Viscosity (15ºC)	2.17×10^{-2} mPa.s
Surface tension (20ºC)	43.35 mN/m
Dielectric constant (20ºC)	35.97
Specific heat (30ºC)	1.418 J/g
Latent heat of fusion	94.1 J/g
Latent heat of vaporization	331 J/g
Flash point (closed cup)	88ºC

Toxicity

Nitrobenzene is a very toxic substance: the maximum allowable concentration for nitrobenzene is 1 ppm or 5 mg.m^{-3} (see International Chemical Safety Cards). It is readily absorbed by contact with skin and by inhalation of vapor, being the primary effects:

- The conversion of hemoglobin to methemoglobin; thus the conversion eliminates hemoglobin from the oxygen-transport cycle. Cyanosis appears when the methemoglobin level reaches 15%.
- Irritation of the skin and eyes.
- Nitrobenzene affects the central nervous system and produces fatigue, headache, vertigo, vomiting, general weakness, and in some cases unconsciousness and coma.

There generally is a latent period of 1-4 hours before signs or symptoms appear. Chronic exposure can lead to spleen and liver damage, jaundice and anemia. (Mark et al., 1992; Ullmann's, 1991)

Uses (OPPT, Chemical Fact Sheets, 1995):

The largest end use for nitrobenzene is in the production of aniline and aniline derivatives, such as methyl diphenyl diisocyanate (MDI). Approximately 95-98% of nitrobenzene is converted to aniline. Nitrobenzene is also used in shoe and floor polishes, leather dressings, paint solvents and other materials to mask unpleasant odors. A significant merchant market for nitrobenzene is its use in the production of the analgesic acetaminophen.

Presence of nitrobenzene in the environment (OPPT, Chemical Fact Sheets, 1995 and references herein):

Nitrobenzene is released into the environment primarily from industrial uses but can also be formed in the atmosphere by the nitration of benzene, a common air pollutant. The largest sources of nitrobenzene release are from its manufacture and primary use as a chemical intermediate in the synthesis of aniline. Smaller amounts are also released from consumer products in which nitrobenzene is used as a solvent. The most familiar of these are metal and shoe polishes.

It can evaporate when exposed to air. Once in air, nitrobenzene breaks down to other chemicals. It dissolves when mixed with water. Most releases of nitrobenzene to the U.S. environment are to underground injection sites. In 1992, only a small percent (6%) of environmental releases of nitrobenzene was to air. It can also evaporate slowly from water and soil exposed to air. Available information indicates that nitrobenzene is moderately toxic to aquatic life. Nitrobenzene may be stored in plants, but is not expected to accumulate in fish.

About the stability of nitrobenzene in water, it has been estimated that its half life varies from one day for natural channels, as it has been confirmed by works carried out by Zoeteman et al. (1980) in the Rhin river (Holland), and 3.8 days in an aerated lagoons (Davis et al., 1983). Because it is a liquid that does not bind well to soil, nitrobenzene that makes its way into the ground can move through the ground and enter groundwater. In surface water, nitrobenzene was detected in only 0.4% of surface water stations and in 1.8% of reporting stations on industrial wastewaters. In Table 1.5, those industries in whose effluents nitrobenzene has been detected are indicated. Furthermore, the presence of nitrobenzene in municipal wastewaters in a concentration between 20 and 100 $\mu g.L^{-1}$ has been detected.

Table 1.5. Concentration of nitrobenzene in different industrial effluents (Howard, 1989).

Industry	Average concentration ($\mu g.L^{-1}$)
Oil refining	7.7
Leather tanning	3.7
Nonferrous metals	47.7
Organics and plastics	3876.7
Pulp and paper	124.3
Auto and other laundries	40.4
Pesticides manufacture	16.3
Explosives	51.7
Organic chemicals	43.7
Inorganic chemicals	1995.3

As it has been commented before, aromatic nitro compounds have been included in the priority pollutants selected by the European union (see Table 1.1). Nevertheless, these compounds have been little studied, paying more attention to those compounds in whose composition halogens are present. Recently, the US EPA (United States Environmental Protection Agency) has included it in a the reduced list of drinking water contaminants to be assessed during the next five years for a possible future regulation (Hayward, 1999).

Chemical properties

Nitrobenzene reactions involve substitution on the aromatic ring and reactions involving the nitro group. Under electrophilic conditions, the substitution occurs at a slower rate than for benzene, and the nitro group promotes meta substitution. Nitrobenzene can undergo halogenation, sulfonation and nitration, but it does not undergo Friedel-Craft reactions. Under nucleophilic conditions, the nitro group promotes ortho and para substitution.

The withdrawing character of the nitro group depletes the aromatic ring of electron density. Hence, the aromatic ring of nitrobenzene is generally more susceptible to nucleophilic rather than electrophilic substitution. Direct ozonolysis is an electrophilic reaction of the oxidant, whereby ozonolysis would occur at the meta position. The mechanism of the OH radical on aromatic compounds is analogous to an electrophilic substitution. It does not imply that it is positively charged – its electrophilic behavior is not surprising in view of the high electron affinity of this species. The electrophilic substitution reactions are retarded by electron-accepting substituents.

1.2.2. Chlorophenols. 2,4-Dichlorophenol

Some chlorophenols are used as pesticides. Others are used in antiseptics. Small amounts are produced when water is disinfected with chlorine. They are also produced while bleaching wood pulp with chlorine to make paper. They have obtained notoriety as hazardous substances, because most of them are toxic and present long persistence in the environment. Laboratory studies carried out with animals showed that they developed liver and immune system effects. High levels of chlorophenols given to pregnant female rats in their drinking water reduced the number of babies they had, and caused low birth weights (ATSDR, 1999).

The presence of these substances has been detected in surface and ground waters (Howard, 1989). In Table 1.6, data related to the presence of these substances in different industrial and municipal effluents is presented.

Table 1.7 presents the solubilities of some of these compounds, which will determine its presence in different types of water. As it can be observed, they are in general readily soluble in water.

Table 1.6. Concentration of chlorophenolic compounds in different effluents (Howard, 1989)

Industry	Concentration of 2-chlorophenol (μg.L^{-1})	Concentration of 2,4,6-trichlorophenol (μg.L^{-1})
Secondary sewage effluent	1.7	-
Herbicide production waste	2.88	-
Leather tanning and finishing	-	2200 – 5900
Foundries	-	240 - 1400
Aluminium forming	-	260 - 1800

Table 1.7. Solubility of some chlorophenols in water (Ullmann's, 1991)

Compound	Solubility at 20ºC (g.L^{-1})
2-Chlorophenol	28.5
3-Chlorophenol	26.0
4-Chlorophenol	27.1
2,4-Chlorophenol	4.5
2,4,6-Trichlorophenol	0.8
Pentachlorophenol	0.014

2,4-Dichlorophenol (DCP)

2,4-Dichlorophenol is used in manufacturing 2,4-dichlorophenoxyacetic acid (2,4-D) and 2-(2,4-dichlorophenoxy)propionic acid (2,4-DP). Industrially, 2,4-dichlorophenol can be obtained by chlorinating phenol, *p*-chlorophenol, *o*-chlorophenol, or a mixture of these compounds in cast-iron reactors.

Physical properties.

2,4-dichlorophenol is solid at ambient temperature (colourless crystals) and has a strong characteristic odor. It is slightly soluble in water, but highly soluble in alcohols. Some physical properties of nitrobenzene are as follows (see Table 1.8).

Table 1.8. Physical properties of 2,4-dichlorophenol (Ullmann's, 1991)

Physical property	Value
Melting point	45ºC
Boiling point	
at 101 kPa	210.9ºC
at 13 kPa	146ºC
at 0,13 kPa	53ºC
Density (50ºC)	1.388 g.mL^{-1}
Vapor Pressure (53ºC)	133 kPa
Specific heat (20ºC)	190 J.mol^{-1}.K^{-1}
Viscosity (50ºC)	2.65 mPa.s
Solubility in water (20ºC)	4.5 g.L^{-1}
Flash point (closed cup)	113ºC

Toxicity

In chlorophenol production, irritation symptoms of the nose, eyes, respiratory tract, and skin resulting in chloroacne have been observed. The results of epidemiology studies on the long-term effects of chlorophenols are quite contradictory and have not allowed the experts to reach any firm conclusions (Mark et al, 1992).

The substance can be absorbed into the body by inhalation of its aerosol, through the skin and by ingestion (see International Chemical Safety Cards). TLV (Threshold Limit Value) has not been established. Lethal dose (LD_{50}) for rats has been found to be 580 mg.kg^{-1} (oral) and 1730 mg.kg^{-1} (percutaneous). Insuffiicent data are available on the effect of this substance on human health, therefore utmost must be taken. Increasing attention is devoted at the present time to the risks of 2,4-dichlorophenol in relation to skin adsorption under the EPA's testing program for high-production-volume chemicals.

EPA recommends that drinking water contain no more than 0.03 mg.L^{-1}

Uses

As it has been commented above, the main use of 2,4-dichlorophenol is as a key intermediate in the synthesis of chloride-based herbicides, such as 2,4-dichlorophenoxyacetic acid (2,4-D) and 2-(2,4-dichlorophenoxy)propionic acid (2,4-DP). It is also found in the selective postemergence herbicide (applied between the emergence of a seedling and the maturity of a crop plant), diclofop-methyl and as a selective preemergence herbicide (used before emergence of seedling above ground), oxadiazon.

Environmental considerations of chlorophenols (Ullmann’s, 1991)

Chlorophenols constitute a group of organic substances that are introduced into the environment as a result of several man-made activities, such as waste incineration, uncontrolled use of wood preservatives, pesticides, fungicides and herbicides, etc, as well as by-products formed during bleaching of pulp with chlorine and in the disinfection by chlorination to get drinking water (Ahlborg and Thunberg, 1980).

All chlorophenol possess bactericidal activities that increase with the degree of chlorination. Chlorophenols are highly toxic to algae. Most of plants are very sensitive to the phytotoxicity of chlorophenols. As for aquatic organisms, fish and other aquatic organisms absorb chlorophenols through their gills, gastrointestinal tract or skin. The EPA recommends that a maximum average 2,4-dichlorophenol concentration in surface waters not exceed 2.02 $mg.L^{-1}$.

Chlorophenols may be present in the aquatic environment in many forms. They may be dissolved in free or complexed form, adsorbed on suspended inert solid or benthic sediments, or carried in biological tissues. Volatilization transfers the chlorophenol from the water to the air but does not otherwise affect it. Biodegradation is the principal means by which chlorophenols are removed. It must be induced because the antimicrobial activities of these products require that the bacteria adapt.

Chemical properties (Ullmann’s, 1991)

Chlorophenols are versatile intermediates in chemical syntheses because both the hydroxyl group and the aromatic ring can react by both electrophilic and nucleophilic substitution. They are readily oxidized.

Electrophilic substitution is favored by the presence of chlorine atoms on the aromatic nucleus. Nucleophilic substitution for one or more of the chlorine atoms, although disfavored by the presence of the other chlorine atoms, is nevertheless used widely, for example to prepare various substituted diphenyl ethers, which serve as efficient herbicides.

1.3. Removal of refractory organic pollutants from water: NB and DCP

Refractory or recalcitrant compounds in this context are those which resist aerobic microbial degradation in conventional biological treatment processes and the natural environment. Both nitrobenzene and 2,4-dichlorophenol have been found to be non-biodegradable and inhibitory under our testing conditions (see section 5). Its low biodegradability makes necessary to find out other alternative techniques to the biological oxidation. The chosen method will depend on the characteristics of the contaminant itself.

1.3.1. Adsorption of organic compounds onto activated carbon

Carbon adsorption is an advanced waste water treatment method used for the removal of the refractory organic compounds as well as residual amounts of inorganic compounds such as nitrogen, sulfides, and heavy metals. This is a separation method in which the contaminant is transferred from a water phase, where it is dissolved, to the surface of active carbon where is accumulated for its subsequent extraction or destruction. The adsorption onto activated carbon is widely used for waste water treatment. Thus, it is used in the control of color and odors, in the removal of organic compounds or trihalomethanes precursors, to remove chlorine and in general to remove toxic compounds.

The adsorption of nitrobenzene (NB) and 2,4-dichlorophenol (DCP) onto activated carbon has been widely studied. Both NB and DCP showed to be well adsorbable compounds onto activated carbon, e.g. in the studies carried out by Sacher et al. (2001) and Speth et al. (2001). This method has been also combined with ozone, showing that the removal efficiency of nitrobenzene by O_3/activated carbon process was significantly higher than by ozonation (Sui and Ma, 2001). Removal of DCP has been performed as well by means of biological activated carbon (Ha et al., 2000; 2001), with the advantage of the bioregeneration of the activated carbon. Recently, GAC (granular activated carbon) has been also combined with photocatalysis (Malato et al., 2001).

1.3.2. Wet oxidation

In the wet oxidation processes, organic and inorganic compounds are oxidized in aqueous phase, with oxygen or air, at high pressure and temperature conditions. The temperature depends on the nature of the compounds to degrade, however it oscillates between 150 and 350ºC. Pressure goes from 20 to 200 bar. COD (chemical oxidation demand) removal ranges from 75 to 90% (Li et al., 1991). The mechanism of wet oxidation has been deeply studied and seems to take place by means of a free radical process. Among the compounds that have been catalogued as readily oxidizable by means of wet oxidation are aliphatic, aliphatic chlorides and aromatic which do not contain halogenated functional groups, such as phenols or anilines. Compounds contain halogen and nitro functional groups have been found to be difficult to be degraded by this method (Scott, 1997).

1.3.3. Supercritical water oxidation (SCWO)

It is about an innovative technique for the rapid destruction of organic pollutants without the production of harmful products. Pure water is considered to be supercritical when its temperature exceeds 374.2ºC and its pressure 221 bar. At this point, volume is three times higher that at room temperature, with a density of 0.322 $g.mL^{-1}$ and a dielectrical constant of only 5.3. As a result, this water can dissolve a lot of organic compounds and gases, such as oxygen, as water acts as a dense gas with the characteristic solvation of a non-polar organic compound.

Nitrogen containing compounds have shown to be difficult to be mineralized by SCWO. Koo and Lee (1994) pointed out that temperature substantially higher than 500ºC and/or catalysts are required for the faster and complete destruction of nitrogen containing aromatic compounds by SCWO. Chen and co. (2001) found that it was extremely difficult to oxidize NB to CO_2 and H_2O at temperatures lower than 923.15 K. Different studies concerning the degradation and modeling of DCP by SCWO have been performed (Li et al., 1994; Lin et al., 1998). Other oxidants, as hydrogen peroxide, can be added to the system. For DCP, conversions higher than 99.995% were obtained with hydrogen peroxide at 450ºC as compared to 87.6% conversion with oxygen at 500ºC in the study carried out by Lee and co. (1990).

1.3.4. Electrochemical oxidation

One of the main advantages of the electrochemical processes is that electrons are given or consumed within the electrodes, supplying a clean reactant which does not increase the number of chemical molecules involved in the process. Nevertheless, they present some disadvantages, as:

- The electrochemical treatment is expensive in comparison with other processes and the mechanism in water is rather complex
- The necessity of the effluent to be conductor, therefore in case that the stream to be treated does not present a good conductivity a salt should be added

The electrochemical oxidation of the organic compounds is thermodynamically favored against the competitive reaction of oxygen production by oxidation of water. However, the kinetics of oxidation of water is much faster than the kinetics of oxidation of the organic compounds, among other reasons because of its higher concentration (Palau, 1998).

The mechanism of the electrochemical processes involves three stages: electrocoagulation, electroflotation and electrooxidation. (Prousek, 1996):

$$\begin{aligned}&RH \xrightarrow{-e^-} RH^+\\&RH^+ \xrightarrow{-H^+} R^\bullet\\&R^\bullet + R^\bullet \rightarrow R-R\end{aligned}$$

The anodic oxidation is generally considered to be a direct technique, involving the direct transfer of an electron from the organic molecule to the electrode, thus generating a cationic radical. In the direct way, the fate of the cationic radical, the pH and the nature of the electrodes influence in a decisive manner on the formed products. The latter radical-radical combinations have been frequently observed.

Few studies have been found in the literature regarding the electrochemical oxidation of NB (Comninellis, 1994; Colucci et al., 1999) and DCP. While Huang and Chu (1992) showed that phenolic compounds were electrochemical oxidizable, Rodgers and co. (1999) proposed the electrochemical oxidation as a remediation method for chlorinated phenols but it was found to be hampered by anode fouling.

1.3.5. Photochemical processes

The addition of energy as radiation to a chemical compound is the principle of the photochemical processes. The molecules absorb this energy and reach excited states the enough time to be able to carry out chemical reactions.

A large amount of studies (Legrini et al., 1993 and references herein) dealt with the degradation of chemicals in water using the Hg emission at 253.7 nm produced by low-pressure mercury lamps. However, results showed that 253.7-nm irradiation alone cannot be used as an effective procedure for the removal of organics from water: it may be useful for the degradation of substituted aromatic, however it is totally inefficient for effective removal of chlorinated aliphatics. It should, however, be noted that low-pressure Hg lamps are quite efficient for water disinfection purposes. Medium and high pressure lamps, with a broader emission spectrum, have been more frequently used for the degradation of contaminants. Medium-pressure Hg lamps emit particularly strongly in the spectral region between 254 and 400 nm and are not only effective in generating hydroxyl radicals from e.g. hydrogen peroxide or ozone, but also by causing electronic transitions in a large number of organic molecules.

In the photochemical reactions, hydroxyl radicals are generated by water photolysis (Cervera and Esplugas, 1983):

$$H_2O \xrightarrow{h\nu} H^{\bullet} + OH^{\bullet} \qquad [1.1]$$

This reaction is a poor source of radicals, and in the reaction medium large quantity of reaction intermediates that absorb part of the radiation are generated, which decreases considerably the photooxidation kinetics of the contaminants. That fact makes the process valid only for effluents with low concentration of pollutants.

The photochemical treatment, although partially solving the problem of the refractory compounds, has some negative aspects in its practical application, as the high cost of UV radiation production. Furthermore, not all the emitted radiation is used, only the absorbed radiation, and only a fraction of this radiation produces chemical changes. This fact makes that some photodegradation reactions have a very slow kinetics. To accelerate the process, other oxidants like hydrogen peroxide and/or ozone, metallic salts or semiconductors like TiO_2 can be added, giving rise to the so-called Advanced Oxidation Processes. Instead of UV lamps, solar light could be used as radiation energy to degrade some compounds.

No effect was observed during direct photolysis of NB with a 150-W mercury-xenon lamp in the study carried out by Lipczynska-Kochany (1992). However, the degradation of NB by different irradiation sources has been studied by Rodríguez and co. (2002a), achieving a TOC removal of 53%, 60% and 76% by irradiation with 253.7-nm UV light, Xe lamp and solar light. With regard to DCP, Shen and co. (1995) pointed out that the photolytic properties of chlorophenols were highly dependent on the pH. Kuo (1999) reported a 48% and 77% of DCP removal at pH 6 and 9, respectively, by direct irradiation with a 150-W medium pressure mercury lamp.

1.3.6. Chemical oxidation: Advanced Oxidation Processes (AOPs)

They are generally used when biological processes have little efficiency. Chemical oxidation is the most effective process for the removal of organic pollutants present as traces in water. Chemical oxidation aims at the mineralization of the contaminants to carbon dioxide, water and inorganics or, at least, at their transformation into harmless products. They can be divided in two classes:

- Classical Chemical Treatments
- Advanced Oxidation Processes

Classical chemical treatments consist generally on the addition of an oxidant agent to the water containing the contaminant to oxidize it. Among the most widely used it is possible to emphasize (Chamarro et al., 1996):

- Chlorine: Strong and cheap oxidant, its main disadvantages are its little selectivity, that high amounts of chlorine are required and it usually produces carcinogenic organochloride by-products.
- Potassium permanganate: It is a strong but expensive oxidant, which works properly in a wide pH range. It is difficult to be handled and adds manganese to treated water.
- Oxygen: It is a mild oxidant that requires large investments in installations. Its low operating cost make the process attractive.
- Hydrogen peroxide: It is a multipurpose oxidant for many systems. It can be applied directly or with a catalyst. However, peroxide without catalyst does not attack some organic compounds.
- Ozone: It is a strong oxidant that presents the advantage of, as hydrogen peroxide and oxygen, not introducing new ions in the medium. It presents the disadvantage of being a unstable gas, and it has to be on-site produced. At basic pH produces hydroxyl radicals, thus it will be considered an AOP.

It has been frequently observed (Andreozzi et al., 1999 and references herein) that contaminants not amenable to biological treatments may also be characterized by high chemical stability and/or by strong difficulty to be completely mineralized. In these cases, it is necessary to adopt reactive systems much more effective than those adopted in conventional purification processes.

<u>Advanced Oxidation Processes</u> (AOPs) were defined by Glaze and co. (1987) as near ambient temperature and pressure water treatment processes which involve the generation of highly reactive radicals (specially hydroxyl radicals) in sufficient quantity to effect water purification. $OH^{\cdot}$ radicals are extraordinarily reactive species, that attack most of the organic molecules. The kinetics of reaction is generally first order with respect to the concentration of hydroxyl radicals and to the concentration of the specie to be oxidized. Rate constants are usually in the range of $10^8 – 10^{11}$ $M^{-1}.s^{-1}$, whereas the concentration of hydroxyl radicals lays between 10^{-10} and 10^{-12} M, thus a pseudo-first order constant

between 1 and 10^{-4} s^{-1} is obtained (Glaze and Kang, 1989). As it can be seen from Table 1.9, hydroxyl radicals are more powerful oxidants than the chemical agents used in traditional chemical processes.

Table 1.9. Oxidation power of selected oxidizing species (Beltrán et al., 1997a; Munter et al., 2001 and references herein)

Oxidation species	Oxidation power (V)
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.77
Permanganate	1.67
Hypobromous acid	1.59
Chlorine dioxide	1.50
Hypochlorous acid	1.49
Hypoiodous acid	1.45
Chlorine	1.36
Bromide	1.09
Iodine	0.54

Hydroxyl radicals are also characterized by a little selectivity of attack, attractive feature for an oxidant to be used in waste water treatment. Several and different organic compounds are susceptible to be removed or degraded by means of hydroxyl radicals, as it is shown in Table 1.10. Nevertheless, some of the simplest organic compounds, such as acetic, maleic and oxalic acids, acetone or simple chloride derivatives as chloroform or tetrachloroethane, cannot be attacked by OH radicals (Bigda, 1995).

Once hydroxyl radicals are generated, they can attack virtually all organic compounds. Depending on the nature of the organic species, two types of initial attack are possible: they can abstract a hydrogen atom, as in the case of alkanes and alcohols, or they can attach itself to a molecule, as in the case of aromatic compounds.

The versatility of AOPs is also enhanced by the fact that they offer different ways of OH radicals production, thus allowing a better compliance with the specific treatment requirements. It has to be taken into account, though, that a suitable application of AOPs to waste water treatment make use of expensive reactants as hydrogen peroxide and/or ozone, and therefore they should not replace, whenever possible, the more economic treatments as the biological degradation.

Table 1.10. Oxidizable compounds by hydroxyl radicals (Bigda, 1995)

Compounds	
Acids	Formic, gluconic, lactic, malic, propionic, tartaric
Alcohols	Benzyl, *tert*-butyl, ethanol, ethylene glycol, glycerol, isopropanol, methanol, propenediol
Aldehydes	Acetaldehyde, benzaldehyde, formaldehyde, glyoxal, isobutyraldehyde, trichloroacetaldehyde
Aromatics	Benzene, chlorobenzene, chlorophenol, creosote, dichlorophenol, hydroquinone, p-nitrophenol, phenol, toluene, trichlorophenol, xylene, trinitrotoluene
Amines	Aniline, cyclic amines, diethylamine, dimethylformamide, EDTA, propanediamine, n-propylamine
Dyes	Anthraquinone, diazo, monoazo
Ethers	tetrahydrofuran
Ketones	Dihydroxyacetone, methyl ethyl ketone

Another aspect regarding the application of these AOPs is that referring to the pollutant load of wastes, normally expressed as COD (chemical oxygen demand). Only wastes with relatively small COD contents (≤ 5 g.L^{-1}) can be suitably treated by means of these processes since higher COD contents would require the consumption of too large amounts of expensive reactants. In those cases, it would be more convenient to use wet oxidation or incineration: waste water with COD higher than 20 g.L^{-1} may undergo autothermic wet oxidation (Mishra et al., 1995).

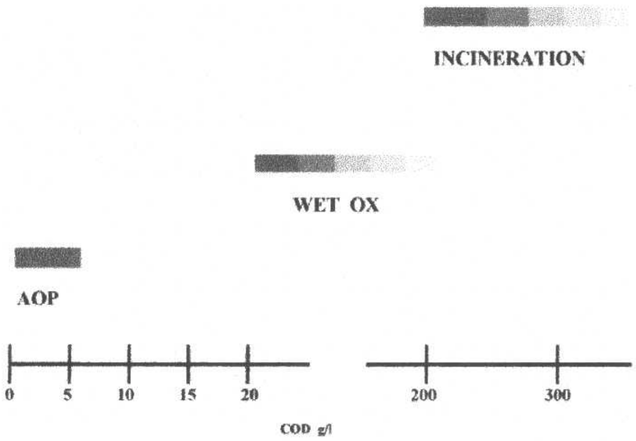

Figure 1.1. Suitability of water treatment technologies according to COD contents (Andreozzi et al., 1999)

As hydroxyl radicals are so reactive and unstable, they must be continuously produced by means of photochemical or chemical reactions. The main processes of producing these radicals are described below.

1.3.6.1. *Photochemical AOPs*

As it has been commented previously, the slow kinetics achieved by photochemical reactions can be enhanced by the addition of hydrogen peroxide and/or ozone, metallic salts or semiconductors.

1.3.6.1.1. UV/H_2O_2 process

This AOP involves the formation of $OH^{\cdot}$ radicals by hydrogen peroxide photolysis and subsequent propagation reactions. The mechanism most commonly accepted for the photolysis of H_2O_2 is the cleavage of the molecule into hydroxyl radicals:

$$H_2O_2 \xrightarrow{h\nu} 2\,OH^{\bullet} \quad [1.2]$$

The rate of photolysis of aqueous hydrogen peroxide has been found to be pH dependent and increases when more alkaline conditions are used, probably because at 253.7 nm, the peroxide anion HO_2^- has a higher molar absorption coefficient (240 vs 18.6 $M^{-1}.cm^{-1}$ (Glaze et al., 1987). Next, hydroxyl radical can attack hydrogen peroxide, giving rise to the next series of equations [1.3-1.5]:

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad [1.3]$$

$$H_2O_2 + HO_2^{\bullet} \rightarrow OH^{\bullet} + O_2 + H_2O \quad [1.4]$$

$$2\,HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad [1.5]$$

The different generated radicals will react with the organic pollutants present in the medium. On the other hand, hydrogen peroxide is known to decompose by a dismutation reaction [1.6] with a maximum rate at the pH of its pK_a value (11.6) (Legrini et al., 1993):

$$H_2O_2 + HO_2^{-} \rightarrow H_2O + O_2 + OH^{\bullet} \quad [1.6]$$

The radical-radical recombination has to be taken into account as well:

$$2\,OH^{\bullet} \rightarrow H_2O_2 \quad [1.7]$$

The major drawback of this process is that if the solution presents a strong absorbance this can compete with hydrogen peroxide for the radiation, thus cloudy waters or containing compounds which absorb UV radiation can present problems at being treated by this method.

Lipczynska-Kochany (1992) reported a 25% of NB removal by the UV/H_2O_2 a 150-W mercury-xenon lamp and 8 mM H_2O_2 concentration. Rodríguez and co. (2000) achieved a ca. 98% NB removal with 2.4 mM H_2O_2 and four 15-W 253.7-nm Hg lamps. A 60% TOC removal of a 100-ppm NB solution has been reported by Rodríguez and co. (2002) with a 21 mM H_2O_2 concentration and solar light. Benítez and co. (2000b) compared the removal of DCP with other chlorophenols by the UV/H_2O_2 process and first-order rate constants were determined. Hirvonen and co. (2000) reported that rates achieved by the UV/H_2O_2 process in alkaline conditions with DCP were comparable to those achieved by direct DCP irradiation (20-W 254 nm lamp) while at acidic pH the addition of hydrogen peroxide increased the reaction rate by one order of magnitude.

1.3.6.1.2. <u>Photocatalysis</u>

The basis of photocatalysis is the photoexcitation of a semiconductor solid as a result of the absorption of radiation, often but not exclusively in the near ultraviolet spectrum. Under near UV irradiation, a suitable semiconductor material may be excited by photons possessing energies of sufficient magnitude to produce conduction band electrons and valence band holes. These charge carriers are able to induce reduction or oxidation, respectively, and react with both water and organic compounds. The holes are extremely oxidants and should thus be able to oxidize almost all chemicals, as well as water, resulting in the formation of hydroxyl radicals (Munter et al., 2001). Many catalysts have been tested, although TiO_2 in the anatase form seems to possess the most interesting features, such as high stability, good performance and low cost (Andreozzi et al., 1999 and references herein). It presents the disadvantage of the catalyst separation from solution, as well as the fouling of the catalyst by the organic matter.

Minero and co. (1994) studied the photocatalytic degradation of NB on TiO_2 and ZnO, reporting that complete mineralization with TiO_2 was achieved. Mathew (1990) also reported more than 90% of NB mineralization was achieved with TiO_2 and sunlight. Regarding DCP, almost complete mineralization was achieved in the study carried out by Ku and Hsieh (1992) with TiO_2 and 6-W 254 nm Hg lamp and showed to be faster in alkaline solutions. Giménez and co. (1999) also tested the photocatalytic treatment of DCP by using TiO_2 and solar light, proving that reaction was first order with respect to DCP concentration and comparing the efficiencies of two different photocatalytic reactors.

1.3.6.1.3. Photoassisted Fenton processes

Over one century ago, H.J. Fenton (1884) reported that by using hydrogen peroxide and an iron salt as catalyst several organic molecules could be oxidized. More recently, it has been discovered that the oxidation mechanism that Fenton discovered is based in hydroxyl radicals generation by catalyst decomposition of H_2O_2 in acidic medium according to the global reaction (Walling and Goosen; 1973; Walling, 1975):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad [1.8]$$

This process can be started from ferric salts as well in the so-called Fenton-like process.

The degradation rate of an organic pollutants by means of Fenton or Fenton-like is strongly enhanced by the addition of UV-visible light, at wavelengths above 300 nm: these are the photo-Fenton and photo-Fenton-like processes. Under these conditions, the photolysis of the Fe(III) complexes allows the regeneration of Fe(II) in the next series of reactions (Chen and Pignatello, 1997):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad [1.8]$$

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + H^+ + OH^\bullet \qquad [1.9]$$

$$H_2O_2 \xrightarrow{h\nu} 2\,OH^\bullet \qquad [1.2]$$

The involvement of many additional free-radical reactions in the Fenton process has been discussed extensively in the literature. Literature recommends to maintain pH in the range 2.6-3 (Pignatello, 1992).

Chamarro and co. (2001) used the Fenton process for the degradation of phenol, 4-chlorophenol, 2,4-dichlorophenol and nitrobenzene. The stoichiometric coefficient for the Fenton reaction was approximately 0.5 mol of organic compound/mol H_2O_2. The process was found to eliminate the toxic substances and increased the biodegradability of the treated water. A rate equation for removal of NB has been established by Rodríguez and co. (2002b). A 95% TOC reduction of a 100-ppm NB solution has been reported by Rodríguez and co. (2000a) by the photo-Fenton process with solar light (21 mM H_2O_2, Fe(II-III) 1 mM). Ormad and co. (2001) compared the degradation of a DCP solution by Fenton and photo-Fenton process: while in the dark only a small abatement of DCP was observed, a 78% mineralization was achieved by the photo-Fenton process (10 mM H_2O_2, Fe(II) 10 mg.L^{-1}, 36-W black light lamp).

An improvement of photoassisted Fenton processes is the UV-vis/ferrioxalate/H_2O_2 system, which has been recently demonstrated to be more efficient than photo-Fenton for the abatement of organic pollutants (Zepp et al., 1992; Safarzadeh-Amiri et al, 1996b).

Recently, two new electrochemical procedures for the detoxification of acidic waste waters, the so-called electro-Fenton and photoelectro-Fenton processes, where H_2O_2 is electrogenerated, have been developed and have shown their good efficiencies for the mineralization of aniline (Brillas et al., 1998a), 4-chlorophenol (Brillas et al., 1998b) and 2,4-D (Brillas et al., 2000).

1.3.6.1.4. Vacuum ultraviolet process (VUV)

The VUV consists on the UV spectral domain where air (oxygen) strongly absorbs radiation; its border with the UV-C is at 190 nm, and spectroscopic work at shorter wavelengths can only be performed in vacuum or in non-absorbing gases. VUV photochemical processes are becoming possible with the development of excimer light sources emitting in this domain (Legrini et al., 1993).

It is an interesting method for the degradation of organic pollutants in liquid or gaseous phase. Besides the photolyis of the target compound, VUV photolysis of water is a highly efficient way of hydroxyl radical generation [1.10], which can then attack the substrate:

$$H_2O \xrightarrow{hv} \frac{1}{2}H_2 + OH^{\bullet} \qquad [1.10]$$

The complete photomineralization of 2,4-DCP by VUV oxidation has been reported by Baum and Oppenlaender (1995).

1.3.6.2. *Ozone-based AOPs*

1.3.6.2.1. Ozonation

Ozone is a very powerful oxidizing agent, which is able to participate in a great number of reactions with organic and inorganic compounds. Among the most common oxidizing agents, it is only surpassed in oxidant power by fluorine and hydroxyl radicals (see Table 1.9). Since the beginning of the century the disinfectant power of ozone has been known, however is during the last two decades when this chemical agent has acquired notoriety in waste water treatment. Thus, the ozonation of dissolved compounds in water can constitute an AOP by itself, as hydroxyl radicals are generated from the decomposition of ozone, which is catalyzed by the hydroxyl ion or initiated by the presence of traces of other substances, like transition metal cations (Staehelin and Hoigné, 1985). As the pH increases, so does the rate of decomposition of ozone in water. At pH 10, for example, the half-life of ozone in water may be less than one minute.

In an ozonation process two possible pathways have to be considered: the direct pathway through the reactions with molecular ozone, and the radical pathway through the reactions of hydroxyl radicals generated in the ozone decomposition and the dissolved compounds (see Figure 1.2). The combination of both pathways for the removal of a compound will depend on the nature of this, the pH of the medium and the ozone dose (Beltrán et al., 1997a). Thus, molecular ozone can directly react with dissolved pollutants by electrophilic attack of the major electronic density positions of the molecule. This mechanism will take place which pollutants such as phenols, phenolates or tiocompounds. Reactions of molecular ozone normally take place through ozonolysis of a double bond or attack of nucleophilic centers, where aldehydes, ketones or carboxylic acids are obtained from double bonds; amides from nitriles; amine oxides from amines, etc (Bailey, 1972). The radical mechanism predominates in less reactive molecules, such as aliphatic hydrocarbons, carboxylic acids, benzenes or chlorobenzenes (Hoigné and Bader, 1979). Normally under acidic conditions (pH<4) the direct pathway dominates, above pH 10 it changes to the radical. In ground and surface water (pH≈7) both pathways can be of importance (Staehelin and Hoigné, 1983a). In special waste waters, even at pH=2 the radical oxidation can be of importance, depending much on the contaminants present (Gottschalk et al., 2000). Both pathways should be always considered when developing a treatment scheme. In Table 1.11, the second order kinetic constants for ozone and hydroxyl radical of a series of organic compounds is presented.

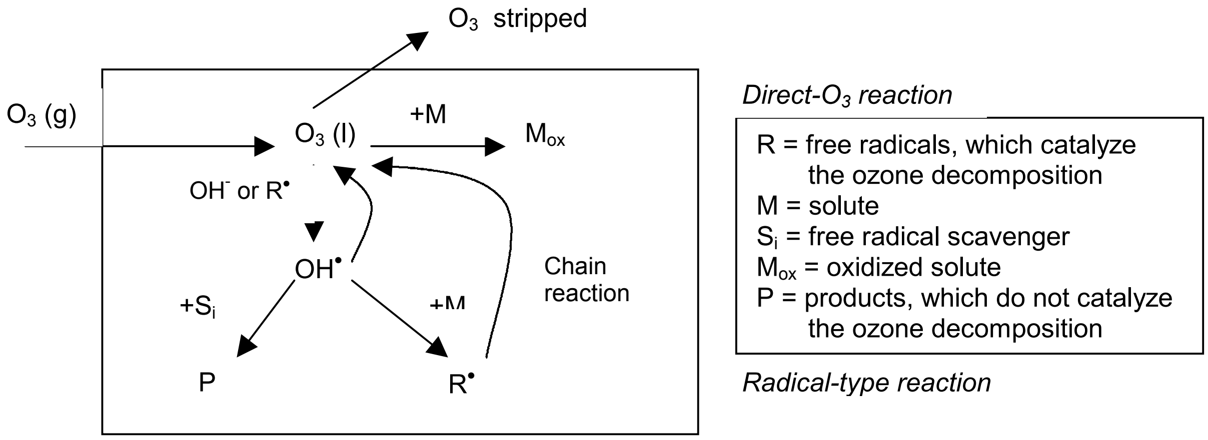

Figure 1.2. Scheme of reactions of ozone added to an aqueous solution (Hoigné and Bader, 1983a).

Table 1.11. Second order rate for ozone and hidroxil radical OH$^\bullet$ for a variety of compounds

Organic compound	**Rate constant ($M^{-1}.s^{-1}$)**	
	O_3 $^{(a)}$	**$OH^{\bullet\,(b)}$**
Benzene	2	$7.8.10^9$
Toluene	14	$7.8.10^9$
Chlorobenzene	0.75	4.10^9
Trichloroethylene	17	4.10^9
Tetrachloroethylene	<0.1	$1.7.10^9$
n-Butanol	0.6	$4.6.10^9$
t-Butanol	0.03	$0.4.10^9$

(a) From (Hoigné and Bader, 1983)

(b) From (Andreozzi et al., 1999)

The mechanism of decomposition of ozone will be deeply commented in section 2.2.2. The rate of attack by hydroxyl radicals is typically 10^6 to 10^9 times faster than the corresponding reaction rate for molecular ozone. A great deal of studies have been undertaken about the reactivity of ozone with many pollutants and reaction-rate constants of several organic and inorganic compounds have been establish (e.g. Hoigné and Bader, 1983a,b). Besides the oxidation process, ozone decreases color and turbidity.

The ozone treatment may be enhanced by the addition of hydrogen peroxide and/or UV radiation. As ozone is the basis of the AOPs that have been studied in the present work, a chapter about ozone has been developed, where the main features of ozone about physical and chemical properties, chemistry, generation, ozone gas transfer, toxicology and ozone in the treatment of waters and waste waters is being discussed (see chapter 2).

Only few articles have been found in the literature regarding the ozonation of NB. Studies regarding the ozonation of NB (Caprio et al., 1984, Baozhen et al.,1988; Beltrán et al., 1998a) and DCP (e.g. Trapido et al., 1997; Benítez et al., 2000, Qiu et al., 2002) will be deeply commented in the discussion section (chapter 5) and compared with the results obtained in the present study.

1.3.6.2.2. O_3/H_2O_2 process

Addition of hydrogen peroxide to ozone offers another way to accelerate the decomposition of ozone, leading to the formation of OH radicals. Hydrogen peroxide in aqueous solution is partially dissociated in the hydroperoxide anion (HO_2^-), which reacts with ozone, decomposing this and giving rise to a series of chain reactions with the participation of hydroxyl radicals. Figure 1.3 shows an scheme of this mechanism.

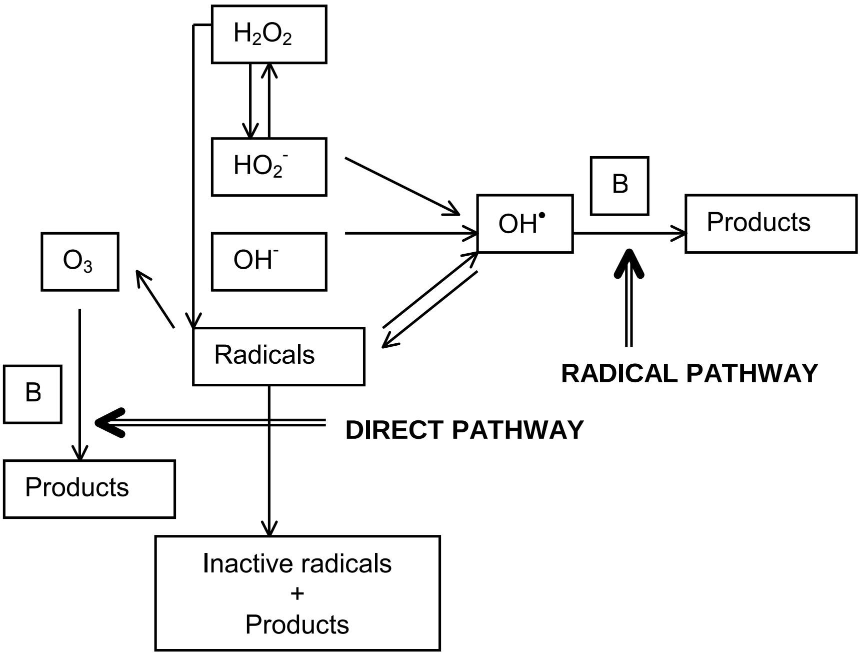

Figure 1.3. Scheme of the mechanism of oxidation in water by the O_3/H_2O_2 process (Beltrán et al, 1997b)

In the global reaction two ozone molecules produce two hydroxyl radicals [1.11]

$$H_2O_2 + 2\,O_3 \rightarrow 2\,OH^\bullet + 3\,O_2 \qquad [1.11]$$

with the following initiating steps (Staehelin and Hoigné, 1982; Glaze and Kang, 1989):

$$H_2O_2 \rightarrow HO_2^- + H^+ \qquad pKa= 11.8 \qquad [1.12]$$

$$HO_2^- + O_3 \rightarrow HO_2^\bullet + O_3^\bullet \qquad [1.13]$$

As this system does not depend on the UV radiation transmission to activate the ozone or hydrogen peroxide molecules, its greatest advantage is to be able to work with turbid waters without problems.

One of the fields where this process has been studied most is the degradation of pesticides and herbicides. For example, Beltrán and co. (1994) studied the degradation of mecropope in water by ozone and O_3/H_2O_2 and determined the optimal hydrogen peroxide amount. Paillard and co. (1988) undertook an study about the degradation of herbicides with the group s-triazine, establishing that the optimal ratio mg H_2O_2/mg O_3 was around 0.5.

However, few articles have been found in the literature regarding the degradation of NB and DCP by means of O_3/H_2O_2. Beltrán and co. (1998b) have studied the effect of hydrogen peroxide concentration, pH and hydroxyl radical scavengers in the removal of NB by this combination. A kinetic model has also been proposed by Beltrán and co. (1999).

1.3.6.2.3. O_3/UV process

The O_3/UV process is an effective method for the oxidation and destruction of toxic and refractory organics in water. Basically, aqueous systems saturated with ozone are irradiated with UV light of 253.7 nm. The extinction coefficient of O_3 at 253.7 nm is 3300 $M^{-1}cm^{-1}$, much higher than that of H_2O_2 (18.6 $M^{-1}.cm^{-1}$). The decay rate of ozone is about a factor of 1000 higher than that of H_2O_2 (Guittoneau et al., 1991).

The AOP with ozone and UV radiation is initiated by the photolysis of ozone. The photodecomposition of ozone leads to two hydroxyl radicals, which do not act as they recombine producing hydrogen peroxide (Peyton and Glaze, 1988):

$$H_2O + O_3 \xrightarrow{h\nu} 2\,OH\bullet + O_2 \qquad [1.14]$$

$$2\,OH^{\bullet} \rightarrow H_2O_2 \qquad [1.7]$$

This system contains three components to produce OH radicals and/or to oxidize the pollutant for subsequent reactions: UV radiation, ozone and hydrogen peroxide. Therefore, the reaction mechanism of O_3/H_2O_2 as well as the combination UV/H_2O_2 is of importance. Considering that hydrogen peroxide photolysis is very slow compared with the rate at which ozone is decomposed by HO_2^- , it seems that a neutral pH reaction of ozone with HO_2^- is the main pathway. The radical reactions mechanism that takes place is shown in Figure 1.4.

Table 1.12 summarizes the relative molar amounts of ozone, UV radiation (photons) and hydrogen peroxide involved in the ozone-hydrogen peroxide-UV processes, whereas Figure 1.5 presents an scheme of the oxidation of an organic pollutant RH_2.

Table 1.12. Theoretical amount of oxidants and UV required for the formation of hydroxyl radicals in ozone-peroxide-UV systems (Glaze et al., 1987)

System	Mols of oxidant consumed per mol $OH^{\cdot}$ produced		
	Ozone	**UV (254 nm) (photon)**	**H_2O_2**
Ozone-hydrogen peroxide	1.0	-	0.5
Ozone-UV	1.5	0.5	(0.5)[a]
UV-hydrogen peroxide	-	0.5	0.5

[a)] Hydrogen peroxide formed *in situ*

$$\begin{array}{rcl}
O_3 + H_2O & \xrightarrow{h\nu} & H_2O_2 + O_2 \\
H_2O_2 & \xrightarrow{h\nu} & 2\,OH\bullet \\
OH\bullet + O_3 & \longrightarrow & HO_2\bullet + O_2 \\
HO_2\bullet & \longleftrightarrow & H^+ + O_2^- \\
HO_2\bullet + O_3 & \longrightarrow & OH\bullet + 2\,O_2 \\
O_2^- + O_3 & \longrightarrow & O_3^- + O_2 \\
H^+ + O_3^- & \longleftrightarrow & HO_3 \\
HO_3 & \longrightarrow & OH\bullet + O_2 \\
2\,OH\bullet & \longrightarrow & H_2O_2 \\
2\,HO_2\bullet & \longrightarrow & H_2O_2 + O_2 \\
HO_2\bullet + O_2^- & \longrightarrow & O_2 + HO_2^- \\
HO_2^- + O_3 & \longrightarrow & \bullet O_3^- + HO_2\bullet \\
H_2O_2 + OH\bullet & \longrightarrow & HO_2\bullet + H_2O
\end{array}$$

Figure 1.4. Radical mechanism of the O_3/UV process (Glaze et al., 1987)

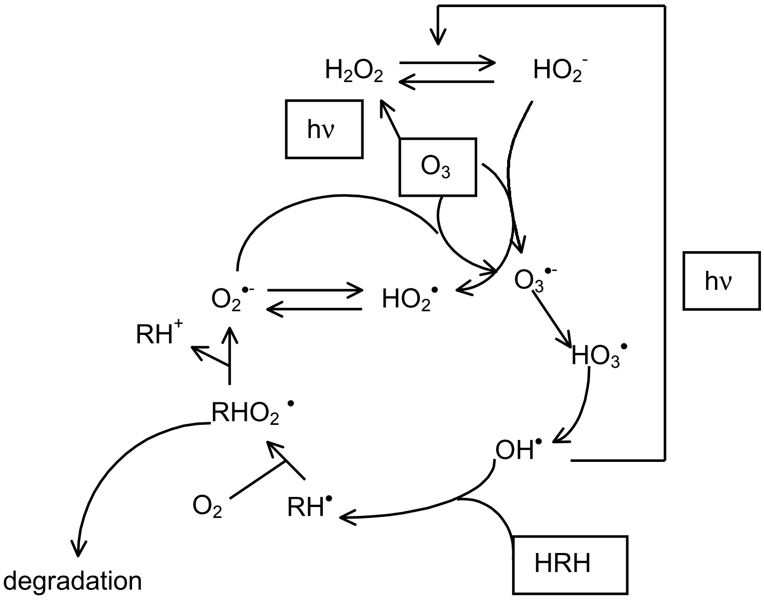

Figure 1.5. Scheme of the degradation mechanism by means of the O_3/UV process (Peyton and Glaze, 1988)

The efficiency of this process with different aromatic compounds has been studied by several authors. Gurol and Vatistas (1987) studied the photolytic ozonation of mixtures of phenol, p-cresol, 2,3-xylenol and catechol at acidic and neutral pH. Guittoneau and co. (1990) reported that the O_3/UV process was found to be more efficient than the UV/H_2O_2 system for the degradation of p-chloronitrobenzene.

Nevertheless, few articles have been found as well in the literature regarding the degradation of NB and DCP by means of the O_3/UV process. Beltrán and co. (1998b) have studied the effect of ozone feed rate, pH and hydroxyl radical scavengers in the removal of NB by this combination. A kinetic model has also been proposed by Beltrán and co. (1999). Studies regarding DCP removal by the O_3/UV process (e.g. Trapido et al., 1997; Hautanemi et al., 1998; Kuo, 1999) will be deeply commented in the discussion section (chapter 5) and compared with the results obtained in the present study.

1.3.6.2.4. O_3/UV/H_2O_2 process

The addition of H_2O_2 to the O_3/UV process accelerates decomposition of ozone resulting in increased rate of $OH^\cdot$ radicals generation. In processes targeted at pollutants that are weak absorbers of UV radiation, it is more cost effective to add hydrogen peroxide externally at reduced UV flux. This is a very powerful method, that allows a considerable reduction of the TOC. This process is the combination of the binary systems O_3/UV and O_3/H_2O_2. By combination of equations [1.12-1.14], the global equation for the $O_3/UV/H_2O_2$ is obtained [1.15]:

$$2\,O_3 + H_2O_2 \xrightarrow{h\nu} 2\,OH^\bullet + 3\,O_2 \qquad [1.15]$$

Zeff and Barich (1990) studied the oxidation of different organic compounds (methylene chloride, chlorobenzene, benzene, toluene, ethylbenzene,…) by means of this system, which proved to be more efficient that the treatment of each oxidant alone or in binary combinations. Mokrini and co. (1997) presented the degradation of phenol by means of this process at different pHs, establishing the optimal H_2O_2 amount. A 40% of TOC reduction was achieved by this method. Trapido and co. (2001) reported the combination of ozone with UV radiation and hydrogen peroxide was found to be more effective for the degradation of nitrophenols than single ozonation or the binary combinations, increasing the reaction rate and decreasing the ozone consumption when using low pH values. With regard to NB and DCP, no articles have been found in the literature about the oxidation of these compounds by means of this process.

1.3.6.2.5. O_3/UV/Fe process

The combination of ozone with light and iron as catalyst improves the oxidative capability of the catalytic ozonation O_3/Fe. Three process may account for this improvement of the efficiency of the process. On one hand, Fe(III) species undergo a photoredox process with UV and near-UV light, giving rise to Fe(II) and $OH^{\cdot}$ radicals according to equation [1.16] (Safarzadeh-Amiri et al., 1996; Mazellier et al., 1997):

$$Fe^{3+} \xrightarrow[H_2O]{hv} Fe^{2+} + OH^{\bullet} + H^{+} \qquad [1.16]$$

On the other hand, Fe(III) is considered to increase the number of hydroxyl radicals through the reduction of O_3 with the Fe^{2+} generated by the photoreduction of Fe^{3+} (Abe and Tanaka, 1999), similar to the mechanism proposed for the photo-Fenton reaction. The mechanism is quite unclear (Ruppert et al., 1994 and references herein)

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \qquad [1.17]$$

$$FeO^{2+} + H_2O \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \qquad [1.18]$$

If hydrogen peroxide is present in the medium, directly or by ozone photolysis, it can react with Fe(II) by Fenton reaction [1.8], regenerating Fe(III) and closing a loop mechanism Fe(III)/Fe(II) while hydroxyl radicals are generated.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + OH^{\bullet} \qquad [1.8]$$

Besides this, the initial oxidation of organic pollutants generates oxygenated intermediates, e.g. intermediates with carboxylic functional groups, which can react with Fe(III) and form complexes. These complexes are also photoactive and produce CO_2, organic radicals and ferrous ions on irradiation, contributing to the mineralization of these pollutants without the participation of hydroxyl radicals (Safarzadeh-Amiri et al., 1996a; Abe and Tanaka, 1999).

$$RCO_2Fe(III) \xrightarrow{hv} R^{\bullet} + CO_2 + Fe(II) \qquad [1.19]$$

The addition of iron ion (Fe^{3+} or Fe^{2+}) has been reported to accelerate the UV-enhanced ozonation of several pollutants (Abe and Tanaka, 1997, 1999). Ruppert and co. (1994) studied the degradation of 4-chlorophenol solutions by means of different AOPs. The O_3/UV/Fe(II) was found to be the most effective method, achieving complete mineralization in few minutes. Complete mineralization of DCP among other chlorophenols was achieved also by O_3/UV/Fe(III) as reported by Abe and Tanaka (1997), where the effect of Fe(III) was found to depend on its concentration. Abe and Tanaka as well (1999) studied the effect of this combination with nitrophenols, attributing the main effect to the photodegradation of aliphatic intermediates by Fe(III) complex. The degradation of aniline and 4-chlorophenol has been studied by Sauleda and Brillas (2001) by means of O_3/UVA/Fe(II), reporting that both quickly mineralized by the O_3/UVA and O_3/UVA/Fe(II).

1.3.7. AOPs combined with biological treatments

Biological treatment of wastewater, groundwater, and aqueous hazardous wastes is often the most economical alternative when compared with other treatment options. The ability of a compound to undergo biological degradation is dependent on a variety of factors, such as concentration, chemical structure and substituents of the target compound. The pH or the presence of inhibitory compounds can also affect the biological degradation. Although many organic molecules are readily degraded, many other synthetic and naturally occurring organic molecules are biorecalcitrant (Adams et al., 1997).

Several chemical processes, which use oxidizing agents such as ozone, hydrogen peroxide, etc. have been carried out to mineralize many synthetic organic chemicals. However, costs associated with chemical oxidation alone can often be prohibitive for wastewater treatment. A potentially viable solution is the integration of chemical and biological treatment processes as an economical means for treating biorecalcitrant organic chemicals in wastewater. The chemical process would be used as a pre-treatment in order to increase the biodegradability of the wastewater. The oxidation of organic compounds in water with AOPs usually produces oxygenated organic products and low molecular weight acids that are more biodegradable (Gilbert, 1987; Heinzle et al., 1995; Marco et al., 1997; Ledakowicz, 1998; Beltrán et al., 2000b). With the AOPs, toxic compounds would be removed until no inhibition due to its toxicity was there and/or non-biodegradable compounds turned into more biodegradable. This feature is economically interesting, as investment and operating costs are much lower for a biological process than a chemical one: investments costs for biological processes range from 5 to 20 times less than chemical ones such as ozone or hydrogen peroxide, while treatment costs range from 3 to 10 times less (Scott and Ollis, 1996; Marco et al., 1997).

In these combined processes, if we want to determine the variation of biodegradability as a function of the chemical reaction conditions (time of pre-treatment, concentration of the oxidizing agent, temperature, etc), a biodegradation test is required.

Methods for measuring biodegradability in these systems have been proposed by a number of authors. BOD and BOD/COD or BOD/TOC are commonly used (Gilbert, 1987; Marco et al., 1997, Yu and Yu, 2000; Chamarro et al., 2001). Other biodegradability measures including substrate destruction, oxygen uptake, EC_{50} toxicity measurements, cell growth counts and intracellular ATP levels also have been used (Scott and Ollis, 1995).

During the last decade studies in this field have increased. It is proper to cite, for example, the effect of single ozonation on black-olive waste waters (Beltrán-Heredia et al., 2000), landfill leachates (Baig and Liechti, 2001), sodium dodecylbenzenesulfonate (Beltrán et al., 2000c); or the effect of ozone-based AOPs on table olive waste waters (Beltrán et al., 1999b) or textile waste waters (Ledakowicz and Gonera, 1999).

Hu and Yu (1994) reported that pre-ozonation of chlorophenolic compounds was found to enhance the effectiveness of a subsequent biological treatment. Marco and co. (1997) increased biodegradability of DCP measured as BOD_5/COD up to ca. 0.4 by means of single ozonation. Chamarro and co. (2001) reported that BOD_5/COD ratio of a DCP solution was increased up to 0.4 by means of Fenton reagent. No studies regarding the effect of ozone-based AOPs on the biodegradability of NB solutions have been found in the literature.