Advanced Oxidative Degradation Processes: Fundamentals and Applications

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Abstract – *This text is a brief review on the use of Advanced Oxidative Degradation Processes (AOPs) applied to the treatment of sewage and industrial and domestic wastewaters. A quick introduction to the importance of wastewater treatment to the environment is discussed, followed by the benefits and limitations of treatment techniques. Chemical fundamentals are focused on the generation of hydroxyl radicals, hydrogen atom abstraction, electrophilic addition of hydroxyl radicals, electrical transfer, and radical-radical reactions. AOPs are herein divided into two categories: homogeneous and heterogeneous. Homogeneous methods are based on the use of radical generators like hydrogen peroxide, ozone, the combined use of these oxidants, Fenton's reagent and photo-Fenton. Heterogeneous systems focus on the use of semiconductors, and results concerning the use of semiconductors in AOPs are discussed at the end. **Copyright © 2013 Praise Worthy Prize S.r.l. - All rights reserved.***

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I. Introduction

In recent decades, problems affecting the environmental quality of ecosystems have become increasingly critical and frequent.

An ecosystem consists of abiotic and biotic components (including human influences) that present an interconnected and interdependent network through soil, air and water.

Changes to only one of these segments can result in changes in the ecosystem as a whole. These problems are due in large part to the impact of anthropic activities, mainly due to population growth and increased industrial activity [1], [2].

One of the major environmental problems today refers to the impact associated with the disposal of industrial wastewater and other residues into superficial and underground waterbodies.

Solutions to this issue require combined approaches, concerning generation, treatment, and disposal into the environment not only of effluents but passive residues produced by specific treatments: physical (resulting primarily from the formation of low-solubility solids and auxiliary reagent for flocculation and precipitation); chemical (promising, but still undergoing up-scaling as emergent processes); microbiological (the most commonly used on industrial scale in terms of versatility and cost); or combined hybrid process.

Several techniques are available for wastewater treatment (as mentioned before, chemical, physical and biological processes) as well as the use of combinations of these techniques to an optimal result.

When organic compounds in wastewaters present recalcitrant characteristics precluding treatments by conventional biological methods, chemical oxidation can be used as pre- or post-treatment, decreasing toxicity before applying a conventional biological process or conditioning the effluent to required maximum concentrations (i.e., oxidize non-biodegradable residues).

Chemical oxidation can also be used as a post-treatment to oxidize non-biodegradable residues present in wastewater treated by biological processes. Each treatment technique has positive aspects and constraints in relation to applicability, efficiency and cost [3].

In this context, Advanced Oxidative Degradation Processes (AOPs) comprise a set of techniques that, under certain conditions, could transform the vast majority of organic contaminants into carbon dioxide, water, and inorganic ions as a result of oxidation reactions, which involve transitory oxidant species, as discussed in this text.

Existing literature presents a very large volume of data related to Advanced Oxidative Degradation. New results are aggregated continuously, reflecting the theoretical principles and the applications of these techniques.

This paper is thus free of the pretension to cover the issue.

Rather, the focus of this review is on the chemical fundamentals involved, on examples in which these techniques are applied, as well as on recent results related to the use of semiconductors in AOPs.

II. Advanced Oxidative Degradation Processes: Positives Aspects and Limitations

Several authors have pointed out the advantages and disadvantages of different AOP systems, such as UV/H_2O_2, UV/TiO_2, photo-Fenton ozone-based processes Examples are the works of [4]-[15].

In general, the literature has highlighted the following positive aspects of AOPs [16]-[19]:

- Unlike conventional technologies which use strongly oxidant species, under certain conditions AOPs can provides the complete mineralization of pollutants;
- Used for the destruction of refractory compounds resistant to other treatments, such as biological processes;
- Allow the conversion of recalcitrant compounds and refractory contaminants submitted to biodegradation systems;
- Can be used in combination with other processes for pre-or post-treatment;
- Possess strong oxidizing power with high reaction rates;
- Ideal to decrease the concentration of compounds formed by alternative pre-treatment, such as disinfection;
- The formation of by-products can be minimized if optimized amounts of reactants are employed;
- In many cases, AOPs consume less energy compared to thermal destruction processes (incineration) of liquid wastewaters and,
- Enable *in situ* treatment.

However, like any other form of treatment, AOPs cannot be indiscriminately applied to arbitrary residue processing.

There are conditions that limit their implementation as highlighted by previous works [20], [21]:

- Not all processes are readily scaled-up to commercial or industrial needs;
- Costs can be high, mostly due to the consumption of electric energy by radiating sources in the case of photo-oxidative degradation processes;
- Restrictions are present under conditions of high pollutant concentrations;
- In some cases strict control of oxidant concentration and pH correction are required for the operation of the process as for post-processing or disposal of treated effluent (e.g., Fenton and photo-Fenton);
- Process limitations are also related to pH changes, such as particle aggregation and modification of surface properties of catalysts used in heterogeneous

systems, and the distribution of iron complexes in Fenton systems (and their UV-visible radiation properties as well), or even iron precipitation.

III. Chemical Fundamentals

III.1.Hydroxyl Radical: Generation and Interferences

AOPs exhibit an elevated capacity to produce hydroxyl radicals (OH) [22], [23]. Due to its high standard reduction potential (Eq. (1)), this radical oxidizes a wide variety of organic compounds to CO_2, H_2, and inorganic ions from any heteroatoms:

$$•OH + e^- + H^+ \rightarrow H_2O$$
$$k = 7 \times 10^9 \text{ L mol s}^{-1} \quad E^o = 2.8 \text{ V} \tag{1}$$
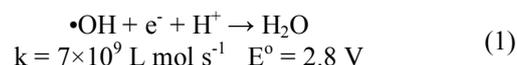
This is a great advantage in relation to treatments that simply transfer pollutants from one phase to another, like filtration, adsorption, precipitation, coagulation, flocculation, sedimentation, flotation, membrane separation, centrifugation, inverse osmosis, distillation, extraction, and evaporation [16].

In most of these operations, the final disposal of passive solid phases remains an unresolved problem [24].

Hydroxyl radicals are obtained from strong oxidants such as H_2O_2 and O_3, combined or not with UV radiation, iron II or III salts, semi-conductor photo catalysts (such as TiO_2) or from the photolysis of water with vacuum UV radiation [25]-[29].

Table I presents the oxidation potential of some species. After fluorine, hydroxyl radical (OH) is the strongest oxidant [30].

According to Kiwi and co-workers [31], the efficiency of AOPs is strongly influenced by the presence of high concentrations of hydroxyl radicals scavengers, such as carbonate, bicarbonate and ionic chloride species, reducing the process efficiency.

Essam and co-workers [32] investigated the AOP-oxidation of treated wastewater containing chloride ions, noting that there is a marked reduction in the oxidation of organic load as a function of Cl^- concentration.

TABLE I
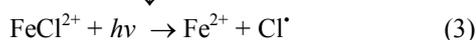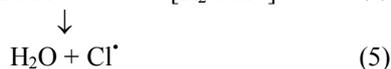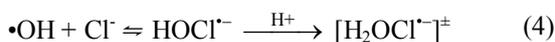STANDARD REDUCTION POTENTIAL OF SELECTED OXIDANT SPECIES
(DORFMAN AND ADAMS, 1973)

Species	E^* (V, 25 °C)[1]
Fluorine (F_2)	3.03
Hydroxyl radical (•OH)	2.80
Atomic oxygen (O_2)	2.42
Ozone (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.78
Perhydroxyl radical (HO_2)	1.70
Chlorine dioxide	1.57
Hypochlorous acid (HClO)	1.49
Chlorine (Cl_2)	1.36
Bromine (Br_2)	1.09
Iodine (I_2)	0.54

[1]Potential refers to the standard hydrogen electrode (SHE)

In the Fenton and photo-Fenton systems, chloride ions can form complexes with iron ($FeCl^{2+}$), which effectively compete with the •OH radical. In fact, in the typical pH range of the photo-Fenton reaction (2.8 to 3.2), the complexes $Fe(OH)^{2+}$ and $FeCl^{2+}$ coexist and can undergo photochemical reactions as shown by Equations (2) and (3):

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + HO\bullet \qquad (2)$$

$$FeCl^{2+} + hv \rightarrow Fe^{2+} + Cl\bullet \qquad (3)$$
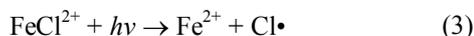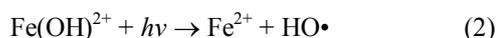
The $FeCl^{2+}$ complex generates Fe(II) and Cl• radicals from photon absorption, with a quantum yield $\Phi = 0.50$ at 347 nm. At that same wavelength, the complex $Fe(OH)^{2+}$ generates hydroxyl radicals less efficiently with quantum yield $\Phi = 0.21$. The species Cl• combines with chloride ions in solution, giving the radical anion $Cl_2\bullet^-$, with standard reduction potential equal to 2.10 V (SHE). This species can generate undesirable chlorinated oxidation products thus competing with hydroxyl radicals. Moreover, as reported by Kiwi and co-workers [31], the same hydroxyl radical reacts with chloride ions in solution generating $HOCl^{\bullet}$ species, that, in an acidic medium, generate Cl• radicals (Equations (4) to (6) and (3)).

$$\bullet OH + Cl^- \rightleftharpoons HOCl^{\bullet-} \xrightarrow{H+} [H_2OCl^{\bullet-}]^{\pm} \qquad (4)$$
$$\downarrow$$
$$H_2O + Cl^\bullet \qquad (5)$$
$$\downarrow$$
$$Cl^\bullet + Cl^- \rightarrow Cl_2^{\bullet-} \qquad (6)$$
$$\downarrow$$
$$FeCl^{2+} + hv \rightarrow Fe^{2+} + Cl^\bullet \qquad (3)$$

This behavior has been observed in the oxidation of 2.4-DCF (2.4-dichlorophenol) and PCF (pentachlorophenol) by the photo-Fenton reaction [33]. The oxidation of pentachlorophenol was very fast in the first 15 minutes and more than half of the initial concentration of the PCF was removed, after approximately 30 minutes.

Depending on the structure of the organic contaminant, different reactions may occur involving the hydroxyl radical, such as hydrogen atom abstraction, electrophilic addition to substances containing unsaturated and aromatic rings, electron transfer, and radical-radical reactions.

Ramos and co-workers [34] used molecular modeling techniques to study the reactions of hydroxyl radicals during phenol oxidation.

III.2. Abstraction of Hydrogen Atoms

Hydroxyl radicals are capable of oxidizing organic compounds by hydrogen abstraction, producing organic radicals (Eq. (7)).

Subsequent addition of molecular oxygen form peroxyl radicals (Equation (8)); reactive intermediates initiate chain reactions leading to thermal degradation to CO_2, water, and inorganic salts. The reaction by hydrogen abstraction usually occurs with aliphatic hydrocarbons [35]:

$$HR + \bullet OH \rightarrow R^\bullet + H_2O \qquad (7)$$

$$R^\bullet + O_2 \rightarrow RO_2^\bullet \qquad (8)$$

III.3. Electrophilic Addition of Hydroxyl Radical

The electrophilic addition of hydroxyl radical to organic compounds containing π bonds results in the formation of organic radicals (Eq. (9)). This usually occurs with hydrocarbons containing unsaturated bonds or aromatic systems [35]:
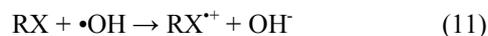

$$(9)$$

Fast dechlorination of chlorophenols is also promoted by the electrophilic generating chloride ions (Eq. 10) [35]:
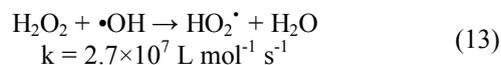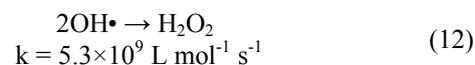

$$(10)$$
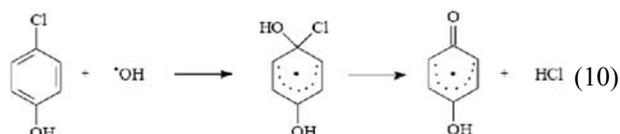
III.4. Electron Transfers

Electron transfer reactions occur when electrophilic addition and hydrogen abstraction are deprived, as in the case of chlorinated hydrocarbons (Eq. (11)) [35]:

$$RX + \bullet OH \rightarrow RX^{\bullet+} + OH^- \qquad (11)$$

III.5. Radical-Radical Reactions

Other radical reactions can also occur (Eqs. (12) and (13)). However, such reactions are undesirable from the point of view of the oxidation of organic compounds due to •OH consuming and subsequent impairment of the photodegradation process efficiency:

$$2OH\bullet \rightarrow H_2O_2$$
$$k = 5.3 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1} \qquad (12)$$

$$H_2O_2 + \bullet OH \rightarrow HO_2^\bullet + H_2O$$
$$k = 2.7 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1} \qquad (13)$$

The predominance of one or another reaction depends on several factors, among which the concentration of organic substrate, as well as its recalcitrant character.

IV. Systems Used in AOPs

The systems used in AOPs are divided into two major groups, depending on the number of phases involved: a) homogeneous processes and b) heterogeneous processes.

These different processes have been used alone or in combination, resulting in different treatments systems. In each group, a source of radiation, such as ultraviolet (UV) or ultraviolet-visible (UV-Vis) may or may not be used. Table II presents examples of treatment systems based on AOPs.

TABLE II
SYSTEMS USED IN THE GENERATION OF HYDROXYL RADICAL [36]

	Irradiated	Non Irradiated
Homogeneous Systems	O_3/UV	O_3/H_2O_2
	H_2O_2/UV	O_3/OH^-
	H_2O_2/Fe^{2+}/UV	H_2O_2/Fe^{2+}
Heterogeneous Systems	* Sc/O_3/UV	Electro-Fenton
	* Sc/H_2O_2/UV	-
	* Sc/UV	-

* Sc: semiconductor (e.g., TiO_2, ZnO).
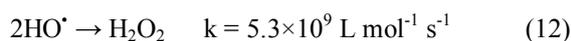
V. Homogeneous Systems and Radical Generators

Homogeneous processes occur in a single phase, and use ozone (O_3), hydrogen peroxide and UV (UV/H_2O_2) or Fenton reagent (mixture of H_2O_2 with Fe(II) salt) generate hydroxyl radicals. Some combinations of technologies like photo-Fenton and UV/ozone are also included in this group.

V.1. Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) under ultraviolet radiation in the wavelength range of 200 to 300 nm is a simple hydroxyl-radicals generator.

The photolysis of hydrogen peroxide by UV radiation involves breaking of the O-O bond, to yield two radicals •OH for every molecule of H_2O_2 (Eq. (14)) [37]-[39].
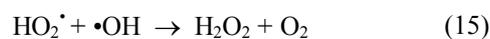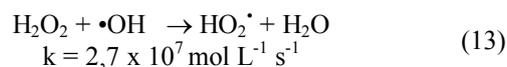
However, at high concentrations •OH radicals can recombine to give H_2O_2 (Eq. (12)):

$$H_2O_2 + hv \rightarrow 2HO^\bullet \tag{14}$$

$$2HO^\bullet \rightarrow H_2O_2 \quad k = 5.3\times10^9 \text{ L mol}^{-1} \text{ s}^{-1} \tag{12}$$

Should be emphasized that, in high concentrations, hydrogen peroxide has the ability to consume the formation of hydroxyl radicals and superoxide radicals, thus reducing the possibility of oxidation (Eq. (13)).

Also, the reaction can occur among the hydroxyl radical superoxide (Eq. (15)) [40]. Thus, in many cases, oxidation occurs quickly at the beginning of the reaction and in others, degradation is slow. In case of the peroxide, to obtain an efficient oxidation, its dosage

must be performed slowly throughout the experiment to ensure higher efficiency of the process. Therefore, the optimal H_2O_2 concentration depends on the amount of pollutant to be oxidized, the goal is preferably an experimentally-derived concentration:

$$H_2O_2 + \bullet OH \rightarrow HO_2^\bullet + H_2O$$
$$k = 2,7 \text{ x } 10^7 \text{ mol L}^{-1} \text{ s}^{-1} \tag{13}$$

$$HO_2^\bullet + \bullet OH \rightarrow H_2O_2 + O_2 \tag{15}$$

If not possible, the adequate H_2O_2 concentration can be obtained from literature data or estimated considering the stoichiometric equivalence between carbon concentration (TOC) and hydrogen peroxide concentration (Eq. (16)) [41]:

$$C + 2H_2O_2 \rightarrow CO_2 + 2H_2O \tag{16}$$
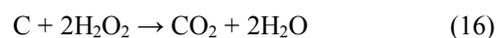
Giroto and co-workers [42] presented experimental results on the photodegradation of poly(ethylene glycol) (PEG) in aqueous solutions by the photo-Fenton and H_2O_2/UV processes.

HPLC analyses enabled the authors to identify acetic and formic acids in both processes. On the other hand, glycolic and malonic acids were detected in the photo-Fenton or H_2O_2/UV systems, respectively, confirming different reaction pathways in each case. In the literature, it is possible to find many studies using and comparing UV/H_2O_2 to other AOPs to treat diverse effluents. Vogna and co-workers [43] studied the UV/H_2O_2-induced degradation of carbamazepine, a worldwide used antiepileptic drug, recently found as contaminant in many municipal sewage treatment plant (STP) effluents and other aquatic environments. The oxidation treatment caused an effective removal of the drug. At complete abatement of the substrate after 4 min treatment, a 35% value of removed total organic carbon (TOC) was obtained.

Ahmed and co-workers [44] studied the degradation and mineralization of organic pollutants contained in actual pulp and paper mill wastewaters by a UV/H_2O_2 process. The results suggested that several steps are involved in the photochemical oxidation of organics, starting with degradation of lignin derivatives and tannins to obtain aromatic intermediates that then undergo oxidative ring opening, leading to aliphatic carboxylic acids. In the final steps, carboxylic acids are mineralized into CO_2 and H_2O.

The AOPs processes have been also studied for microbiological pollutants removal in drinking waters.

However, the formulation of the photokinetic rates of a photochemical process is one of the most difficult parts of reactor design and involves determination of the absorbed light intensity causing chemical conversion, e.g. the generation of highly reactive hydroxyl radicals. Actinometric measurements may often cause problems

due to the polychromatic emission of medium-pressure Hg-arcs, which are used in oxidative degradation procedures. Gahr and co-workers [45] studied the practical use of filter solutions as an appropriate method for approaching monochromatic conditions with polychromatic radiation. The experiments were carried out with the annular photoreactor of a pilot plant for drinking water treatment.

AOPs have been studied for effluents from industries that use dyes. As a few examples, one can find the works of Muruganandham and Swaminatham [46] and Marmitt and co-workers [47].

V.2. Ozone

Ozone (O_3) is a gas composed of three oxygen atoms. Two oxygen atoms form the basis for the oxygen molecule present in the air we breathe. The third atom, very unstable, is easily separated from ozone to connect to other molecules such as organic substances.

The lifetime of the ozone molecule is directly related to temperature. For example, the half-life of ozone at 0°C is 140 minutes and only 40 minutes at 20°C [48]. Due to its instability (approximately 3 s in the gas phase), storage is not an option.

Thus, ozone must be generated *in situ* [49] by three different techniques: exposure of O_2 to ultraviolet radiation, electrolysis of perchloric acid, and electrical discharge. These processes involve fast reactions and are not selective [50]. Among these different processes, electrical discharge (known as corona effect) is the most widely used by most commercial generators. According to this method, ozone is generated by passing air or pure oxygen between two electrodes with a high potential difference (approximately 10 kV), as given by Equations (17) and (18) [51], [52]:

$$O_2 \rightarrow O^\bullet + O^\bullet \qquad (17)$$

$$O^\bullet + O_2 \rightarrow O_3 \qquad (18)$$

This technique produces more ozone in the oxygen conversion process as compared with other methodologies mentioned here [53]. Yields range between 1 and 4% (m m^{-1}) for air-fed systems and between 6 and 14% (m/m) for systems powered by pure oxygen [49], [50], [53]. Although the use of ozone presents a series of advantages, it also has limitations.

The low solubility and low stability in water, combined with the high costs involved in its production and the partial oxidation of organic compounds present in water can make its implementation economically unfeasible [54]. Another limiting factor comes from the low stability of ozone in the reaction medium, which depends on several factors. Among them, special attention is given to pH, since hydroxyl ions initiate the decomposition of ozone molecules [55].

The oxidation of inorganic and organic compounds during ozonation can occur via molecular ozone (direct reaction, prevalent in an acidic medium) or by hydroxyl radicals (indirect reaction, prevalent in alkaline medium). In practice, these two mechanisms are the most favored [55].

The direct reaction (electrophilic attack by molecular ozone) is assigned to compounds that contain double bonds (C=C), specific functional groups (OH, CH$_3$, OCH$_3$), and atoms with high negative charge density (N, P, O and S).

The indirect reaction is non-selective, leading to reactions with organic compounds 10^6 to 10^9 times faster than known oxidizing agents such as H_2O_2 and O_3 (Masten and Davies, 1994). However, each oxidant species takes different significance depending on the specific application of ozone [56].

The interactions between O_3 and OH$^-$ in aqueous solution initiate a series of radical reactions leading to the formation of hydroxyl radicals. This reaction sequence is complex and can be influenced by a number of experimental factors and by the nature and concentration of chemical species present [57], [54].

While disinfection processes occur predominantly via molecular ozone oxidation, oxidative processes can occur either through molecular ozone or hydroxyl radicals [58]. Recent advances in ozone generation systems have reduced the energy required for their production, leading to a considerable reduction in the costs involved in specific applications, making ozone-based processes very attractive and benefit to industry.

In addition to ozonation via molecular O_3 (direct reaction) and via hydroxyl radical (indirect reaction) other possibilities of ozone application in wastewater remediation are available. Such combinations can produce effective results in the remediation of some industrial wastewaters. Ozone can be used in conjunction with ultraviolet radiation (O_3/UV) [59], [29], hydrogen peroxide (O_3/H_2O_2) (Eq. (19)) [60], or a combination of these (O_3/UV/H_2O_2), in addition to O_3/ultrasound and O_3/TiO$_2$. These techniques increase the generation of •OH [61], [62]. Emerging technologies, such as heterogeneous nanocatalyst and catalytic ozonation using ozone are quite promising, and represent nowadays the current trend of ozonation processes [53]:

$$H_2O_2 + 2\,O_3 \rightarrow 3O_2 + 2\bullet OH \qquad (19)$$
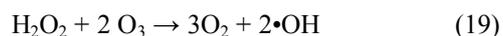
In the presence of ultraviolet (UV) radiation, O_3 might also form hydroxyl radicals. However, in this case, the organic matter decomposition occurs at very slow rates. The combination of UV radiation with H_2O_2 promotes more efficient oxidation of organic pollutants when compared with systems under UV irradiation only.

This mechanism begins with the photolysis of ozone producing hydrogen peroxide.

Then the hydroperoxide ion (HO_2^-) can react with ozone to produce O_3^- and hydroxyl radicals.

These species start a chain reaction and, as a result, compounds normally refractory to simple ozonation are rapidly converted to CO_2 and H_2O [63], [29].

A simplified representation of the reaction in this case is given by Eq. (20) [64]:

$$3O_3 + H_2O + h\nu \rightarrow 2\bullet OH + 4O_2 \qquad (20)$$

The limitations of direct oxidation by ozone can be circumvented by using high reactive indirect ozone reactions in basic aqueous medium. In this case, the reaction between O_3 and OH^- triggers a series of radical reactions that lead to the formation of hydroxyl radicals.

This reaction route is quite complex and is influenced by a number of experimental factors and the nature or concentration of chemical species [29].

In simple terms, the mechanism can be divided into three parts: initiation, propagation, and termination [65]. Al-Hayek and co-workers [66] showed that phenol ozonation in the presence of Fe (III) / Al_2O_3 catalyst leads to a significant increase in TOC removal as compared to ozonation alone. Bhat and Gurol [67] studied the ozonation of chlorobenzene in the presence of goethite and found that the catalytic ozonization was more effective than ozonation alone.

Naydenov and Mehandjiev [68] and Thompson and co-workers [69] observed mineralization of benzene and 1,4-dioxane, respectively, obtained by ozonisation in the presence of MnO_2 in aqueous solution.

Ma and Graham [70] demonstrated that the MnO_2 formed *in situ* by atrazine ozonization in the presence of small amounts of Mn (II) leads to a much higher degree of atrazine oxidation as compared to the ozone only.

The authors have given these results to the generation of highly oxidative intermediate species. Andreozzi and co-workers [71] reported a significant improvement in the oxalic acid ozonation in acidic medium induced by the presence of MnO_2. Pines and co-workers [72] indicated that the combination of O_3/metal-TiO_2 is particularly interesting for the hydrophilic compounds oxidation (biodegradable). However, under these combination, the efficiency observed for the hydrophobic compounds was low.

V.2.1. Initiation

The reaction between the hydroxide anion and ozone leads to the formation of superoxide radical anions ($O_2^{\bullet-}$) and hydroperoxide radicals ($HO_2^\bullet$), according to Eq. (21) [73]:

$$O_3 + OH^- \rightarrow HO_4^\bullet \rightarrow O_4^{\bullet-} + HO_2^\bullet$$
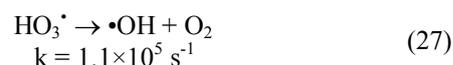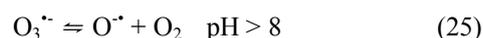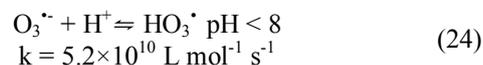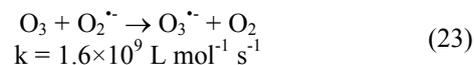$$k = 1.1 \times 10^5 \ s^{-1} \qquad (21)$$
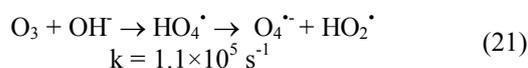
The hydroperoxide radical shows acid-base equilibrium (Eq. (22)) [74]:

$$HO_2^\bullet \rightleftharpoons O_2^- + H^+ \qquad ka = 1.6 \times 10^{-5} \qquad (22)$$
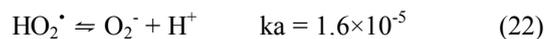
V.2.2. Propagation

The radical anion ozonide ($O_3^{\bullet-}$), formed from the reaction between ozone and the superoxide radical anion ($O_2^{\bullet-}$), quickly decomposes to form hydroxyl radicals (Equations (23) to (27)) [73]-[75]:
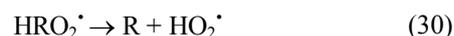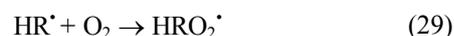
$$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2$$
$$k = 1.6 \times 10^9 \ L \ mol^{-1} \ s^{-1} \qquad (23)$$

$$O_3^{\bullet-} + H^+ \rightleftharpoons HO_3^\bullet \quad pH < 8$$
$$k = 5.2 \times 10^{10} \ L \ mol^{-1} \ s^{-1} \qquad (24)$$

$$O_3^{\bullet-} \rightleftharpoons O^{\bullet-} + O_2 \quad pH > 8 \qquad (25)$$

$$O^{\bullet-} \rightarrow HO^\bullet + OH^- \qquad (26)$$

$$HO_3^\bullet \rightarrow \bullet OH + O_2$$
$$k = 1.1 \times 10^5 \ s^{-1} \qquad (27)$$

The radical •OH can react with the ozone as follows (Eq. (28)):

$$\bullet OH + O_3 \rightarrow HO_4^\bullet \rightarrow O_2 + HO_2^\bullet \qquad (28)$$
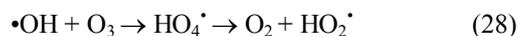
with the formation of O_2 and $HO_2^\bullet$ from $HO_4^\bullet$, a chain reaction can be repeated. Substances which convert •OH to radical anions $O_2^{\bullet-}$ and/or $HO_2^\bullet$ promote chain reactions. Organic molecules (R) can also act as promoters (Eq. (7)):

$$HR + OH^\bullet \rightarrow R^\bullet + H_2O \qquad (7)$$

According to Emanuel and Gál [76] and Singh and Bahari [77], if oxygen is present, organic peroxyl radicals ($ROO^\bullet$) can be formed and then react, eliminating $O_2^{\bullet-}$/$HO_2^\bullet$ and entering into chain reaction (Eqs. (29) to (31)):

$$HR^\bullet + O_2 \rightarrow HRO_2^\bullet \qquad (29)$$

$$HRO_2^\bullet \rightarrow R + HO_2^\bullet \qquad (30)$$

$$HRO_2^\bullet \rightarrow RO + OH^\bullet \qquad (31)$$

V.2.3. Termination

Some organic and inorganic substances react with the hydroxyl radical and form secondary radicals that do not produce $O_2^{\bullet-}$/$HO_2^\bullet$ [78], acting as inhibitors of chain reactions (Eqs. (32) and (33)):

$$\bullet OH + CO_3^{2-} \rightarrow OH^- + CO_3^{\bullet-} \qquad (32)$$

$$\bullet OH + HCO_3^- \rightarrow OH^- + HCO_3^\bullet \qquad (33)$$
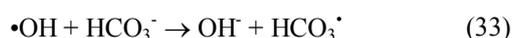
Another possibility for the termination reaction is the combination of two radicals [79] (Eq. (15)):

$$•OH + HO_2^• \rightarrow O_2 + H_2O \qquad (15)$$

In general, three moles of ozone produce two moles of hydroxyl radicals [80], according to Eq. (34):

$$3O_3 + OH^- + H^+ \rightarrow 2•OH + 4O_2 \qquad (34)$$

A change in solution pH is usually the simplest approach (although not the most efficient) to obtain hydroxyl radicals from ozone. Generally, under acidic conditions (pH ≤ 4), the direct mechanism predominates. Above pH 10, it becomes predominantly indirect [65].

V.3. The Combined Use of O₃/H₂O₂

Regardless of H_2O_2 being a powerful oxidant, it is also an unstable compound which dissociates with maximum rate at pH equal to its pKa [20], as given by Equations (35) to (37):
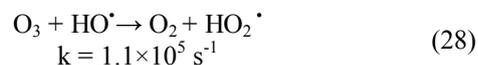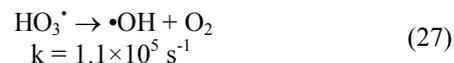
$$\begin{array}{c} H_2O_2 \rightarrow HO_2^- + H^+ \\ pKa = 11.6 \end{array} \qquad (35)$$

$$\begin{array}{c} H_2O_2 + 2e^- + 2H^+ \rightarrow 2\,H_2O \\ E^° = +1.78\ V \end{array} \qquad (36)$$

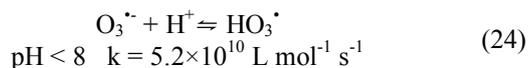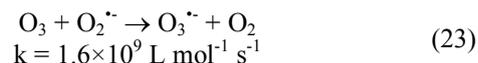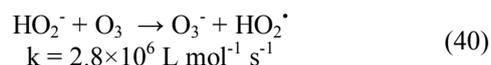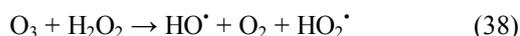$$H_2O_2 + HO_2^- \rightarrow H_2O + O_2 + HO^- \qquad (37)$$
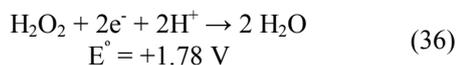
The use of two or more combined oxidants allows using possible synergistic effects among them [18].

For example, Catorceno and co-workers [29] compared phenol oxidation by the O₃, O₃-UV, and O₃-H₂O₂ processes, and found that for low initial dissolved organic carbon (DOC) concentration, the O₃-H₂O₂ process showed a better performance in comparison to the O₃ and O₃-UV systems in terms of DOC removal rates. For DOC removed after two hours, however, a strong dependence on ozone and H₂O₂ concentrations was found.

Hydrogen peroxide can start the decomposition of O₃ by electron transfer.

The reaction generates HO•, with H₂O₂ and O₃ consumed through a chain mechanism (Equations (38), (39), (22), (40), (23), (24), (27), (28) and (41):

$$O_3 + H_2O_2 \rightarrow HO^• + O_2 + HO_2^• \qquad (38)$$

$$\begin{array}{c} H_2O_2 \rightleftharpoons HO_2^- + H^+ \\ ka = 1.6 \times 10^{-12} \end{array} \qquad (39)$$

$$\begin{array}{c} HO_2^• \rightleftharpoons O_2^- + H^+ \\ ka = 1.6 \times 10^{-5} \end{array} \qquad (22)$$

$$\begin{array}{c} HO_2^- + O_3 \rightarrow O_3^- + HO_2^• \\ k = 2.8 \times 10^6\ L\ mol^{-1}\ s^{-1} \end{array} \qquad (40)$$

$$\begin{array}{c} O_3 + O_2^{•-} \rightarrow O_3^{•-} + O_2 \\ k = 1.6 \times 10^9\ L\ mol^{-1}\ s^{-1} \end{array} \qquad (23)$$

$$\begin{array}{c} O_3^{•-} + H^+ \rightleftharpoons HO_3^• \\ pH < 8 \quad k = 5.2 \times 10^{10}\ L\ mol^{-1}\ s^{-1} \end{array} \qquad (24)$$

$$\begin{array}{c} HO_3^• \rightarrow •OH + O_2 \\ k = 1.1 \times 10^5\ s^{-1} \end{array} \qquad (27)$$

$$\begin{array}{c} O_3 + HO^• \rightarrow O_2 + HO_2^• \\ k = 1.1 \times 10^5\ s^{-1} \end{array} \qquad (28)$$

$$O_3 + HO_2^• \rightarrow 2\,O_2 + HO^• \qquad (41)$$

Although it is an expensive process, it is fast and allows treating organic contaminants present at very small concentrations (ppb). The molar ratio O₃/H₂O₂ is approximately 2:1 [81]. The process favors kinetics as pH rises, as observed in Equations (35) and (22) [20].

The adequate pH range of the process is between 7 and 8. In the literature, it is possible to find many works combining the use of O₃ whit ₂O₂. Lee and co-workers [82] investigated the possibility of conventional ozonation and the O₃/H₂O₂ for N-nitrosodimethylamine (NDMA) oxidation, a probable human carcinogen found in surface and drinking water. The authors also and discussed the mechanism for NDMA oxidation during ozonation. In experiments with natural waters, NDMA could not be significantly oxidized during conventional ozonation. In the O₃/H₂O2, ozone doses of 160–320 μM ([O₃]₀/[H₂O₂]₀=2:1) were necessary for >50% NDMA oxidation depending on the •OH scavenging rates of the natural waters. A lot of authors investigated and compared the efficiency of O₃/H₂O₂ to others AOP processes for treating effluents from diverse industries.

As a few examples to illustrate this, treatment of pharmaceutical drugs effluents from penicilin were invastigated by Arslan-Alaton and Dogruel [83]. Diclofenac effluents were treated by Vogna and co-workers. Other wastewaters, as dyeingbath [85], fragances as musk [86] were also studied.

V.4. Catalytic Ozonation

The catalytic ozonization may be regarded as a homogeneous process, which is based on activation of ozone by metal ions present in aqueous solution, or as a heterogeneous process in the presence of supported metal oxides or metal oxides. Catalytic ozonization corresponds to an effective method for removal of various organic compounds in water and in aqueous effluents. However, this method have been used mainly in laboratory scale [87].

The proposed catalysts for homogenous catalytic ozonization process are transition metals such as Fe^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Ag^+, Cr^{3+}, Zn^{2+}.

The nature of the transition metal applied not only determines the rate of reaction, but also the selectivity and consumption of ozone [87].

In the literature are reported ozone molecular reactions with many compounds (over 50 species), with second-order rate constants. Some of these are very reactive, regardless of pH (as sulfite, sulfite and nitrite) while others exhibit low kinetic constant in acidic media and a significant increase in reactivity with increasing pH (such as hypochlorous acid, hypobromous acid and ammonia). Fe (II) and Mn (II), which are present in natural waters, may readily be oxidized by ozone generating insoluble oxides easily removed by filtration. Equations 42 to 48 illustrate proposed reaction mechanisms of Fe^{2+} with ozone [88]. It is worth mentioning that the use of Fe^{2+} in processes of catalytic ozonization is restricted to acid media, since at higher pH values precipitation of these ions occurs [89]:

$$Fe^{2+} + O_3 \rightarrow Fe^{3+} + O_3^- \qquad (42)$$

$$O_3^- + H^+ \leftrightharpoons HO_3 \rightarrow OH + O_2 \qquad (43)$$

$$\underline{Fe^{2+} + OH \rightarrow Fe^{3+} + OH^-} \qquad (44)$$

$$2\ Fe^{2+} + O_3 + 2\ H^+ \rightarrow 2Fe^{3+} + O_2 + H_2O \qquad (45)$$
$$\text{(Balance: (42) to (44))}$$

$$Fe^{2+} + O_3 \rightarrow (FeO)^{2+} + O_2 \qquad (46)$$

$$\underline{(FeO)^{2+} + Fe^{2+} + 2\ H^+ \rightarrow 2Fe^{3+} + O_2 + H_2O} \qquad (47)$$

$$2\ Fe^{2+} + O_3 + 2\ H^+ \rightarrow 2Fe^{3+} + O_2 + H_2O \qquad (48)$$
$$\text{(Balance: (46) to (47))}$$
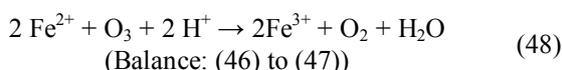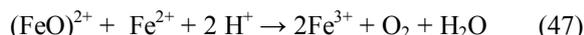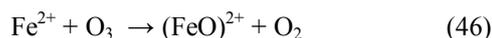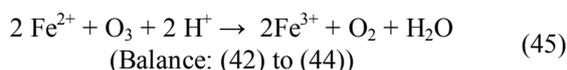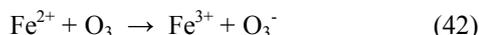
Béltran and co-workers [90] proposed reaction mechanism between Fe (III) and ozone with subsequent formation of hydroxyl radical, according Eq. (49):

$$Fe^{3+} + O_3 \rightarrow (FeO)^{2+} + HO^\bullet + O_2 + H^+ \qquad (49)$$

According Eqs. (42) to (49), the reaction mechanism is the transfer of electrons from the metal reduced to ozone, forming Fe^{3+} ion and radical ion O_3^-, and from this the hydroxyl radical. In the presence of excess Fe^{2+}, hydroxyl radical can oxidize a second Fe^{2+}, providing a stoichiometric ratio of 0.5 moles of ozone per mole of ferrous ion [88].

Catalytic ozonation is a method that has been employed at laboratory scale. It shows to be effective in the removal of several organic compounds present in water and aqueous effluents [87], [54].

The catalysts proposed for catalytic homogeneous ozonization process are transition metals cations such as

Fe(II), Fe(III), Mn(II), Co(II), Cd(II), Cu(II), Ag(I), Cr(III), Zn(II). The nature of the transition metals determine, besides the reaction rate, selectivity and consumption of ozone [87], [54].

Xiang-Feng and Xin-Xua [91] studied phenol degradation using the catalytic ozonation process with Fe^{3+}. The parameters studied to evaluate this effect were pH, Fe^{3+} concentration, and reaction time. The COD was used as a response. The maximum efficiency of COD removal was 55.4% with pH equal to 2.8, ozone concentration equal to 3 g L^{-1}, iron (III) concentration equal to 10 mg L^{-1}, and ozonation time of 20 minutes.

Assalin and co-workers [92] studied the catalytic effect of Mn^{2+} and Cu^{2+} ions for phenol ozonation. The presence of Mn^{2+} ions has significantly increased phenol degradation and reduced the consumption of ozone compared to conventional processes (molecular ozone and hydroxyl radicals). The authors obtained a reduction on the organic load (TOC) of 63% for pH 3 using the metal Mn(II) in just 7 minutes of treatment. The consumption of ozone was also reduced from 229 to 129 mg L^{-1} in the presence of catalyst. The catalyst effect of Cu^{2+} ion was less significant in the degradation of phenol under the same conditions used in this process.

Peixoto and Izario Filho [54] studied the effect of metal cations in the homogenous catalytic ozonation of leachate from the municipal landfill of the City of Guaratinguetá (São Paulo). The experiments considered the effects of metal concentrations (Fe^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Cr^{3+}), pH, ozone flow rate and presence/absence of UV radiation (254 nm). In this work, a maximum reduction of chemical oxygen demand (COD) of 50% was achieved. The conditions which enabled to achieve the best results were ozone flow of 5 L h^{-1} (590 mg h^{-1} O_3) and a ferric ion concentration of 5 mg L^{-1} and pH 5.

It is important to note that the homogeneous catalytic ozonation must be associated to a technique of removing the metal ion from treated effluents. The toxic character of some metals may limit the application of this process. In spite of these limitations, the catalytic ozonation is a promising technology for application in the decontamination of aqueous effluents.

In the literature, it is possible to find works concerning the use of different catalytic AOPs processes. As an example, we can cite the work of Lee and co-workers [82], that developed an innovative advanced catalytic oxidation, with iron oxide coated granular activated carbon (FeGAC) and/or hydrogen peroxide (H_2O_2) process. The developed process was employed to treat the landfill leachate from central Taiwan. Experimental results indicated that the FeGAC/H_2O_2 process could effectively remove organic compounds from landfill leachate.

The presence of iron oxide coated granular activated carbon (FeGAC) greatly improved the oxidative ability of H_2O_2 for the removal of humic acids, fulvic acids and non-humic substance from leachate.

For instance, at pH 6, the removal efficiencies of FeGAC/H_2O_2 and H_2O_2 processes were 70%, and 8%, respectively. FeGAC/H_2O_2 combined both advantages of FeGAC and H_2O_2 where FeGAC had good organics adsorption ability and could effectively catalyse the hydrogen peroxide oxidation reaction for organics removal.

Kim and co-workers [93], investigated the feasibility of microporous silicates as a potential catalyst for a catalytic ozonation process. Organophosphorus insecticide, dichlorvos (DDVP), was employed as a model chemical for assessing conventional ozonation and catalytic ozonation, because its oxidative intermediate is toxic and is not degraded by direct ozonation.

It was found that ozone was well adsorbed and simultaneously decomposed in microporous silicates, resulting in the production of possible radical species. In the presence of microporous silicates, radical reactions by decomposed ozone were evidenced by phosphate ion release that shows a degradation of a toxic intermediate of DDVP. Accordingly, cytotoxicity was successfully decreased.

In a continuous treatment process combining a conventional ozonation vessel and a microporous silicate column for an effective use of residual ozone, enhanced degradation of DDVP was demonstrated by a decrease of DOC, an increase of the PO_4^{3-} concentration and reduction in the cytotoxicity.

The works cited above are just a few examples. The catalytic AOP have been employed for treating a variety of effluents, as biotrated textile effluentes [94] or pharmaceutical drugs as Fuoxetine in aqueous media [95].

V.5. Fenton Reaction

A century ago, the catalytic oxidation of tartaric acid in the presence of ferrous salts and hydrogen peroxide was reported by Fenton [96]. In the Fenton reaction (Equation 50), hydroxyl radicals are generated from the reduction of hydrogen peroxide.

However, this spontaneous reaction was only proposed 40 years after the report of Fenton [97]:
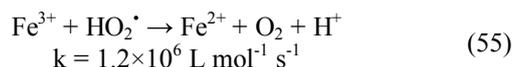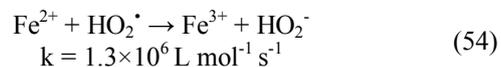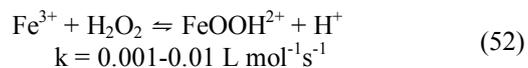
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$$
$$k = 76 \text{ L mol}^{-1} \text{ s}^{-1} \tag{50}$$
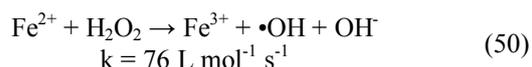
In the absence of a substrate or in the presence of high concentrations of Fe^{2+}, the hydroxyl radicals formed can oxidize other ferrous ions to ferric ion, as in Equation (51):

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^-$$
$$k = 3.2 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} \tag{51}$$
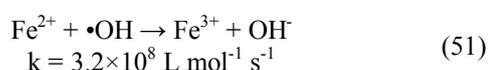
The ferric ions formed can catalytically decompose H_2O_2 to H_2O and O_2 (Eqs. (52) to (55)), also forming ferrous ions and radicals. In this case, the iron species in aqueous solution (Fe^{2+}, Fe^{3+}) exist as aquo-complexes.

The rate constants for these reactions were determined by different authors [98], [99]:

$$Fe^{3+} + H_2O_2 \rightleftharpoons FeOOH^{2+} + H^+$$
$$k = 0.001\text{-}0.01 \text{ L mol}^{-1}\text{s}^{-1} \tag{52}$$

$$FeOOH^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet} \tag{53}$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^-$$
$$k = 1.3 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1} \tag{54}$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+$$
$$k = 1.2 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1} \tag{55}$$

In accordance with these reactions, iron acts as a catalyst. However, as the reduction of Fe^{3+} with H_2O_2 is usually much slower than the oxidation of Fe^{2+}, the iron exists in solution mostly in the form of Fe^{3+}.

According to Equation 13, hydrogen peroxide can also act as consumer of hydroxyl radicals, forming hydroperoxide radicals ($HO_2^{\bullet}$). These species have lower standard reduction potential (E° = 1.42 V) in comparison to •OH and its formation occurs mainly in the presence of excess of H_2O_2. In this case, Fe^{2+} concentration in the reaction medium is low in relation to that of Fe^{3+}, making the reaction slower. This occurs because the reaction between Fe^{3+} and H_2O_2 (Equation 52) is slower than the decomposition of H_2O_2 in the presence of Fe^{2+}. The prejudicial effect of excess of H_2O_2 in the degradation of organic compounds was observed by various authors [100], [101], who focused particularly attention to establish adequate concentrations.

The Fenton oxidation has been applied with success to the treatment of textile effluents [102]-[104]. Teixeira and co-workers [105] have successfully applied the Fenton reaction to the treatment of aminosilicone-containing water emulsions.

The key aspect of the Fenton process is credited to the relation among $[Fe^{+2}]$, $[Fe^{+3}]$, $[H_2O_2]$ and characteristics of reaction medium (pH, temperature and amount of organic and inorganic constituents). These parameters determine the efficiency of the global reaction. From a practical point of view, the Fenton process requires prior optimization of the variables to be effective.
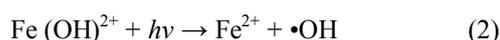
V.6. Photo-Fenton Reaction

The oxidation of organic compounds under UV irradiation in the presence of ferric ion in acidic medium was observed in the 1950s, when it was postulated that the electron transfer initiated by irradiation results in the generation of •OH, responsible for the oxidation reactions [106].

In aqueous solution, in the absence of other ligands and acidic medium, the ferric ion exists as aqueous complexes, for example, $[Fe(H_2O)_6]^{3+}$. With pH increase, hydrolysis occurs by the formation of hydroxylate species, whose proportion depends on pH. The first hydrolysis equilibrium is represented by Equation (56) [107]:

$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+ \tag{56}$$
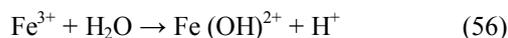
when Fe(III) complexes are irradiated, there is the promotion of an electron from an orbital centered in the ligand to a metal-centered orbital, which is called *ligand to metal charge transfer* (LMCT) and involves the reduction of Fe (III) to Fe (II) and ligand oxidation (Eq. (2)), forming hydroxyl radicals [108]:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \cdot OH \tag{2}$$

The Fe^{2+} generated during irradiation reacts in the presence of hydrogen peroxide, the Fenton reaction. In this context, the photochemical reaction establishes a cycle in which Fe^{2+} is regenerated. The use of Fe^{2+}/Fe^{3+} in the presence of hydrogen peroxide under irradiation is called photo-Fenton reaction.

Photon absorption by ferric ions can extend into the visible region of the spectrum, depending on pH and ligands. As discussed above, pH influences the formation of hydroxylate species, which have a higher absorption in the visible spectrum. The species $Fe(OH)^{2+}$ shows maximum absorbance at about 300 nm extending to 400 nm, which enables solar-irradiated photo-Fenton reactions. More information about the role of iron as a function of pH is described in the work of Poulopoulos and co-workers [33].

Particularly, many photochemical reactions may occur in the photo-Fenton system, depending on the emission spectrum of the radiation source and on the absorbance of existing chemical species. The photolysis of H_2O_2, which generates two hydroxyl radicals, can occur simultaneously with the photo-Fenton reaction. However, its low molar absorption coefficient (18.7 L mol^{-1} cm^{-1} at 254 nm) makes this step less important in the photo-Fenton process, especially if one considers the absorption of light by iron and organic compounds.

Since Fenton and photo-Fenton are catalyzed by Fe^{2+}/Fe^{3+} ions and considering that these are hydrolyzed to form insoluble hydroxides, the pH of the medium has an important role in the reactions, thus affecting the rate of degradation of organic compounds. The influence of pH was evaluated in several studies, where it was found that a narrow pH range between 2.5 and 3.0 provides maximum efficiency [17].

This limited range is also related to the precipitation of Fe (III) at pH above 5.0, drastically reducing their interactions with hydrogen peroxide and, thus, the production of •OH radicals.

Below pH 2.5, the degradation rate also decreases although Fe remains in solution as soluble complexes.

This decrease in the rate of degradation occurs since high concentrations of H^+ may adduct hydroxyl radicals. Futhermore, species like $Fe(H_2O)_6^{3+}$ limit radiation absorption. In conclusion, the narrow pH range in which the maximum efficiency of the Fenton and photo-Fenton reactions is verified constitutes the major limitation of these processes. Fe(III) complexes as a function of pH ($[Fe^{3+}]_{TOT}$ = 1 mmol L^{-1}, T = 25 °C) are shown in Fig. 1 [109].
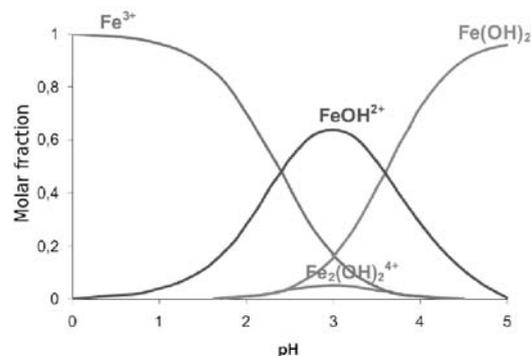
Fig. 1. Fe(III) complexes as a function of pH ($[Fe^{3+}]_{TOT}$ = 1 mmol L^{-1}, T = 25 °C). Adapted from. [109]

This narrow pH range is maintained by adjusting the pH throughout the whole reaction time. Moreover, there is the need to neutralize the pH of the treated wastewater before discarding to waterbodies.

To overcome these limitations, some strategies have been studied, such as the use of iron complexes with organic ligands, in order to stabilize pH close to neutrality, or the immobilization of Fe on membranes or other supports [17].

The UV/visible absorption spectra for Fe(III) complexes in aqueous solution, and the total absorbance for an optical length of 1 cm given by $\varepsilon_{total}[Fe(III)] = \varepsilon_1[Fe^{3+}] + \varepsilon_2[FeOH^{2+}] + \varepsilon_3[Fe(OH)^{2+}] + \varepsilon_4[Fe(OH)_2^{4+}]$ are shown in Fig. 2 [110].

The photo-Fenton process is effective in removing organic load of dairy effluent. According to Dalla Villa an co-workers [111], the concentration of iron which already exists in effluent is not sufficient to promote mineralization; a complement of iron salt is thus necessary.

The authors observed that TOC removal after 3 hours of reaction remains the same for iron concentrations in the range 1.5-6 mmol L^{-1}. High initial concentrations of H_2O_2 do not favor the removal of the organic load. However, multiple additions of hydrogen peroxide (0.25 mol L^{-1}) revealed to be more efficient for TOC removal than an addition of 0.5 mol L^{-1}, especially for low iron concentrations. The photo-Fenton process was also efficient for high organic loads.This aspect is considered important since in general, biological processes loose efficiency with an increase of organic load.
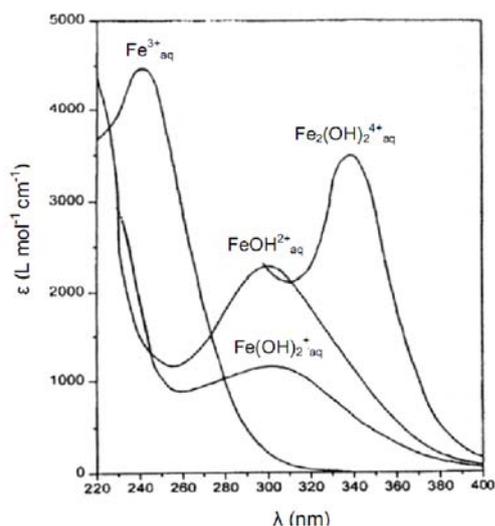
Fig. 2. UV-visible absorption spectra of Fe(III) complexes in aqueous solutions. Fe^{3+} corresponds to the hexa-aquo complex (ferric ion), $Fe_2(OH)_2^{4+}$ is the tetra-aquo-dihydroxi-complex, and $FeOH^{2+}$ is the monohydroxy- penta-aquo complex. Adapted from. [110]

Furthermore, the rate of the photo-Fenton treatment improved the performance of global treatment, once the biological treatments are mostly slow.

Manenti and co-workers [112] studied the removal of organic pollutants in the effluent from industrial food processing based on the photo-Fenton technique using artificial irradiation at laboratory scale. A complete 2^3-factorial design was applied to optimize the process, on the basis of the effects of pH and Fe^{2+} and H_2O_2 concentrations on the removal of chemical oxygen demand (COD), color and turbidity. The best performance was achieved for Fe^{2+} and H_2O_2 concentrations of 0.26 g L^{-1} and 22 g L^{-1}, respectively, and initial pH 3.0, with 93% reduction of COD, 95% color removal and 98% reduction of turbidity.

Teixeira and co-workers [63], [105] have also demonstrated the applicability of the photo-Fenton process to the degradation of aminosilicone polymers in concentrated and diluted water emulsions, irradiated by medium pressure mercury lamps or sunlight. Giroto and co-workers [42], [113], [114] studied the photo-Fenton degradation of water soluble polymers (polyvinil alcohol, poly(ethylene glycol), polyacrylamide, and polyvinylpyrrolidone).

Silva and co-workers [115] studied the use of the photo-Fenton process to reduce the toxicity of oil field produced water by oxidation of organic compounds. In the petroleum industry, water production represents 98% of all waste generated. According to the authors, when using solar irradiated reactors, this process resulted in low residual generation and low cost. According to the authors, the analysis of treated water showed acceptable levels of contamination for use in irrigation.

In the work of Nogueira and co-workers [116], the solar driven photo-Fenton process was applied to the oxidation of phenol in a parabolic trough solar reactor (PTR). The effects of Fe(II) (0.04-1.0 mmol L^{-1}), H_2O_2 (7-270 mmol L^{-1}), initial phenol concentration (100 and 500 mg C L^{-1}), solar radiation, and operation mode (batch and fed-batch) were studied. More than 90% of the dissolved organic carbon (DOC) was removed within three hours of irradiation or less.

Martín and co-workers [117] studied the degradation of a complex mixture of pesticides by combining a pretreatment with photo-Fenton and a final biologically activated sludge process. Four commercial pesticides were chosen, at an initial concentration of 200 mg L^{-1}: *laition*®, *metasistox*®, *sevnol*® and *ultracid*. The biotreatment started once photocatalytic mineralization achieved 31%, and remained for 5 h in a stirred tank reactor in batches of 6 L with non-acclimated activated sludge. In this way, the effluent produced by the photo-Fenton treatment was completely remediated. The time involved in the biological treatment was shorter than typically found values in municipal wastewater treatment plants (usually 8 to 10 h). However, the evaluation of this technology has been limited by the use of only one concentration of the contaminants, not considering the effect of higher concentrations of pesticides.

Teixeira and co-workers [118] studied the degradation of a fungicide (tebuconazole) and an insecticide/ acaricide (methamidophos) in aqueous solution by the photo-Fenton process. For the fungicide, a rapid removal of both DOC (89% after 180 minutes) and COD (86%) was achieved; the non-irradiated thermal Fenton process resulted in the poorest performance, with only 20% DOC removal after 180 minutes. On the other hand, the degradation of methamidophos occured without significant mineralization.

In fact, for [Fe(II)]=0.55 mmol L^{-1} a ten-fold increase in initial H_2O_2 concentration enabled only a slight improve of the photo-Fenton degradation, with final DOC and COD removals of 6% and 24% ($[H_2O_2]_0$=55 mmol L^{-1}), respectively, and of 18% and 46% ($[H_2O_2]_0$=550 mmol L^{-1}), respectively.

Navarro and co-workers [119] studied the oxidation of phenol by the photo-Fenton process. A molar ratio of phenol:Fe(II):H_2O_2 equal to 1:0.5:15, and pH controlled at 3 were used, and TOC analyses showed almost complete mineralization of phenol after 2 h with controlled pH to 3. Organic acids of low molecular weight, particularly oxalic acid, suabproducts of phenol degradation, were also destroyed. Huang and co-workers [120] studied the degradation of both hypophosphite binary components and citrate in aqueous solution by the advanced oxidation processes Fe^{2+}/H_2O_2, $UV/Fe^{2+}/H_2O_2$ and electro-Fenton. The authors found that the Fenton process could not degrade citrate completely in the presence of hypophosphite since this species caused a serious inhibition. On the other hand, both the photo-

Fenton and the electro-Fenton processes could overcome the inhibition by hypophosphite, especially the electro-Fenton, due to the degradation of hypophosphite and catalytic activation.

VI. Heterogeneous Systems

Heterogeneous processes use semiconductor catalysts [121]. As examples of heterogeneous systems, UV/titanium dioxide (TiO_2) and UV/zinc oxide (ZnO) are included. Once the semiconductor is exposed to UV radiation, it is promoted to an electronically excited state, characterized by the generation of electron-hole pairs (e^-, h^+), due to the promotion of electrons from the valence band (VB) to the conduction band (CB) by photon absorption. The energy difference between the two bands corresponds to the bandgap energy (Fig. 3).

With the electron promoted to the BC and the hole (h^+) generated in BV with a strongly oxidizing character, reducing and oxidizing sites are created, respectively, capable of inducing chemical reactions with adsorbed species. Holes can oxidize water molecules or hydroxide anions, with the formation of hydroxyl radicals; organic pollutants can be oxidized by the later or directly by the holes.

TiO_2 is the most commonly used semiconductor in photo-degradation of organic compounds. Several characteristics contribute to this: the possibility of activation by sunlight, its insolubility in water, chemical stability over a wide pH range, the possibility of immobilization on surfaces, low cost and its non-toxic character [123]-[128]. Many empirical studies with TiO_2 have been developed, but its reaction mechanism is not yet fully understood. However, some steps of the mechanism seem to have been explained and accepted by most researchers: excitation of the semi-conductor and subsequent formation of pairs h^+_{BV} and e^-_{BC}; the recombination between these pairs; the adsorption of O_2, H_2O and organic species on the semiconductor surface and the donation or reception of electrons to/from the pair e^-/h^+, respectively, preventing recombination.
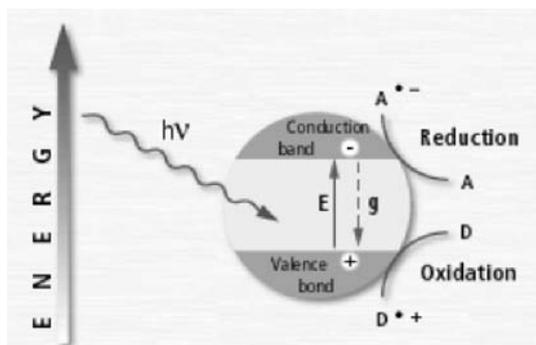

Fig. 3. Electronic principles of a heterogeneous photochemical process employing a photoreactive semiconductor. Adapted from. [122]. BV: Valence band, CB: Conduction band, and e^-: electron (-) h^+: hole (+); hv: UV radiation

It is also believed that O_2 is the main responsible species for continuing the reactions, consuming electrons and reacting with organic radicals formed and leading to complete mineralization [129], [127].

Direct oxidation occurs when the photo-generated hole reacts directly with the organic compound (Eq. (57)) [124]:

$$R_{1\,(ads)} + h^+_{BV} \rightarrow R_{1\,(ads)}^+ \qquad (57)$$
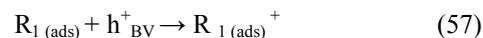
Indirect oxidation occurs when the photo-generated hole in the valence band reacts with H_2O or OH^- anions adsorbed on the surface producing hydroxyl radicals, which oxidize adsorbed organic matter (Eq. (58)) [124], [125], [129]:

$$\bullet OH + R_1 \rightarrow R_2 \qquad (58)$$

Several articles have been published demonstrating the effectiveness of this process, as well as the various combinations of different AOPs to degrade recalcitrant substances [130]-[134], [81].

In spite of positive results, the implementation of photocatalytic processes in industrial scale is still difficult, because the treatment using ultraviolet radiation is expensive. An alternative is the use of the UV component of solar radiation. However, this is still a technical challenge at industrial scales [25], [135]. Another alternative is to search for new semiconductor catalysts which absorb a higher amount of the visible componente of sunlight. Immobilization of the semiconductor with no loss in photocatalytic activity is a widely studied because when in suspension, significant light scattering occurs [136]; there is also the need for the separation of fine catalyst particles [137].

Many studies aiming at avoiding the disadvantages mentioned above have been conducted, mainly involving the development of photocatalysts for greater efficiency (doping), implementation of systems operated with photocatalysts, photocatalysts immobilization and the use of passive photocatalysts activated by sunlight or systems assisted by sensitizers agents [138]-[143].

In Addition to TiO_2, other semiconductors such as CdS, ZnO, WO_3, ZnS, and Fe_2O_3 are mentioned in literature [144]-[149]. There are many studies comparing the effectiveness of TiO_2 and ZnO as photocatalysts [150]-[152]. Such studies have shown various aspects related to the use of these semiconductors: the photo-degradation mechanism of ZnO is similar to TiO_2 [130]; both are efficient semiconductors, inexpensive and non-toxic; the efficiency is increased when nanometric particles are used. The major advantage of ZnO is due to its higher absorption band in comparison with TiO_2 [153].

The metal oxide semiconductor shave shown good photocatalytic activity toward the degradation of harmful organics into less harmful molecules under light

illumination such as TiO_2 and ZnO. These semiconductors with direct wideband gap (3.37 eV) are highly explored n-type semiconductors owing to their high electron–hole binding energy (60 meV), high thermo-mechanical stability, and good piezoelectric [153] and optoelectronic properties [155], [156]. The synthesized ZnO/TiO_2 have been extensively characterized in terms of morphology as well as structural, crystalline and photocatalytic properties. Recently, ZnO nanomaterials applications in photocatalysis have received great deal of interest because of its impressive catalytic activity and quantum efficiency, besides the low cost and low toxicity, compared to that of widely used TiO_2 nanomaterials [157]. It has been reported to display good photoconductivity and high transparency in the visible region and used as transparent electrodes for solar cells. Currently there are number of physical or chemical synthesis methods available to synthesize ZnO nanoparticles. However, in these methods a strictly controlled synthesis environment, high synthesis costs, complexities in synthesis reaction, expensive equipment and complicated operation are required. So far, various ZnO/TiO_2 nano structures have been used to degrade the harmful dyes into less harmful chemicals by photocatalytic reaction under UV light illumination. Sun *et al*. and Kuo *et al*. demonstrated the photo-catalytic degradation of methylene blue (~94%) in 5 h and rhodamine-B (~94%) in 300 min under UV light illumination over the surface of ZnO nanobelts and ZnO nanowires on silicon wafer with assistance of SnO_2/Sn respectively [158], [159]. Various processes for the preparation of catalysts with nanoparticles have been used for treatment of effluent by POA, either by impregnation under inert support, such as metal powders, ceramic tubes, among others, used or as powder in the effluent solution. The facile solution method is used to synthesize ZnO nanoparticles at relatively low temperature using zinc acetate and oxalic acid and which are then utilized as the photocatalyst for the degradation of rhodamine-B dye. Also, Zinc acetate dihydrate, $Zn(CH_3COO)_2 \cdot 2H_2O$ has been used as a precursor to prepare zinc oxide nanoparticles (NPs) by thermal decomposition in air at 400 ^{o}C. Two samples with reaction time of 3 and 12 h are studied. Structural study of ZnO NPs has been analyzed by X-ray diffraction (XRD). The synthesized ZnO NPs are found to possess wurtzite structure. The average crystallite size determined by XRD is found as 29.66 and 32.68 nm corresponding to reaction time of 3 and 12 h, respectively. Optical properties of the ZnO NPs have been investigated by UV–visible spectroscopy and photoluminescence (PL) spectroscopy at room temperature. Blue shift in band gap is observed due to nano size. PL spectra exhibit a UV emission peak at 396 nm (~3.11 eV), and broad visible emission peaks including violet emission at 418 nm (2.96 eV), blue emission at 441 nm (~2.79 eV), blue–green emission 481 nm (~2.56 eV) and green emission at 522 nm (~2.37 eV). Photoconductivity properties have been investigated with several parameters such as voltage dependence of photocurrent and darkcurrent, time-resolved rise and decay of photocurrent and spectral response of photocurrent. Longer reaction time of 12 h manifests in improved photosensitivity as compared to that for sample with reaction time of 3 h.

Though some good results are obtained using these semiconductors studies of Wilcoxon and co-workers [149], Daneshvar and co-workers [160] and Silva and co-workers [152] showed that the applicability of nanoparticles in AOPs may increase the process efficiency and, therefore, minimize the limitations in this type of treatment [100].

VII. Final Considerations

Estimating the importance of an issue for the scientific world is complex. Many criteria can be used, each with advantages and disadvantages. An illustration of the importance and evolution of AOPs can be grasped in a quick search on the page "*Web of Knowledge*" <http://apps.webofknowledge.com> using the terms "*advanced oxidative process* (*processes*)", "*advanced oxidative technology* (*technologies*)", "*advanced oxidation process* (*processes*)" or "*advanced oxidation technology* (*technologies*)" as keywords. The data from this collection are shown in Fig. 4.

Since the first publication (in 1966) until the date of this survey (January 31st, 2013), a total of 7,289 documents were found. Interestingly, in 1966, there were only two papers (corresponding to less than 0.1% of the total).
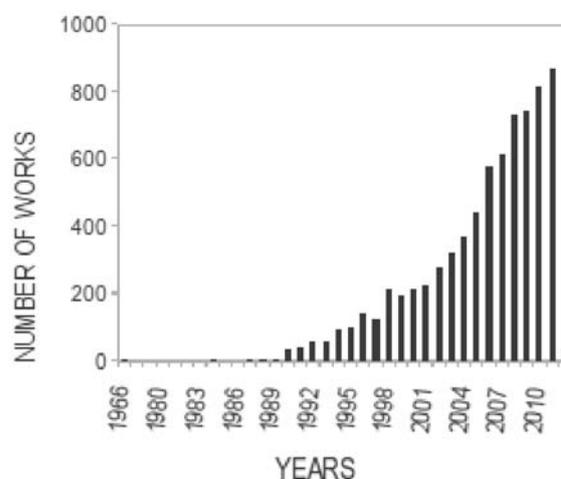
Fig. 4. Number of documents published on the page "Web of Knowledge" from 1966 to the survey date, using the terms "*advanced oxidative process* (*processes*)", "*advanced oxidative technology* (*technologies*)", "*advanced oxidation process* (*processes*)" or "*advanced oxidation technology* (*technologies*)" as keywords. Source: <http://apps.webofknowledge.com>. Data of 2013 are partial, until the date of the survey (January 31st, 2013)

In the next 24 years, few records were found in the database: three records in 1978, one in 1985, two in 1988, three in 1989 and five in 1990. This indicates that for two decades, this topic was almost totally ignored in the international literature. Considering the evolution for decades, the increase of publications is noticeable. From 1991 to 2000, a total of 1054 documents were found (14.5% of total). In the following decade, from 2001 to 2010, there was an increase to 4494 documents, which corresponds to 61.7% of the total. If 2011 untill part of 2013 (from January 1st until the date of this survey) were included as part of the last decade, that number rises to 6,219 (85.3% of total).

These numbers should be understood as a very limited sample to illustrate unequivocally the tremendous growth of research on AOP techniques in the international literature. This increase in works related to AOPs follows a trend observed for the treatment of sewage and toxic waste proceeding from modern society, especially from industry, in general. This is a subject discussed by the scientific community around the world, due to the magnitude of impacts caused as a result of inadequate management [16]. Currently, studies related to AOPs show that there is great potential for the application of scientific information to the use of these dynamic processes. In some regions of the world, mainly in Europe and North America, AOPs are now referred to as "conventional technologies" [161]. Despite all the technological developments fully demonstrated and discussed here, and in accordance with this database, surveys are still conducted at bench scale (around 95% at this stage). Thus, it is still necessary that the scientific community, together with sponsors and the private sector, continue the intense and ongoing search for immediate solutions to make those technologies operational, so far proved to be kinetically feasible and economically viable.

It is important to stand out that good policies on waste management involve several aspects. The first aspect is awareness, that is, full disclosure, with the help of the political sphere leading to topical exposure in pre-school to television broadcasting and electronic entertainments. The minimization of waste generation as well as the possibility of reuse or recycling, whether domestic, commercial or industrial, is a major issue. Finally, after the proper disposal of such wastes it is necessary to propose appropriate treatments for the remaining waste [16]. Since each type of oxidation reaction applied to numerous types of effluents and wastes generated under different regional or national conditions, requires specific conditioning, still pending important information to complement the intense state of the art of AOPs, especially with regard to information such as cost/benefit analysis and scale-up. Obtaining such information will remain very important, considering the incidents and accidents emerging and imminent in the planet's interconnected environmentes (air, soil and water).

In this context, the scientific advisers have undeniable importance in the dissemination of knowledge generated by researchers. Even if it were possible to address the technical knowledge with economic, social and political factors, important aspects for the solution of environmental issues at hand would be missing.

The embracing of solutions probably starts with a sufficiently critical mass of the planet's inhabitants who end up involved, either spontaneous or not spontaneous.

Finding solutions falls to various population segments, such as researchers, teachers, government officials, organizations and industries or anyone concerned with polluting materials generation. This will ultimately create the conditions necessary to drive awareness into viable solutions.

This awareness needs to occur at fundamentally deep levels, many of which are opaque to the great mass of humanity. Only in this way it will be possible to move from theory to practice. Everyone is responsible, and everyone feeds the process.

All are co-creators of the world we live in, everyone contributing a small portion of the whole.

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References

[1] F. Al-Momani, E. Touraud, J. R. Degorce-Dumas, J. Roussy, O. Thomas, Biodegradability enhancement of textile dyes and textile wastewater by VUV photolysis, *Journal of Photochemistry and Photobiology, A: Chemistry 153 (2007) 191–197.*

[2] W. Mulbry, S. Kondrad, C. Pizarro, E. Kebede-Westhead, Treatment of dairy manure effluent using freshwater algae: Algal productivity and recovery of manure nutrients using pilot-scale algal turf scrubbers, *Bioresource Technology 99 (2008) 8137-8142.*

[3] A. Rey, M. Faraldos, J. A. Casas, J. A. Zazo, A. Bahamonde, J. J. Rodryguez, Catalytic wet peroxide oxidation of phenol over Fe/AC catalysts: Influence of iron precursor and activated carbon surface, *Applied Catalysis B: Environmental 86 (2009) 69-77.*

[4] R. Bauer, H. Fallmann, The photo-Fenton oxidation: a cheap and efficient wastewater treatment method, *Research on Chemical Intermediates 23 (1997) 341-354 .*

[5] R. Bauer, G. Waldner, H. Fallmann, S. Hager, M. Klare, T. Krutzler, S. Malato, P. Maletzky, The photo Fenton reaction and the TiO₂/UV process for waste water treatment: novel developments, *Catalysis Today 53 (1999) 131-144.*

[6] H. Fallmann, T. Krutzler, R. Bauer, Detoxification of pesticed containing effluents by solar driven Fenton process, *Zeitschrift für Physikalische Chemie 213, (1999) 67-74.*

[7] J. Araña, E. T. Rendon, J. M. D. Rodriguez, J. A. H. Melian, O. G. Diaz, J. P. Pena, Highly concentrated phenolic wastewater treatment by the photo Fenton reaction, mechanism study by FTIR"ATR, *Chemosphere 44 (2001) 1017-1023.*

[8] R. Andreozzi, A. D'apuzzo, R. A. Marotta, Oxidation of aromatic substrates in water/goethite slurry by means of hydrogen peroxide, *Water Research 26 (2002) 4691-4698.*

[9] C. A. O. Nascimento, A. C. S. C. Teixeira, R. Guardani, F. H. Quina, O. Chiavone Filho, A. M. Braun, Industrial wastewater treatment by photochemical processes based on solar energy,

Journal of Solar Energy Engineering 129 (2007) 45-52.

[10] F. T. Silva, L. R. Mattos, T. C. B. Paiva, Treatment of an ECF effluent by combined use of activated sludge and advanced oxidation process, *Water Science and Technology 55 (2007) p.151-156.*

[11] M. R. Barreto, F. T. Silva, T. C. B. Paiva, Combined zero-valent iron and fenton processes for the treatment of Brazilian TNT industry wastewater, *Journal of Hazardous Materials 165 (2008) 1224-1228.*

[12] M. R. Barreto, J. V. B. Souza, E. S. Silva, F. T. Silva, T. C. B. Paiva, Combined photocatalytic and fungal processes for the treatment of nitrocellulose industry wastewater, *Journal of Hazardous Materials 161 (2009) 1569-1573.*

[13] M. B. Rodrigues, F. T. Silva, T. C. B. Paiva, Optimization of Brazilian TNT industry wastewater treatment using combined zero-valent iron and fenton processes, *Journal of Hazardous Materials 168 (2009) 1065-1069.*

[14] L. F. R. Cavalotti, M. B. Rodrigues, T. C. B. Paiva, P. G. Peralta-Zamora, Degradação de espécies nitroaromáticas e remediação de efluentes da indústria de explosivos, utilizando-se processos redutivos-oxidativos fundamentados no uso de ferro metálico, *Química Nova 32 (2009) 1504-1508.*

[15] C. F. Melo, F. T. Silva, T. C. B. Paiva, Treatment of wastewater from a cotton dyeing process with UV/H_2O_2 using a photoreactor covered with reflective material. *Water Science and Technology 64 (2011) 460-468.*

[16] C. P. A. B. Teixeira, W. F. Jardim, *Processos Oxidativos Avançados: Conceitos Teóricos* (Instituto de Química, Laboratório de Química Ambiental, Universidade de Campinas, 2004) 82p.

[17] S. A. Parsons, *Advanced Oxidation Process for Water and Wastewater Treatment* (Iwa Publishing, United Kingdon, 2005) 356p.

[18] H. Gabardo Filho, *Estudo e Projeto de Reatores Fotoquímicos para Tratamento de Efluentes Líquidos*, MsC dissertation (Faculdade de Engenharia Química, Universidade Estadual de Campinas, 2005) 175p.

[19] J. J. Pignatello, E. Oliveros, A. Mackay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, *Critical Reviews in Environmental Science and Technology 36 (2006) 1-84.*

[20] X. Domènech, W. F. Jardim, M. I. Litter, M.I., *Procesos Avanzados de Oxidación para la Eliminación de Contaminantes: Eliminiación de Contaminantes por Fotocatálisis Heterogênea* (Rede CYTED, La Plata, 2001). Cap. 1.

[21] J. L. Morais, *Estudo da potencialidade de processos oxidativos avançados, isolados e integrado com processos biológicos tradicionais, para tratamento de chorume de aterro sanitário*, PhD thesis (Departamento de Química, Universidade Federal do Paraná, Curitiba, 2005) 229f.

[22] S. G. Poulopoulos, F. Arvanitakis, C. J. Philippopoulos, Photochemical treatment of phenol aqueous solutions using ultraviolet radiation and hydrogen peroxide, *Journal of Hazardous Materials B 129 (2006) 64-68.*

[23] H. Kusic, N. Koprivanac, L. Srsan, Azo dye degradation using Fenton type processes assisted by UV irradiation: A kinetic study, *Journal of Photochemistry and Photobiology A: Chemistry 181 (2007) 195-202.*

[24] A. Kunz, P. Peralta-Zamora, S. G. Moraes, N. Duran, Novas Tendências no Tratamento de Efluentes Têxteis, *Química Nova 25, 1, (2002) 78-82*

[25] R. P. Nogueira, W. F. Jardim, A fotocálise heterogênea e sua aplicação ambiental, *Quimica Nova 21 (1998) 69-72.*

[26] I. V. L. Ferreira, L. . Daniel, Fotocátalise heterogênea com TiO_2 aplicada no tratamento de esgoto sanitário secundário, *Engenharia Sanitária Ambiental 9, 4 (2004) 335-342 .*

[27] I. B. S. Will, J. E. F. Moraes, A. C. S. C. Teixeira, R. Guardani, C. A. O. Nascimento, Photodegradation of wastewater containing organic compounds in solar reactors, *Separation and Purification Technology 34 (2004) 51-57.*

[28] B. C. B. Salgado, S. O. Aguiar, K. A. Rodrigues, G. M. M. S. Sampaio, R. S. Araujo, Degradação de corantes azo e índigo via processos oxidativos avançados (POA's), *17th Congresso Brasileiro de Engenharia Química. Recife, Brazil, September 14-*

17 (2008).

[29] L. L. C. Catorceno, K. R. B. Nogueira, A. C. S. C. Teixeira, Treatment of aqueous effluents containing phenol by the O_3, O_3-UV, and O_3-H_2O_2 processes: experimental study and neural network modeling, *Separation Science and Technology 45 (2010) 1521-1528.*

[30] L. M. Dorfman, G. E. Adams, Reactivity of the Hydroxyl Radical, *National Bureau of Standards, Report No. NSRDS-NBS-46 (1973).*

[31] J. Kiwi, A. Lopez, V. Nadtochenko, Mechanism and kinetics of the OH⁻ radical intervention during Fenton oxidation in the presence of a significant amount of radical scavenger (Cl⁻), *Environmental Science Technology 34 (2000) 2162-2168 .*

[32] T. Essam, M. A. Amin, E. O. Tayeb, B. Mattiasson, B. Guieysse, Solar-based detoxification of phenol and p-nitrophenol by sequential TiO_2 photocatalysis and photosynthetically aerated biological treatment, *Water Research 41, 8, (2007) 1697-1704.*

[33] S. G. Poulopoulos, M. Nikolaki, D. Karampetsos, C. J. Philippopoulos, Photochemical treatment of 2-chlorophenol aqueous solutions using ultraviolet radiation, hydrogen peroxide and photo-Fenton reaction, *Journal of Hazardous Materials 153, 1–2 (2008) 582-587.*

[34] B. Ramos, J. P. S. Farah, A. C. S. C. Teixeira, Estimating reaction constants by Molecular Modeling: a study on the oxidation of phenol to catechol and hydroquinone in Advanced Oxidation Processes, *Brazilian Journal of Chemical Engineering 29 (2012) 113-120.*

[35] O. Legrini, E. Oliveros, A. M. Braun, Photochemical processes for water treatment, *Chemical Reviews 93 (1993) 671–698.*

[36] C. Comninellis, A. Kapalka, S. Malato, S. A. Parsons, I. Poulios, D. Mantzavinos, Advanced oxidation processes for water treatment: advances and trends for R&D, *Journal of Chemical Technology & Biotechnology 83 (2008) 769–776.*

[37] L. M. Carneiro, *Utilização de processos oxidativos avançados na degradação de efluentes provenientes das indústrias de tintas*, MsC dissertation, Escola de Engenharia de Lorena, Lorena, SP, 2007. 118f.

[38] C. Liao, M. D. Gurol, Chemical oxidation by photolytic decomposition of hydrogen peroxide, *Environmental Science & Technology 29 (1995) 3007-3014.*

[39] N. H. Ince, M. I. Stefan, J. R. J. Bolton, UV/H_2O_2 degradation and toxicity reduction of textile azo dyes: Remazol Black – B, a case study, *Journal Advanced Oxidation Technology 2 (1997) 442-448.*

[40] Y. S. Shen, D. K. Wang, Development of photoreactor design equation for the treatment of dye wastewater by UV/H_2O_2 process, *Journal of Hazardous Materials B89 (2002) 267-277.*

[41] E. Chamarro, A. Marco, S. Esplugas, Use of Fenton reagent to improve organic chemical biodegradability, *Water Research 35, 4 (2001) 1047-1051.*

[42] J. A. Giroto, A. C. S. C. Teixeira, C. A. O. Nascimento, R. Guardani, Degradation of poly(ethylene glycol) in aqueous solution by photo-Fenton and H_2O_2/UV processes, *Industrial & Engineering Chemistry Research 49 (2010) 3200-3206.*

[43] D. Vogna, R. Marotta, R. Andreozzi, A. Napolitano, M. d'Ischia, Kinetic and chemical assessment of the UV/H_2O_2 treatment of antiepileptic drug carbamazepine, *Chemosphere 54 (2004a) 497–505.*

[44] B. Ahmed, H. Mohamed, E. Limem, B. Nasr, Degradation and mineralization of organic pollutants contained in actual pulp and paper mill wastewaters by a UV/H_2O_2 process, *Industrial & Engineering Chemistry Research 48, 7, (2009) 3370-3379.*

[45] A. Gahr, L. Weil, R. Nie&sBligner, Polychromatic actinometry with filter solutions, *Water Research 29, 9 (1995) 2125-2137.*

[46] M. Muruganandham, M. Swaminathan, Photocatalytic decolourisation and degradation of reactive Orange-4 by TiO_2/UV process, *Dyes and Pigments 68, 2 (2006) 133-142.*

[47] S. Marmitt, L. V. Pirotta, S. Stülp, Aplicação de fotólise direta e UV/H_2O_2 a efluente sintético contendo diferentes corantes alimentícios, *Quimica Nova 33, 2 (2010) 384-388.*

[48] V. Bocci, *Ozone: A New Medical Drug* (Springer, Berlin, 2005) 295p.

[49] T. Robinson, G. Mcmullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment

technologies with a proposed alternative, *Bioresource Technology* 77 (2001) 247-255.

[50] P. A. Balakrishnan, A. Arunagiri, P. G. Rao, Ozone generation by silent electric discharge and its application in tertiary treatment of tannery effluent, *Journal of Electrostatics 56 (2002) 77-86.*

[51] M. Horvath, *Ozone* (Elsevier Science, Amsterdam, The Netherlands, 1980).

[52] J. S. Chang, S. Masuda, Mechanism of the ozone formations in a near liquid nitrogen temperature medium pressure glow discharge positive column. *Pure and Applied Chemistry 60, 5 (1980) 645-650.*

[53] E. Almeida, M. R. Assalin, M. A. Rosa, Tratamento de efluentes industriais por Processos Oxidativos na presença de ozônio, *Química Nova 27, 8 (2004) 818-824.*

[54] A. L. C. Peixoto, H. J. Izário Filho, Statistical evaluation of mature landfill leachate treatment by homogeneous catalytic ozonation, *Brazilian Journal of Chemical Engineering 27 (2010) 531-534.*

[55] U. Von Guten, Ozonation of drinking water: part II. Disinfection and by-product formation in presence of bromide, iodine or chlorine, *Water Research 37 (2003) 1469-1487.*

[56] S. J. Masten, S. H. R. Davies, The use of ozonation to degrade organic contaminants in wastewaters, *Environmental Science & Technology 28 (1994) 180A–185A.*

[57] I. S. Oliveira, M. B. Silva, H. J. Izário Filho, O. L. C. Guimarães, A. L. C. Peixoto, Integração da Fotocatálise homogênea e processo biológico na remediação de resíduos gerados nos laboratórios da EEL-USP, *4th EPOA Encontro Sobre Aplicações Ambientais de Processos Oxidativos Avançados, Cubatão, SP, Brazil (2007), v.1, p.POA-028-028.*

[58] J. Hoigne, H. Bader, Ozonation of water: selectivity and rate of oxidation of solutes, *Ozone-Science & Engineering 1 (1979) 73-85.*

[59] Aguiar, D.T.; Giudici, F.; Will, I.B.S. Sistema de degradação de efluentes industriais contendo polímeros utilizando o processo UV/H_2O_2, *3rd PIC-EPUSP Produção de Iniciação Científica da Escola Politécnica da Universidade de São Paulo, São Paulo, SP, Brazil (2006).*

[60] W. H. Glaze, J. W. Kang, D. H. Chapin, The chemistry of water-treatment processes involving ozone, hydrogen-peroxide and ultraviolet-radiation, *Ozone-Science & Engineering 9, 4 (1987) 335-352.*

[61] T. Kurbus, Y. M. Slokar, A. M. Le Merechal, D. B. Voncina, The use of experimental design for the evaluation of the influence of variables on the H_2O_2/UV treatment of model textile waste water, *Dyes And Pigments 58 (2003) 171-178.*

[62] A. Rathi, H. K. Rajor, R. K. Sharma, Photodegradation of direct yellow-12 using UV/H_2O_2/Fe^{2+}, *Journal of Hazardous Materials 102 (2003) 231-241.*

[63] A. C. S. C. Teixeira, R. Guardani, C. A. O. Nascimento, Photo-fenton remediation of wastewaters containing silicones: experimental study and neural network modeling, *Chemical Engineering and Technology 27 (2004) 800-810.*

[64] H. Ching-Rong, S. Hung-Yee, The reaction kinetics, decomposition pathways and intermediate formations of phenol in ozonation, UV/O_3 and UV/H_2O_2 processes, *Journal of Hazardous Materials 41, 1 (1995) 47-64.*

[65] A. Mahmoud, R. S. Freire, Métodos emergentes para aumentar a eficiência do ozônio no tratamento de águas contaminadas, *Química Nova 30, 1 (2007) 198-205 .*

[66] N. Al-Hayek, B.Legube, M. Doré, Ozonation catalytique (FeIII/Al_2O_3) du phénol et de ses produits d'ozonation, *Environmental Technology Letters 10 (1989) 415-426.*

[67] N. Bhat, M. D. Gurol, Oxidation of chlorobenzene by ozone and heterogeneous catalytic ozonation, *27th Industrial Waste Mid-Atlantic Conference, Bethlehem, PA, USA, July (1995) p.371.*

[68] A. Naydenov, D. Mehandjiev, Complete oxidation of benzeneon manganese dioxide by ozone, *Applied Catalysis A: General 97 (1992) 17-22.*

[69] P. E. Thompson, P. N. Sharaatt, J. Hutchison, Heterogeneous catalytic oxidation of organic pollutants in aqueous solutions, *1st ICHEME Research Event, European Conference, Eddinburg, Scotland, January* **5-6** *(1995) p.297.*

[70] J. Ma, N. J. D. Graham, Preliminary investigation of manganese-catalyzed ozonation for the destruction of atrazine, *Ozone Science*

& *Engineering 19 (1997) 227-240.*

[71] R. Andreozzi, A. Insola, V. Caprio, R. Marotta, V. Tufano, The use of manganese dioxide as a heteogeneous catalyst for oxalic ozonation in aqueous solution, *Applied Catalysis A: General 138 (1996) 75-81.*

[72] D. Pines, R. Humayan, D. A. Reckhow, C. Spangenberg, A catalytic oxidation process for removal of ozone by-products, *2004 WQTC Water Quality Technology Conference, San Francisco, CA, USA, November 6–10 (1994) part II – session 4A, p.1493.*

[73] K. Sehested, H. Corfitzen, J. Holcman, C. H. Fischer, C. J. Hart, The primary reaction in the decomposition of ozone in acidic aqueous solutions. *Environmental Science and Technology 25 (1991) 1589-1595.*

[74] B. Langlais, D. A. Reckhow, D. R. Brank, *Ozone in Water Treatment: Application and Engineering* (Lewis Publishers, 1991) 569p.

[75] J. Hoigne, H. Bader, The role of hydroxil radical reactions in ozonation processes in aqueous solutions, *Water Research 10 (1976) 377-386.*

[76] N. M. Emanuel, D. Gál, *Modelling of Oxidation Processes: Prototype, the Oxidation of Ethylbenzene* (Akademiai Kiado, 1986) p. 184, 209, 377 .

[77] A. Singh, K. Bahari, *Polymer Blends Handbook* (Academic Publishers, Netherlands, LA, 2003) 1500p.

[78] F. Tang, H. Fudouzi, T. Uchikoshi, Y. Sakka, Preparation of porous materials with controlled pore size and porosity, *Journal of the European Ceramic Society 24, 2 (2004), 341-344.*

[79] Duca, G. *Homogeneous Catalysis with Metal Complexes: Fundamental and Applications* (Springer, New York, 2012) 490p.

[80] C. Gottschalk, J. A. Libra, A. Saripe, *Ozonation of Water and Waste Water: A Practical Guide to Understanding Ozone and its Applications* (Wiley-VCH, Weinheim, 2009) 378p.

[81] R .F. S. Salazar, H. J. Izário Filho, Aplicação de processo oxidativo avançado (POA) como pré-tratamento de efluente de laticínio para posterior tratamento biológico, *Analytica 45 (2010) 60-61.*

[82] C. Lee, C. Schmidt, J. Yoon, U. von Gunten, Oxidation of N-Nitrosodimethylamine (NDMA) precursors with ozone and chlorine dioxide: kinetics and effect on NDMA formation potential, *Environmental Science & Tecnology 41, 6 (2007) 2056–2063.*

[83] I. Arslan-Alaton, S. Dogruel, Photodegradation of hydrophobic disperse dyes and dye-bath effluents by silicadodecatungstate (SiW$_{12}$O$_{40}$$^{4-/5-}$) nanoparticles, *Water Science & Technology 49, 4 (2004) 171-176.*

[84] D. Vogna, R. Marotta, A. Napolitano, R. Andreozzi, M. d'Ischia, Advanced oxidation of the pharmaceutical drug diclofenac with UV/H_2O_2 and ozone, *Water Research 38 (2004b) 414–422.*

[85] I. A. Alaton, I. A. Balcioglu, D. W. Bahnemann, Advanced oxidation of a reactive dyebath effluent: comparison of O_3, H_2O_2/UV-C and TiO_2/UV-A processes, *Water Research 36, 5 (2002) 1143-1154.*

[86] J. Santiago-Morales, M. J. Gómez, S. Herrera, A. R. Fernández-Alba, E. García-Calvo, R. Rosal, Oxidative and photochemical processes for the removal of galaxolide and tonalide from wastewater, *Water Research 46, 14 (2012) 4435-4447.*

[87] B. Kasprzyk-Hordern, M. Ziólek, J. Nawrocki, Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment, *Applied Catalysis B: environmental 46 (2003) 639-669.*

[88] B. Legube, N. K. V. Leitner, Catalytic ozonation: a promising advanced oxidation technology for water treatment, *Catalysis Today 53, 1 (1999) 61–72.*

[89] M. R. Assalin, N. Durán, Novas tendências para aplicação de ozônio no tratamento de resíduos: ozonização catalítica, *Revista Analytica 26 (2007) 76-86.*

[90] F. J. Béltran, F. J. Rivas, O. Gimeno, Comparison between photocatalytic ozonation and other oxidation processes for the removal of phenols from water, *Journal of Chemical Technology 80, 9 (2005) 973-984.*

[91] Z. Xiang-Feng, X. Xin-Xua, The mechanism of Fe(III)-catalyzed ozonation of phenol, *Journal of Zhejiang University Science 5, 12 (2004) 1543-1547.*

[92] M. R. Assalin, P. L. Silva, N. Durán, Comparação da eficiência do

processo de ozonização e ozonização catalítica (Mn II e Cu II) na degradação de fenol, *Química Nova 29 (2006) 24-27.*

[93] B. S. Kim, H. Fujita, Y. Sakai, A. Sakoda, M. Suzuki, Catalytic ozonation of an organophosphorus pesticide using microporous silicate and its effect on total toxicity reduction, *Water Science & Technology 46,* 4-5 (2002) 35-41.

[94] I. Arslan-Alaton, O. Seremet, Advanced treatment of biotreated textile industry wastewater with ozone, virgin/ozonated granular activated carbon and their combination, *Journal of environmental science and health. Part A, Toxic/hazardous substances & environmental engineering 39,* 7 (2004) 1681-1694.

[95] F. Méndez-Arriaga, T. Otsu, T. Oyama, J. Gimenez, S. Esplugas, H. Hidaka, N. Serpone, Photooxidation of the antidepressant drug Fluoxetine (Prozac®) in aqueous media by hybrid catalytic/ozonation processes, *Water Research 45,* 9 (2011) 2782-2794.

[96] H. J. H. Fenton, Oxidation of tartaric acid in presence of iron, *Journal of Chemical Society, Transactions 65 (1894) 899-910.*

[97] A. M. F. M. Guedes, *Oxidação química com reagente de Fenton: aplicações às águas de cozimento da cortiça,* MsC dissertation, Faculdade de Engenharia da Universidade do Porto, Portugal, 2000. 134f.

[98] T. Rigg, W. Taylor, J. Weiss, The rate constant of the reaction between hydrogen peroxide and ferrous ions, *Journal of Chemical Physics 22 (1954) 575-577.*

[99] G. V. Buxton, C. L. Greenstock, W. P. Helman, A. B. Ross, Critical review of rate constants of reactions of hydrated electrons, hydrogen atoms and hydroxylradicals (OH/O-) in aqueous solution, *The Journal of Physical Chemistry 17,* 2 (1988) 513-886.

[100] E. L. Machado, W. Sales Dambros, L. T. Kist, E. A. Alcayaga Lobo, S. B. Tedesco, C.C. Moro, Use of ozonization for the treatment of dye wastewaters containing rhodamine B in the agate industry, *Water, Air & Soil Pollution 223,* 4 (2012) 1753-1764.

[101] A. L. C. Peixoto, R. A. Brito, R. F. S. Salazar, O. L. C. Guimarães, H. J. Izário Filho, Prediction of chemical oxygen demand in mature landfill leachate doped with Fenton's reagent, using empirical mathematical model obtained by full factorial design, *Química Nova 31,* 7 (2008) 1641-1647.

[102] A. Aleboyeh, M. B. Kasiri, M. E. Olya, H. Aleboyeh, Prediction of azo dye decolorization by UV/H$_2$O$_2$ using artificial neural networks, *Dyes and Pigments 77 (2008) 288–294.*

[103] I. Arslan-Alaton, B. H. Gursoy, J. Schmidt, Advanced oxidation of acid and reactive dyes: Effect of Fenton treatment on aerobic, anoxic and anaerobic processes, *Dyes and Pigments 78 (2008) 117-130.*

[104] W. Baran, A. Makowski, W. Wardas, The effect of UV radiation absorption of cationic and anionic dye solutions on their photocatalytic degradation in the presence TiO$_2$, *Dyes and Pigments 76 (2008) 226–230.*

[105] A. C. S. C. Teixeira, R. Guardani, A. M. Braun, E. Oliveros, C.A.O. Nascimento, Degradation of an aminosilicone polymer in a water emulsion by the Fenton and the photochemically enhanced Fenton reactions, *Chemical Engineering and Processing 44 (2005a) 923-931.*

[106] H. G. C. Bates, N. Uri, Oxidation of Aromatic Compounds in Aqueous Solution by Free Radicals Produced by Photo-excited Electron Transfer in Iron Complexes, *Journal of the American Chemistry Society 75,* 11 (1953) 2754-2759.

[107] C. W. Jones, *Applications of Hydrogen Peroxide and Derivatives* (The Royal Society of Chemistry, Cambridge, UK, 1999) 264p.

[108] C. H. Langford, J. H. Carey, The charge transfer photochemistry of the hexaaquoiron(III) ion, the chloropentaaquoiron(III) ion, and the μ-dihydroxy dimer explored with tert-butyl alcohol scavenger, *Canadian Journal of Chemistry 53 (1975) 2430-2435.*

[109] A. Machuleck Jr., J. F. Moraes, C. Vautier-Giongo, C. A. Silerio, L. C. Friedrich, C. A. O. Nascimento, M. C. Gonzales, F. H. Quina, Abatement of the inhibitory effect of chloride anions on the photo-Fenton process, *Environmental Science Technology 41 (2007) 8459-8463.*

[110] S. Göb, *Optimierung und Modellierung der Photochemisch Beschleunigten Fenton-reaktion,* dissertation, Fakultät für Chemieingenieurwesen der Universität Fridericiana Karlsruhe, Fulda, 2001) 88p.

[111] R. Dalla Villa, M. R. A. Silva, R. F. Pupo Nogueira, Potencial de aplicação do processo foto-Fenton/solar como pré-tratamento de efluente da indústria de laticínios, *Química Nova 30,* 8 (2007) 1799-1803.

[112] D. R. Manenti, F. B. Borba, A. N. Módenes, F. R. Espinoza-Quiñones, S. M. Palácio, K. S. Crestani, P. R. Schmidt Júnior, R. Nascimento, Optimization of photo-Fenton process with UV irradiation in the treatment of effluents from the processing industry by-products of food, *Revista Ciências Exatas e Naturais 11,* 1 (2009) 112-128.

[113] J. A. Giroto, R. Guardani, A. C. S. C. Teixeira, C. A. O. Nascimento, Study on the photo-Fenton degradation of polyvinil alcohol in solution, *Chemical Engineering and Processing 45 (2006) 523-532.*

[114] J. A. Giroto, A. C. S. C. Teixeira, C. A. O. Nascimento, R. Guardani, Photo-Fenton removal of water soluble polymers, *Chemical Engineering and Processing 47 (2008) 2361-2369.*

[115] D. N. Silva, A. A. E. Neto, G. M. A. Cunha, O. C. Filho, C. A. O. Nascimento, Processo foto-Fenton aplicado ao tratamento de águas produzidas em campos de petróleo, *Revista Brasileira de Ciências Ambientais 14 (2009) 1-14.*

[116] K. R. B. Nogueira, A. C. S. C. Teixeira, C. A. O. Nascimento, R. Guardani, Use of solar energy in the treatment of water contaminated with phenol by photochemical processes, *Brazilian Journal of Chemical Engineering 25 (2008) 671-682.*

[117] M. M. B. Martín, J. A. S. Pérez, J. L. C. López, I. Oller, S. M. Rodríguez, Degradation of a four-pesticide mixture by combined photo-Fenton and biological oxidation. *Water Research 43 (2009) 653-660.*

[118] A. C. S. C. Teixeira, L. M. Z. Mendes, G. Stollar, R. Guardani, C. A. O. Nascimento, Photo-Fenton remediation of wastewaters containing agrochemicals. *Brazilian Archives of Biology and Technology 48 (2005b) 207-218.*

[119] R. R. Navarro, H. Ichikawa, K. Tatsumi, Ferrite formation from photo-Fenton treated wastewater, *Chemosphere 80 (2010) 404-409.*

[120] Y. Huang, H. Su, L. Lin, Removal of citrate and hypophosphite binary components using Fenton, photo-Fenton and electro-Fenton processes, *Journal of environmental sciences 21 (2010) 35-40.*

[121] D. M. Tobaldi, A. Tucci, G. Camera-Roda, D. G. Baldi, L. Esposito, Photocatalytic activity for exposed building materials, *Journal of the European Ceramic Society 28 (2008) 2645–2652.*

[122] R. S. Freire, A. Kunz, N. Duran, Some chemical and toxicological aspects about paper mill effluent treatment with ozone, *Environmental Technology 21,* 6 (2000) p.717-721.

[123] J. C. D'Oliveira, G. Al-Sayyed, P.Pichat, Photodegradation of 2-chlorophenol and 3chlorophenol in TiO$_2$ aqueous suspensions, *Environmental Science & Technology 24 (1990) 990-996.*

[124] M. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, Environmental Applications of Semiconductor Photocatalysis, *Chemical Reviews 95 (1995) 69-96.*

[125] A. L. Linsebigler, G. Lu, J. T. Yates, Pthotocatakysis on TiO$_2$ surfaces: principles, mechanisms and selected results, *Chemical Reviews 95 (1995) 735-758.*

[126] R. L. Ziolli, W. F. Jardim, Mecanismo de fotodegradação de compostos orgânicos catalisada por TiO$_2$. *Quimica Nova 21 (1998) 319-325.*

[127] J. Chen, D. F. Ollis, W. H. Rulkens, H. Bruning, Photocatalyzed oxidation of alcohols and organochlorides in the presence of native TiO$_2$ and metalized TiO$_2$ suspensions. Part (II): Photocatalytic mechanisms, *Water Research 33,* 3 (1999) 669-676.

[128] Y. Wang, C. S. Hong, Effect of hydrogen peroxide, periodate and persulfate on photocatalysis of 2-chlorobiphenyl in aqueous TiO$_2$ suspensions, *Water Research 33 (1999) 2031-2036.*

[129] W. Choi, M. R. Hoffmann, Novel photocatalytic mechanisms of CHCl$_3$, CHBr$_3$, and CCl$_3$CO$_2^-$ degradation and the fate of photogenerated trihalomethyl radicals on TiO$_2$, *Environmental Science Technology 31 (1997) 89-95.*

[130] N. Daneshvar, D. Salari, A. R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO$_2$, *Journal of Photochemistry and Photobiology A: Chemistry 162 (2004) 317-322.*

[131] P. R. S. Sottoriva, *Remediação de efluentes têxteis por Processos Oxidativos Avançados integrados a lodos ativados,* PhD

dissertation, Escola de Engenharia de Lorena, Universidade de São Paulo, Lorena, SP, Brazil, 2006. 192f.

[132] M. A. Behnajady, N. Modirshahla, N. Daneshvar, M. Rabbani, Photocatalytic degradation of C.I. Acid Red 27 by immobilized ZnO on glass plates in continuous-mode, *Journal of Hazardous Materials 140 (2007) 257-263.*

[133] I. T. Peternel, N. Koprivanac, A. M. L. Bozic, H. M. Kusic, Comparative study of UV/TiO₂, UV/ZnO and photo-Fenton processes for the organic reactive dye degradation in aqueous solution, *Journal of Hazardous Materials 148 (2007) 477-484.*

[134] J. S. Carrocci, R. Y. Mori, O. L. C. Guimaraes, H. J. Izário Filho, *Tratamento de vinhaça utilizando processo físico-química e processo Foto-Fenton*, 25th Congresso Brasileiro de Engenharia Sanitária e Ambiental, Recife, PE, Brazil, september 20-25 (2009). v.1.

[135] A. B. Prevot, E. Pramauro, Analytical monitoring of photocatalytic treatments: degradation of 2,3,6-trichlorobenzoic acid in aqueous TiO₂ dispersions, *Talanta 48,* 4 *(1999), p.847-857 .*

[136] P. Peralta-Zamora, E. Esposito, J. Reyes, N. Durán, Remediação de efluentes derivados da indústria de papel e celulose: Tratamento Biológico e Fotocatalítico, *Quimica Nova 20 (1997).*

[137] S. Kagaya, K. Shimizu, R. Arai, K. Hasegawa, Separation of titanium dioxide photocatalyst in its aqueous suspensions by coagulation with basic aluminium chloride, *Water Research 33 (1999) 1753-1755.*

[138] S. Naskar, S. A. Pillay, M. Chanda, Photocatalytic degradation of organic dyes in aqueous solution with TiO₂ nanoparticles immobilized on foamed polyethylene sheet, *Journal of Photochemistry and Photobiology A: Chemistry 113 (1998) 257-264.*

[139] F. Kiriakidou, D. I. Kondarides, X. E. Verykios, The effect of operational parameters and TiO₂-doping on the photocatalytic degradation of azo-dyes, *Catalysis Today 54 (1999) 119-130.*

[140] X. Z. Li, Y. G. Zhao, Advanced treatment of dyeing wastewater for reuse, *Water Science Technology 39,* 10 *(1999) 249-255.*

[141] R. Pelegrini, P. Peralta-Zamora, A. P. Andrade, J. Reyes, N. Duran, Electrochemical assisted photocatalitic degradation of reactive dyes, *Applied Catalysis B: Environmental 22 (1999) 83-90.*

[142] C. A. K. Gouvêa, F. Wypych, S. G. Moraes, N. Durán, N. Nagata, P. Peralta-Zamora, Semiconductor-assisted photocatalytic degradation of reactive dyes in aqueous solution, *Chemosphere 40 (2000) 433-440.*

[143] C. M. Zhu, L. Y. Wang, L. R. Kong, X. Yang, L. S. Wang, S. J. Zheng, F. L. Chen, M. Z. Feng, H. Zong, Photocatalytic degradation of AZO dyes by supported TiO₂ + UV in aqueous solution, *Chemosphere 41,* 3 *(2000) 303-309.*

[144] L. B. Reutergardh, M. Iangphasuk, Photocatalytic decolourization of reactive azo dye: a comparison between TiO₂ and CdS photocatalysis, *Chemosphere 35 (1997) 585-596.*

[145] T. M. Wang, H. Y. Wang, P. Xu, X. C. Zhao, Y. L. Liu, S. Chao, The effect of properties of semiconductor oxide thin films on photocatalytic decomposition of dyeing waste water, *Thin Solid Films 334 (1998) 103-108.*

[146] M. G. Kang, H. E. Han, K. J. Kim, Enhanced photodecomposition of 4-chlorophenol in aqueous solution by deposition of CdS on TiO₂, *Journal of Photochemistry and Photobiology. A: Chemistry 125 (1999) 119-125.*

[147] J. Poulios, I. Tsachpinis, Photodegradation of the textile dye reactive black 5 in the presence of semiconducting oxides, *Journal of Chemical Technology and Biotechnology 74 (1999) 349-357.*

[148] M. C. Yeber, J. Rodriguez, J. Freer, J. Baeza, N. Durán, H. D. Mansilla, Advanced oxidation of a pulp mill bleaching wastewater, *Chemosphere 39, (1999) 1679-1688.*

[149] J. P. Wilcoxon, T. R. Thurston, J. E. Martin, Applications of metal and semiconductor nanoclusters as thermal and photo-catalysts. *Nanostructure Materials 12 (1999) 993-997.*

[150] B. Liu, T. Torimot, H. Yoneyama. *Photocatalytic reduction of CO₂ using surface-modified CdS photocatalysts in organic solvents,* Journal *of Photochemistry and Photobiology A: Chemistry 113 (1998) 93-97.*

[151] W. Huihu, X. Changsheng ; Z. Wei, C. Shuizhou, Y. Zhihong.; G. Yanghai Comparison of dye degradation efficiency using ZnO powders with various size scales. Journal of Hazardous Materials, v.B112 (2004) 269-278.

[152] S. S. Silva, F. Magalhaes, M. T .C. Sansiviero, Nanocompósitos semicondutores ZnO/TiO₂, Testes Fotocatalíticos, *Quimica Nova 33, 1, (2010) 85–89.*

[153] M. A. Behnajady, N. Modirshahla, R. Hamzavi, Kinetic study on photocatalytic degradation of C.I. Acid Yellow 23 by ZnO photocatalyst, *Journal of Hazardous Materials B133 (2006). p.226-232.*

[154] Z. L. Wang, S. Song, Piezoelectric Nanogenerators Based on Zinc Oxide Nanowire Arrays, *Science, 312,* 5771 *(2006) 242-246.*

[155] J. Lv, C. Liu, W. Gong, Z. Zi; X. Chen, K. Huang, T. Wang, G. He, X. P. Song, Z. Q. Sun, Effect of surface topography on wettability of ZnO thin films deposited by hydrothermal method, *Science of Advanced Materials 4 (2012) 757-762.*

[156] P. Zhang, G. D. Zhou, H. B. Gong, H. H. Xu, D. Nakamura, T. Okada, H. B. Zeng, B. Q. Cao, Pressure-induced growth evolution of different ZnO nanostructures by a pulsed laser ablation method, *Science of Advanced Materials 4 (2012) 455-462.*

[157] A. A. Khodja, T. Sheili, J. F. Pilichowski, P. J. Boule, Photocatalytic degradation of 2-phenylphenol on TiO₂ and ZnO in aqueous suspensions, *Journal of Photochemistry and Photobiology A-Chemistry 141 (2001) 231-239.*

[158] T. J. Kuo, C. N. Lin, M. H. Huang, Growth of ultralong ZnO nanowires on silicon substrates by vapor transport and their use as recyclable photocatalysts, *Chemistry of Materials 19 (2007) 5143-5147.*

[159] T. Sun, J. Qiu, C. J. Liang, Controllable fabrication and photocatalytic activity of ZnO nanobelt arrays, *The Journal of Physical Chemistry C, 112 (2008) 715-721.*

[160] N. Daneshvar, M. H. Rasoulifard, A. R. Khataee, F. Hosseinzadeh, Removal of C.I. acid orange 7 from aqueous solution by UV irradiation in the presence of ZnO nanopowder, *Journal of Hazardous Materials 143 (2007) 95–101.*

[161] M. Mohajerani, M. Mehrvar, F. Ein-Mozaffari, An overview of the integration of advanced oxidation technologies and other processes for water and wastewater treatment, *International Journal of Engineering 3,* 2 *(2009) 120-146.*

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The researchers of this review have worked with some environmentally important themes. Especially with oxidative processes applied to industrial effluents and wastes, considering homogeneous and heterogeneous catalysis, in batch and semi-continuous processes. They work with the statistical evaluation of experimental planning, and have also applied a mathematical model to determine the importance of each parameter to the model and its costs.

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