Advanced Oxidation Processes for Wastewater Treatment in the Pulp and Paper Industry: A Review

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Abstract   The effluents of some pulp and paper processes are potentially pollutant, because of their large volume and their refractory nature. Biological processes generally are not capable to remove these compounds. Advanced Oxidation Processes (AOP) are characterized by the capability of exploiting the high reactivity of HO• radicals. AOP can produce a total mineralization, transforming recalcitrant compounds into inorganic substances (CO_2 and H_2O_2), or partial mineralization, transforming them into more biodegradable substances. The high reactivity and low selectivity of these radicals are useful attributes that that make these processes in promising technologies. Due to the differences between pulping processes, the effluents from the various processes and operations of such industries also differ from each other, so that some oxidative processes should be combined to improve the removal efficiency. For the effective oxidation of refractory organic compounds, hydroxyl radicals should be generated continuously in situ due to its chemical instability. Generation of HO• is commonly accelerated by combining oxidizing agents. Among these treatments, UV radiation plus hydrogen peroxide (UV/H_2O_2), Fenton's reagent (H_2O_2/Fe^{+2}), photo-Fenton ($UV/H_2O_2/Fe^{+2}$), and ozone in different combinations (O_3/UV; O_3/H_2O_2) are considered to be effective for the oxidation of effluents from pulp and paper industries.

Keywords   Advanced Oxidation Processes, COD removal, Pulping effluent, Recalcitrant compounds

1. Introduction

The pulp and paper industry has been considered as one of the biggest consumers of natural resources (wood, water), energy (electricity and fossil fuels) and as major contributor of pollutants discharge to the environment. As a result of pulping and manufacture of paper products, it generates a large amount of contaminants, whose composition varies depending on the manufacturing process [1]. The objective of all pulping processes is to separate the fibers, producing a fiber suspension in water. This separation can be accomplished by applying mechanical, thermal, and chemical energy, in different proportions [2].

Depending on the process, the most important sources of contamination from the different stages of the process are: wood preparation, pulping, pulp washing, screening, bleaching, papermaking and coating operations [3].

The characteristics of the waste liquid to be treated depends on the type of wood, the type of process, the amount of water that the mill is able to circulate, the technology used and the selected management practices. Depending on the

raw material and the process involved, untreated waste fluids can have high biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (mainly fibers), fatty acids, tannins, resin acids, lignin, and its derivatives. Some of them are naturally occurring pollutants and others are xenobiotics, which are formed during the pulp and paper manufacturing process [4], [5]. Some substances are recalcitrant to biological degradation and toxic to aquatic species. Some bleaching processes even generate bioaccumulative compounds [6], [7].

The wastewaters of high yield pulping processes are characterized by their suspended solids content (including particles of bark), organic substances, chromophoric compounds (mainly labile extractives and lignin fragments), inorganic compounds (nitrogen and phosphorus, as result of the effluent treatment) and salts. Semichemical processes contain lignosulfonates (derived from lignin) in addition to the above. The Kraft process wastewaters are characterized by their content of solids (including particles of bark), dissolved organics, chromophoric compounds (mainly derived from lignin). If Kraft pulps are bleached with chlorine compounds, they can present organochlorine compounds (dioxins and furans) [8].

Although chromophoric groups are not well defined, they are basically composed by conjugated olefins and quinones, methidic quinones and aromatic rings. While bleaching of

high yield processes uses oxygen as oxidizing agent, in the case of Kraft pulps, chlorine was historically used. The improvements that have been made in the bleaching process in the last 20 years consisted on the complete removal of elemental chlorine by developing technologies as Elemental Chlorine Free (Elemental Chlorine Free, ECF) or Totally Chlorine Free (Totally-Chlorine Free, TCF), combined with oxygen delignification, which reduces the amount of organochlorine compounds released into the environment [9].

The initial values of COD of pulping processes are very different, depending on the origin of the effluent and the type of raw material. For example, the content of phenolic compounds and chlorinated compounds in the wastewater of hardwood Kraft pulping is three to eight times smaller than that of the softwood Kraft pulping [10]. Examples of initial COD of high yield pulping [TMP, CTMP, BCTMP, and NSSC] and Kraft pulping are shown in Table 1.

Table 1. COD of effluents from high yield and chemical pulping processes

Effluent	Process	COD [mg/L]	Reference
Pulp mills	TMP	3340; 3500; 5600; 7210; 3340	[12] [13]
	BCTMP-TMP	2520; 7930	[12]
	TMP-CTMP	4000 y 7800	[12]
	CTMP	4800; 7900; 6000-9000; 12000	[12]
	NSSC	1000 - 5600	[12]
	Kraft bleaching	500 - 700; 1100 - 1700; 1254; 1200	[14],[15], [16],[17]
Pulp and paper mills	TMP	1000 - 5600	[12]
	CTMP	2500 - 13000; 9521	[12], [18]
	NSSC	5020	[12]
	Kraft	1000; 1400; 2210; 1130	[3],[19], [16], [20]

TMP: Thermomechanical pulping, CTMP: chemithermomechanical pulping, BCTMP: Bleached chemithermomechanical pulping, NSSC: neutral sulfite semichemical process

2. Advanced Oxidation Processes

Conventional technologies including biological, thermal, and physicochemical treatments have been traditionally used to remove aqueous contaminants. Some other techniques such as flocculation, precipitation, adsorption, extraction, and reverse osmosis required post-treatments to dispose the separated contaminants. These limitations of conventional methods have been an incentive to develop more efficient systems. Since some of the pollutants in industrial effluents are not biodegradable, conventional treatment processes are not sufficient. In order to meet the increasingly stringent discharge limits, mills are forced to adopt unconventional and technologically advanced treatment systems to reduce refractory organic compounds [20], [21], [22] and color of wastewater processes [23]. Effluents from this industry are highly colored. In general, lignin and its derivatives are responsible for that strong coloration [24]. Biological treatments, such as activated sludge process, remain the most

suitable treatment for the degradable organic matter (measured as BOD5), but the ability of these methods for removing refractory compounds is negligible. For example, using an activated sludge process for the treatment of CTMP pulping effluent, a maximum decrease of 68% was reported (12.000 mgL^{-1} initial COD), and similar values were found for NSSC pulping effluent (14,200 mgL1 of initial COD) [25]. In the case of chemical pulps, decreases of 31% were reported by treating the effluent with activated sludge [26], whereas the treatment in a Upflow Anaerobic Sludge Blanke (UASB) reactor produced an average efficiency of COD removal of 80-86% without recirculation and of 75-78% with recirculation (1.400 mgL^{-1} of initial COD) [27]. The final values of COD reported with the use of biologic treatment, indicate that the degree of degradation achieved is not sufficient to comply with the regulations [28]. It is therefore necessary to identify alternative methods that can degrade these compounds.

Advanced Oxidation Processes (AOP) can produce a total mineralization, transforming recalcitrant compounds into inorganic substances (CO_2 and H_2O_2), or partial mineralization, transforming them into more biodegradable substances. Therefore, three levels of degradation can be defined: [29]: (i) primary degradation, which causes a structural change in the compound, allowing it to be more easily removed by other processes (for example, biological treatment, adsorption, etc.), (ii) acceptable degradation, which involves the decomposition of the compounds, reducing their toxicity, (iii) final degradation, the last step comprising the mineralization of organic compound. AOP are powerful systems capable of transforming pollutants into harmless substances in a short reaction time and can be used to treat effluents from the chemical, petrochemical, textile, and other industries, and also from the pulp and paper mills [30], [31].

AOP exploit the high energy of hydroxyl radicals, which attack most of organic molecules: aromatic rings, polyphenols, halogenated compounds, resin acids, unsaturated fatty acids, compounds resulting from the decomposition process of organic nitrogen, or mutagenic compounds as TNT [32], [33], [34], [35], [36], [37], [38]. They have the ability to destroy dissolved organic contaminants, such as halogenated hydrocarbons (trichloroethane, trichlorethylene), aromatic compounds (benzene, toluene, ethylbenzene, xylene BTXE), volatile organic compounds (VOCs), pentachlorophenol (PCP), nitrophenols, detergents and pesticides, as well as inorganic contaminants such as cyanides, sulfides and nitrites [39], with a constant speed on the order of 106 - 109 M^{-1} s^{-1} [40].

The high reactivity of these radicals and their low oxidation selectivity are useful attributes that made this process a promising technology for the treatment of effluents containing refractory organic compounds [41], [42]. The main strengths of the oxidative processes are that they do not transfer contaminants from one medium to another, as do other techniques such as flocculation or membranes, for example. The formation of sludge does not usually happen,

and in some cases complete mineralization of refractory compounds occurs [43]. As negative aspects of these processes, the high investment and operating costs [a common feature to all processes and their main problem], and the generation of undesirable byproducts may be mentioned [44]. The combination of biological and chemical processes (each process affected by their individual parameters) may result in a more economical option to increase the treatability of refractory effluents, by increasing the BOD_5/COD ratio and /or by the better utilization of the oxygen rate [45]. Therefore, chemical oxidation is affected by the amount of oxidizable organic compounds, the reaction rate between the oxidizing agents and the organic compounds, and by chemical conditions, such as pH and temperature, whereas the biological processes are affected mainly by the pH, the presence of toxic substances, the redox potential and the oxygen available. For each treatment there is an optimal combination of conditions, which in turn can be organized in multiple ways. Therefore, changes in the input composition of the effluent are easily solved by changing the parameters in each stage, thereby allowing a wide range of possibilities and a flexible design of the process [29]. Chemical oxidation has been shown to be an efficient method to increase the treatability of effluents from the pulp and paper industries and to reduce their toxicity [46].

Oxidation is defined as the transfer of one or more electrons from an electron donor (reductant) to an electron acceptor (oxidant), which has a higher affinity for electrons. These electron transfers result in the chemical transformation of both the oxidant and the reductant, producing in some cases chemical species with an odd number of valence electrons. These species, known as radicals, tend to be highly unstable and hence highly reactive because one of their electrons is unpaired. Oxidation reactions that produce radicals tend to be followed by additional oxidation reactions between the radical oxidants and other reactants (both organic and inorganic) until thermodynamically stable oxidation products are formed. The ability of an oxidant to initiate chemical reactions is measured in terms of its oxidation potential. The most powerful oxidants are fluorine, hydroxyl radicals (HO•), ozone, and chlorine, with oxidation potentials of 2.85, 2.70, 2.07 and 1.49 electron volts, respectively [47]. Several technologies such as Fenton, photo-Fenton, ozonation, photocatalysis, etc. are included in the group of the AOP and the main difference between them is the source of radical production [48]

For the effective oxidation of refractory organic compounds, hydroxyl radicals should be generated continuously in situ through photochemical reactions due to its chemical instability. Generation of HO• is commonly accelerated by combining some oxidizing agents such as ozone (O_3), hydrogen peroxide (H_2O_2), UV radiation, and ferrous and ferric salts (Fe^{+2} and Fe^{+3}) [49], and also by radiation sources such as ultrasound, visible, solar and thermal energy. In more advanced processes, the radicals can be generated by gamma radiation, microwave or electron beams [50]. By adjusting the reaction conditions, the HO•

radicals with a significant oxidation potential up to 2.8 V, can attack a wide variety of contaminants. Among these treatments, UV radiation plus hydrogen peroxide (UV/H_2O_2), Fenton's reagent (H_2O_2/Fe^{+2}), photo-Fenton ($UV/H_2O_2/Fe^{+2}$), and ozone combinations (O_3/UV O_3/H_2O_2) are considered to be effective for the oxidation of effluents from the pulp and paper industries [51], [52], [53], [54], [55], [56].

Some examples in which AOP were used to treat pulp and paper effluents are shown in Table 2, whereas the yield achieved in each case is represented in Figure 1. Yields of the processes are represented by the percentage of COD reduction ((final COD/initial COD)*100).

Table 2. Examples of AOP applied to the oxidation of effluents from pulp and paper industries

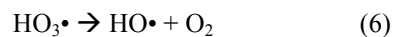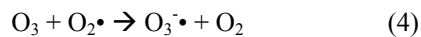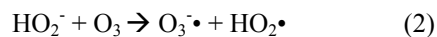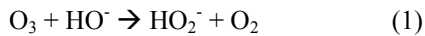| Effluent	Initial COD [mgL^{-1}]	AOP	Reference
a. Recycled paper mill	2319	O_3	[57]
b. Kraft pulp mill	1749	O_3	[57]
c. Resin acids mixture I	1880	O_3	[58]
d. Resin acids mixture II	1542	O_3	[58]
d. Resin acids mixture III	1918	O_3	[58]
e. Resin acids mixture I	1880	UV	[58]
f. Resin acids mixture II	1542	UV	[58]
g. Resin acids mixture III	1918	O_3+UV+H_2O_2	[58]
h. Black liquor	628	Fenton	[59]
i. Kraft bleaching plant*	537	Fenton	[60]
j. Bleaching plant	1150	UV/FeIII/H_2O_2	[36]
k. Kraft bleaching plant *	441	Fenton	[61]
l. Kraft bleaching plant *	441	UV/Fenton	[61]
m. Kraft pulp mill	441	UV/O_3	[62]
n. Kraft pulp mill	441	O_3	[62]
o. Kraft pulp mill	441	UV/Fenton	[62]

* Corresponds to initial total organic carbon (TOC)
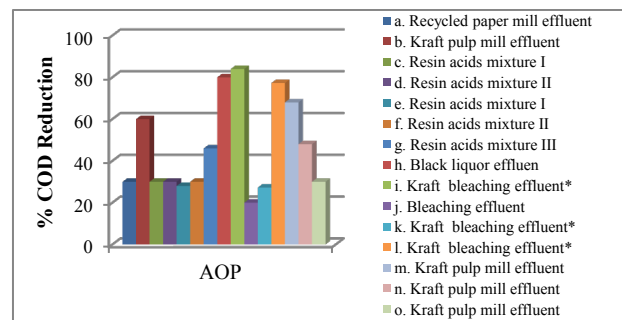
Figure 1.   COD reduction (as percentage) in cases presented in table 2

2.1. Advanced Oxidation by Ozone

Ozone is an oxidizing gas which reacts with inorganic and organic compounds, directly or indirectly, through the formation of hydroxyl radicals. Ozone oxidizes preferentially electron-rich molecules containing carbon-carbon double bonds and aromatic alcohols, but not those have single bonds [58]. It is poorly soluble in water (12 mg dm^{-3}, 25°C), but once in contact with water, it becomes highly unstable and rapidly decomposes through a complex series of reactions [59], in accordance with the mechanism of hydroxide ions (HO$^-$):

$$O_3 + HO^- \rightarrow HO_2^- + O_2 \qquad (1)$$

$$HO_2^- + O_3 \rightarrow O_3^- \bullet + HO_2 \bullet \qquad (2)$$

$$HO_2 \bullet \rightarrow O_2 \bullet + H^+ \qquad (3)$$

$$O_3 + O_2 \bullet \rightarrow O_3^- \bullet + O_2 \qquad (4)$$

$$O_3^- \bullet + H^+ \rightarrow HO_3 \bullet \qquad (5)$$

$$HO_3 \bullet \rightarrow HO \bullet + O_2 \qquad (6)$$

$$O_3 + HO \bullet \rightarrow O_2 + HO_2 \bullet \qquad (7)$$

The chain reaction is sustained by the formation of the $HO_2 \bullet$ radical, which can then initiate further reactions. The hydroxyl radical ($HO \bullet$) is the most important species formed during the ozone decomposition. Therefore, depending on the behavior of the ozone in the aqueous environment, the selectivity of ozonation may be high (direct reaction) or low (indirect reaction) [65].

The main factors affecting ozonation performance are: pH, the nature and concentration of oxidisable organic compounds, ozone dose, competition between the target compound and biodegradable by-products, the presence of oxidant scavengers, and the efficiency of ozone mass transfer [66]. Ozone is effective to decolorize effluents, and can convert wastewater biorefractory compounds into biodegradable ones [67]. Ozone treatment itself seems to have little impact on the reduction of the concentration of total organic carbon (TOC), but a rapid decrease in UV 254 absorbance was observed during the treatment. Although it did not mineralize the organic matter present in the effluent, it altered its chemical structure. Prolonging the duration of the ozone treatment beyond 5 min did not produce aditional benefits. The oxidation products are suspected to be relatively non-reactive to ozone [68]. Many catalysts are used in combination with ozone to enhance the oxidation process. Ultraviolet light and ultrasonic have been used to produce further hydroxyl radicals, thus improving the degradation effect [69].

The ozone dosage played an important role in discoloration. The increase of the ozone dosage in 10-fold produces a 19-fold increase of the discoloration rate. When the liquid is saturated, an excess of ozone dosage do not enhance the discoloration, since ozone solubility is constant at a certain temperature. If ozone concentration is higher than the optimum dose, the amount of $HO \bullet$ radicals and ozone in solution are virtually invariant. When the initial concentration of organic matter is high, more $HO \bullet$ radicals are consumed, so the increase of ozone concentration can have a positive effect in this case [70].

Ozonation best performance occurs at alkaline pH, and is due to the reaction of almost all organic and inorganic compounds with the molecular ozone and the oxygen radicals, including the hydroxyl radical. These phenomena are attributed to the ability of O_3 to initiate hydroxyl radical formation at high pH. These hydroxyl radicals have an oxidation potential ($E° = 2.80$) higher than O_3 ($E° = 2.07$) in the direct reaction under acidic conditions [71]. Conversely, under acidic conditions, the selective reaction of ozonation involves only the ozone with unsaturated organic compounds. Removing color and COD has not been different in a pH range of 4.5 to 11, but the oxidation of phenolic compounds has been favored at pH higher than 9 [26]. With similar reaction conditions (pH = 10-12) the efficiency of the ozone oxidation of phenolic compounds in a liquor corresponding to the first alkaline extraction of a Kraft industry has been proved [72]. Phenolic compounds have been shown to promote O_3 decomposition and increase radical $HO \bullet$ exposure [73].

The action of ozone, which is often limited to a partial oxidation of the organic matter, seems to be a viable technique for the treatment of the papermaker's effluents, as it is able to accomplish the degradation of lignin products and to reduce the organic load. Therefore, ozonation may be used as a first step in the treatment of effluents from the pulp and paper industry, followed by a treatment in an aerobic biological reactor [74] [75]. The combination of ozonation with biological treatment reduces biological regrowth potential, because biological treatment can remove biodegradable organic matter selectively. Ozonation transforms large molecules into smaller ones, thus increasing the biodegradability of the organic matter [76].

Numerous examples of treatment of effluents from paper mills with ozone show that the produced oxidation is able to decrease the quantity of organochlorine organic compounds, extractives, lignin derivatives, resin and fatty acids, color and toxicity, but it cannot reach high values of oxidation [77]. Ozonation combined with biological treatment is an effective method for treating effluent from several pulping processes [78].

The destruction of lipophilic extracts with an increase of biodegradability represented by the BOD/COD ratio [79], and a decrease of 90% of the extractives and 50% of the COD [80] have been reported for two different TMP effluents. A reduction of 12% of TOC, 70% of total phenols, and a 35% in color after 60 minutes of ozonation have been informed for an industry that produces bleached Kraft pulp [81]. Ozonation of wastewater from a similar industry with doses of 0.7 to 0.8 mgL^{-1} for 120 min resulted in a COD removal of about 21% ($\pm$ 5%). By integrating ozonation with a biological treatment, a reduction of 50% TOC has been obtained, i.e. 30% higher than the performance of each individual treatment [82]. It has been found that the use of ozone (dose: 50 - 250 mgL^{-1}) as a pretreatment of a biological reactor is effective for the treatment of a bleached Kraft pulp effluent, as it increase the effluent biodegradability, checked by increasing BOD along with the reduction in COD (reductions close to 11%). With the use of ozone as a postreatment, the reduction percentages were much lower [83].

2.2. Advanced Oxidation by Hydrogen Peroxide

In the case of hydrogen peroxide, the reaction between the generated $HO \bullet$ and many organic contaminants occurs rapidly. However, although the reaction itself produces no direct mineralization of these pollutants, it produces the oxidation of organic products, which can in turn react with

the HO• radical. The use of this agent has emerged as a viable alternative among other advanced oxidation processes, because it is a non-toxic reagent that does not form any harmful by-product, improves the efficiency and reduces the critical conditions of the oxidation reaction [84]. For a given concentration of H_2O_2 and pH, hydroxyl radical production mainly depends on catalyst concentration and reaction temperature. Once the radical is formed, it can react with the unreacted H_2O_2 or the organic matter, resulting in oxidized species.

$$H_2O_2 + HO• \rightarrow HO_2• + H_2O \qquad (8)$$

$$HO_2• + HO• \rightarrow O_2 + H_2O \qquad (9)$$
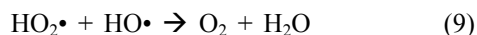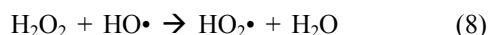
The first reaction is favored when the effluent contains high levels of organic matter, and leads to a high degree of mineralization (desired reaction.) The second is favored when the H_2O_2 is present in large amounts [relative to the organic matter content] or the load of catalyst is low. This reaction affects the efficiency of the overall degradation and acts as a radical scavenger, resulting in a significant increase in operating costs [85], and inhibitory effects on degradation of the compounds [86]. Since hydrogen peroxide itself is not able to oxidize the dissolved matter, radicals should be generated from the direct reaction of another oxidant [such as ozone] and the ionic form of hydrogen peroxide, which is the initiation stage of a radical mechanism [87]. The catalyzed reaction of ozone with hydroxyl ion must be considered as a second step of the radical initiation mechanism, leading to the formation of hydroxyl radicals. The rate of initiation of the reaction of radical generation becomes more important at high pH [88]. The combination of these two oxidizing agents is also beneficial in the treatment of compounds that show little or no reactivity towards the direct attack of the ozone molecule [89].
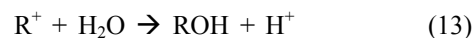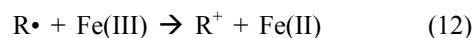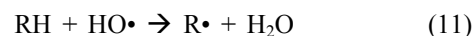
2.3. Advanced Oxidation by catalyzed H_2O_2

Early studies on advanced oxidation processes with H_2O_2 were carried out using metal salts (mostly iron) as homogeneous catalysts in reactions known as Fenton-type reactions. These systems have been successfully applied to the oxidation of various compounds, including phenol and its derivatives. However, it is generally preferred the use of solid catalysts which can be recovered by a simple separation operation and reused in the treatment process. For this reason, variants of catalytic systems that can work with the active ions in a solid support are under study [90]. Among the advanced oxidation processes, the Fenton reaction has been proved to be ease to handle and more effective in terms of removal rate. The main organic pollutants "target" of the Fenton's reagent are soluble substances, aromatic nucleophilic compounds [91], and polyphenols such as lignin [92]. Radicals are formed by the reaction:

$$H_2O_2 + Fe[II] \rightarrow Fe[III] + HO^-+ HO• \qquad (10)$$
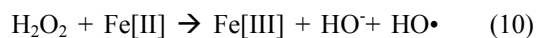
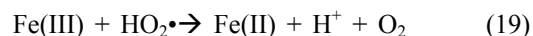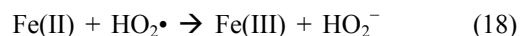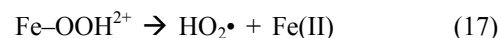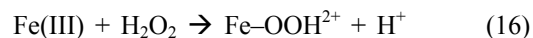The reaction mechanism of this reagent has not been completely explained due to the variety of complex compounds and intermediates which are formed and their subsequent reactions. During the reactions with the H_2O_2 solution and of Fe(II) salts, the organic compounds are oxidized with a radical chain mechanism [93], where the hydroxyl radicals are capable of attacking rapidly to organic substrates. The main stages of the process are [94]:

$$RH + HO• \rightarrow R• + H_2O \qquad (11)$$

$$R• + Fe(III) \rightarrow R^+ + Fe(II) \qquad (12)$$

$$R^+ + H_2O \rightarrow ROH + H^+ \qquad (13)$$

Numerous competing reactions, involving Fe(II), Fe(III), H_2O_2, hydroxyl radicals, and hydroperoxyl radicals ($HO_2•$) derived from the substrate can occur. Hydroxyl radicals can be swept by reaction with Fe(II) or hydrogen peroxide.

$$HO• + Fe(II) \rightarrow HO^- + Fe(III) \qquad (14)$$

$$HO• + H_2O_2 \rightarrow H_2O + HO_2• \qquad (15)$$
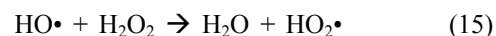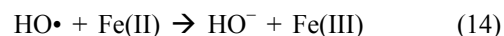
The Fe(III) formed through the mentioned reactions can react with H_2O_2, according to a radical mechanism, consisting of hydroxyl and hydroperoxyl radicals, with the regeneration of Fe(II).

$$Fe(III) + H_2O_2 \rightarrow Fe–OOH^{2+} + H^+ \qquad (16)$$

$$Fe–OOH^{2+} \rightarrow HO_2• + Fe(II) \qquad (17)$$

$$Fe(II) + HO_2• \rightarrow Fe(III) + HO_2^- \qquad (18)$$

$$Fe(III) + HO_2•\rightarrow Fe(II) + H^+ + O_2 \qquad (19)$$

The rapid decomposition of H_2O_2 is attributed to the immediate reduction of Fe(III) to Fe(II) after each cycle of the Fenton reaction. The efficiency of Fenton process depends on the generation rate and the concentration of oxidizing agents formed during Fenton reaction. Operational parameters that directly affect the efficiency of the process are: the source of iron catalyst (e.g. ferrous or ferric salt), iron and hydrogen peroxide concentrations, their ratio, pH, temperature and treatment time [95].

Several studies indicate that high efficiencies of consumption and conversion could be obtained with an oxidant dosage strategy that minimizes the peroxide decomposition into non-oxidizing (parasitic) species [96], [97]. A decrease in pH values due to the formation of acidic intermediates was verified. The increase of the initial H_2O_2 concentration first enhances the oxidation process resulting in an increase of TOC removal until it reaches a maximum, and thereafter, higher hydrogen peroxide concentrations inhibit the degradation of organic compounds in wastewater. It is therefore very important to optimize the applied H_2O_2 dose in order to maximize the oxidation reaction [98].

Lignocellulosic materials may contain reducing agents for Fe[III] in their structure, such as extractives (phenolic compounds or terpenes) or cell wall polymers (lignin), which contribute to the generation of hydroxyl radicals [99].

The main advantage of the Fenton process is that the reagents are safe to handle and environmentally benign. It does not require highly complicated devices or pressurized systems for the oxidation process, making it technologically a viable for direct application on any scale (laboratory industry), [100]. It can also be used as a pretreatment of the

biological stage in order to increase the biodegradability of recalcitrant compounds, reducing the toxicity of the wastewater [101], [102], [103] and for the elimination of the organochlorine compounds and polyphenols contained in effluents from some bleaching processes [104], [105]. Complete oxidation of organic substances by the Fenton's reagent, which lead to the formation of carbon dioxide, is generally inconvenient due to a high consumption of hydrogen peroxide [106]. The potential application of Fenton technology for the treatment of highly polluted industrial effluents requires to achieve high efficiencies of H_2O_2 consumption, since this is the critical component of the operating costs. High temperatures increase TOC and COD removal, since H_2O_2 consumption is more efficient in these conditions. For example, COD removal was 92% at 90ºC compared to 67% at 50ºC [107].

The optimum pH in Fenton reactions for COD and TOC removal seems to be 3 in most studies. At higher pH values, free Fe^{2+} ions concentration decreases due to the formation of ferrous complexes and the precipitation of ferric hydroxides. The oxidation potential of hydroxyl radicals also decreases when pH increases. Hydrogen peroxide stability is high at pH 3–4, but it decomposes when pH increases [108]. Besides the iron salts, other transition metals having at least two oxidation states, such as copper, ruthenium, cerium and manganese, can also promote the generation of hydroxyl radicals from H_2O_2. However, due to economic and environmental constraints, the iron salts are generally preferred for the process [109].

Elements with multiple redox states (like chromium, cerium, copper, cobalt, manganese, and ruthenium) all directly decompose H_2O_2 into HO• through conventional Fenton-like pathways. These systems work efficiently even at neutral pH. The H_2O_2 activation mechanism is very specific to the nature of the catalyst and critically depends on its composition. To achieve an efficient electron transfer to H_2O_2, the ideal Fenton catalyst should exhibit multiple oxidation states because the catalytically-active species with a specific oxidation state can be easily regenerated from an inactive form through a simple redox cycle. To achieve this objective, both active and inactive redox states should be stable over a wide pH range to prevent the precipitation of the catalytic species. In terms of its reactivity towards H_2O_2, redox properties of copper are strikingly similar to those of iron. Both the monovalent (Cu^+) and divalent (Cu^{2+}) oxidation states react easily with H_2O_2. This Fenton-like system should work over a broader pH range, compared to the traditional Fenton system working only in acidic conditions. All copper based Fenton catalysts efficiently generate HO• for the oxidation of various organic pollutants in near-neutral or neutral aqueous solutions. Additionally, Cu^{2+} complexes with organic degradation intermediates (organic acids) are easily decomposed by HO•, whereas the corresponding Fe^{3+} complexes are highly stable [110].

Combinations of an electrochemical process with the Fenton process, named the electro-Fenton method, was developed to enhance the oxidation of organic compounds [111], in which the reactions between hydroxyl radicals and the organic compounds are easily carried out [112]. This method is divided into four categories. In type 1, hydrogen peroxide and ferrous ions are electro generated using a sacrificial anode and a bubbling oxygen cathode.

In type 2, a sacrificial anode is used as a source of ferrous ions and hydrogen peroxide is externally added. In type 3, ferrous ions are externally added and hydrogen peroxide is generated using a bubbling oxygen cathode. In the type 4 [the most used one], Fenton's reagent is used to produce hydroxyl radicals in an electrolytic cell and ferrous ion is regenerated by the reduction of ferric ions at the cathode [113]. Using this method, COD reduction up to 96% in a Kraft pulp mill effluent [initial COD: 1669.7 mgL^{-1}] was achieved [114].

2.4. Advanced Oxidation by UV Radiation

UV radiation alone is popular for water disinfection, but does not have any applicability in the treatment of effluents. UV/H_2O_2, UV/O_3, and their combinations are suitable for treating the organic components of the effluents. An optimization procedure applicable to UV/O_3 or UV/H_2O_2 may be extended to $UV/O_3/H_2O_2$. Combinations UV/O_3 and UV/H_2O_2 processes are qualitatively similar, but show slight quantitative differences in the optimization. Since ozone is a gas, the solubility should be taken into consideration and the influence of pressure on solubility cannot be ignored. Furthermore, H_2O_2 is commonly available as a 30% solution. As it has an unlimited solubility in water, the system pressure is not a variable, providing some simplification in the analysis and experimentation [115]. UV/H_2O_2 treatment is based on the formation of radicals HO• by photolysis of the hydrogen peroxide:

$$H_2O_2 + h\nu \rightarrow 2HO• \qquad (20)$$

H_2O_2 molar absorptivity at 253.7 nm is low, about 20M^{-1} cm^{-1} and the HO• are formed by the absorption of an incident photon. At this wavelength, the speed of photolysis of aqueous hydrogen peroxide is about 50 times slower than that of ozone. UV/H_2O_2 technique requires a relatively higher dose of H_2O_2 and / or longer exposure to UV rays than, for example, the UV/O_3 process. Furthermore, it has been found that the speed of photolysis of hydrogen peroxide is pH dependent and increases in alkaline conditions, because of the formation of HO_2^- anions, which show a molar absorptivity of 240M^{-1} cm^{-1} at 253.7 nm, which is higher than the hydrogen peroxide, by the reaction [116]:

$$HO_2^- + h\nu \rightarrow HO• + O•^- \qquad (21)$$
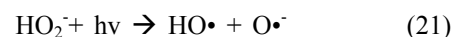
These combined treatments were tested under various conditions on an effluent from a bleaching process, characterized by its high content of chelating agents. Ozone alone was not effective, however, by using UV/O_3 treatment reductions of 95% and 98% in COD and chelating agents respectively were achieved [117]. The oxidation of aromatic compounds such as lignin and phenolic extractives from lignocellulosic materials and TOC reduction, have been
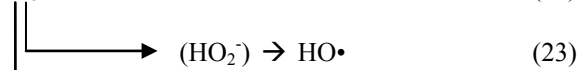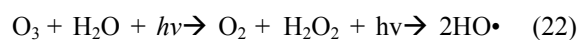
found to be more efficient at pH ≥7 with UV/H$_2$O$_2$ treatment [118].

When using the UV/H$_2$O$_2$ technique is important to note that the synergistic effect between the UV radiation and hydrogen peroxide is beneficial only with contaminants that require a relatively aggressive oxidation conditions (high activation energies). There is a concentration of peroxide beyond which the presence of hydrogen peroxide is detrimental to the oxidation reaction, so the optimal peroxide concentration needs to be selected. The presence of compounds that strongly absorb incident UV light [for example, humic acid] is another factor that must be considered. If these compounds are present in the effluent stream, a higher dose of hydrogen peroxide to achieve the synergistic effect is required [119].

In the treatment of an effluent from a bleaching process (chlorination and alkali extraction stages), the color removal was more influenced by the pH than by UV. This is explained by the increased presence of easily degradable chromophores compounds at basic pH. It was verified that the discoloration constant depends on pH rise, contributing favorably to increase the reaction rate [120]. When treating a phenol solution (40 to 500 mgL^{-1}), almost 25% of phenol was oxidized in 1.5 h, and over 45% of the degradation took place during a period of 4 h due to direct UV photolysis, or by the attack of the hydroxyl radicals.

By using a H$_2$O$_2$/phenol molar ratio of 125, more than 95% of the phenol was oxidized in 40 min. At higher H$_2$O$_2$/phenol ratios (>300), the oxidative process is adversely affected even though the rate of free radicals production is higher. H$_2$O$_2$/UV combinations significantly enhanced the degradation of phenol compared to direct photolysis [121].

O$_3$/UV process is effective for oxidation and destruction of toxic and water-refractory organic compounds. It consists basically of an aqueous system saturated with ozone, which is irradiated with UV light at 253.7 nm. The extinction coefficient of ozone at 253.7nm is 3300m^{-1}cm^{-1}, much higher than that of hydrogen peroxide and its decomposition rate is about 1000 times greater than that of the same reagent. O$_3$/UV combination improves the efficiency of the individual processes. The synergistic effects of the combined treatments increase by increasing pH to basic levels. This is attributed to the catalytic effect of HO- ion on the ozonation initiation [116].

Irradiation of ozone in water produces H$_2$O$_2$ quantitatively. Hydrogen peroxide thus generated is in turn photolyzed, generating radicals HO• and reacts with the excess of ozone generating radicals which contribute to oxidation, according to equation [122]:

$$O_3 + H_2O + h\nu \rightarrow O_2 + H_2O_2 + h\nu \rightarrow 2HO\bullet \quad (22)$$

$$(HO_2^-) \rightarrow HO\bullet \quad (23)$$

$$HO^- \rightarrow HO\bullet \quad (24)$$

Accordingly, the conditions to be considered for O$_3$/UV processes can be summarized as [119]: high partial pressures

and continuous bubbling of ozone; low initial concentration of contaminants (in general, the effluent requires dilution); temperature optimization taking into account the increase in the rate of degradation and the low solubility of ozone at high temperatures; neutral or slightly alkaline pH (range 7-8); minimum presence of radical scavengers because they inhibit the process of degradation. These combined treatments which involve photodegradation are important for removing aromatic hydrocarbons and chlorinated phenolic compounds present in some bleaching effluents of kraft pulp [123]. Bleaching processes using chlorine generate bioaccumulative and carcinogenic substances (such as chlorophenols), which are difficult to remove with a biological treatment or by oxidative treatments applied individually [124].

The efficiency of degradation of Fenton process is also accelerated by irradiation with UV light [125]. It is expected also a improvement of the efficiency in the oxidation reaction, because in this case two different pathways contribute to the generation of free radicals (UV radiation and iron salts) and, therefore, its concentration should be high [126]. Fenton and photo Fenton efficiencies have been monitored in the treatment of an effluent from a TMP pulping process. The increase in discoloration produced by the last one was attributed to the increased radical attack to the double bonds of the lignin in the effluent, responsible for its color [23]. Color removal was also verified when treating bleach effluents from unbleached Kraft pulping processes [127]. Some stages in the pulp and paper mill require recirculating water of high quality. In these cases, reverse osmosis systems are implemented as the final step of the different treatments applied for the reduction of recalcitrant toxic compounds. The photo-Fenton system has been proved to be a viable alternative in these cases requiring strict processing conditions [128]. Fenton oxidation has also been evaluated for oxidation of chelants, reaching reductions of about 90%. The oxidation rate was increased by photo-Fenton treatment [129]. This oxidation treatment is also highly efficient when applied to the effluents of a wastepaper plant (TOC concentration: 332mgL^{-1} and COD: 1286mgL^{-1}). Generally, over 90% of TOC can be removed with optimized conditions, especially at temperatures about 50°C. Because the temperature of the effluent is normally between 40 and 50ºC, no energy input is required. Therefore, efficient TOC removal is highly possible under the usual operation conditions [53].

When testing various oxidizing systems on a solution of phenol (93-105 mgL^{-1}), it was found that no combination of ozone (O$_3$/H$_2$O$_2$, O$_3$/UV and O$_3$/UV/H$_2$O$_2$) enhanced the rate of degradation with respect to the use of ozone alone. Concerning peroxide treatment, the degradation rate of the UV/H$_2$O$_2$ process was almost five-fold higher than with UV. Fenton's reagent resulted in a degradation 40-fold faster than the UV process. The highest percentages of reduction achieved were, O$_3$: 100%; O$_3$/H$_2$O$_2$: 92.5% UV: 24.2%; UV/H$_2$O$_2$: 90.6%; O$_3$/UV/H$_2$O$_2$: 99.4% Fe (II) / H$_2$O$_2$: 100% [130].

Various oxidative systems have been evaluated on different streams of wastewaters from pulp and paper mills. Applying different iron doses (1.3, 20, and 50 mgL^{-1}) in the Fenton's reagent on an outgoing effluent from a biological treatment (initial COD: 898,9 mgL^{-1}), COD removal achieved was 4, 18, and 36%, respectively. This low rate of degradation observed was attributed to the poor regeneration of ferrous ions (reduction of Fe(III) to Fe(II)) in the absence of UV light. On the contrary, when photo-Fenton was applied with 5 and 10 mgL^{-1} of Fe(II), COD removal rates exceeded 90% [131]. The use of hydrogen peroxide alone resulted in too low removal values, also the UV treatment was ineffective by itself, producing unacceptably low color and TOC reductions (initial TOC: 110 mgL^{-1}), UV/H_2O_2 treatment performance was also unsatisfactory and the same results were verified in the treatment with ozone of organochlorine compounds. Both, Fenton or photo-Fenton treatments can be used for effective removal of color, organochlorine compounds and TOC of those wastewaters, reaching reductions of about 80% in all parameters. However, the photo-Fenton treatment seems to be more advantageous because requires much less time to react and smaller reactor volumes, compared to Fenton treatment [51].

The degradation of the organic compounds in the bleaching effluents from a Kraft pulp mill has been successfully carried out by applying photo-Fenton and Fenton treatments. Temperature is a key parameter that significantly increases reaction rates whereas UV irradiation improves TOC removal. At high temperature the system has similar reaction rates in both, Fenton and photo-Fenton. In all experiments, the color of the samples was reduced over 90% at the end of the reaction [61].

The effect of the initial concentration of hydrogen peroxide in UV/H_2O_2, Fenton and Photo-Fenton in the treatment of the effluent from a recycled cardboard mill (COD: 10300 mgL^{-1}) has been reported. Photo-Fenton treatment produced the greatest reduction in COD (76%) compared with UV/H_2O_2 and Fenton, in 45 minutes [132]. With the same purpose, a papermaking effluent with a COD of 950 mgL^{-1} was treated by the Fenton method, obtaining color and COD reductions of 95% and 50% respectively [133].

3. Efficiency and Cost

In all AOP processes, the hydroxyl radical is the main oxidizing agent [134], no contaminants are transferred from one phase to the other, the production of hazardous sludge is reduced [135], and the doses of H_2O_2 are critical. By increasing H_2O_2 concentration, hydroxyl radicals are more available for the oxidation of pollutants and the efficiency of removal of recalcitrant compounds also increases. However, when H_2O_2 exceeds a certain level, scavenger compounds are generated in the system, the sweep occurs and the efficiency of oxidation accordingly decreases. The amount of peroxide considered optimum depends on the system, that

is, the catalyst chosen, the concentration of recalcitrant compounds present, the reaction temperature and other parameters [136], [137].

Although classical Fenton reactions have been widely used for the treatment of effluents, they have two major disadvantages for large scale application: the high cost of H_2O_2 generation and the narrow operating range for pH, because iron ions precipitate as a hydroxide under certain conditions [138]. The main parameters that govern this system are the initial concentrations of H_2O_2 and Fe (II), and the temperature [60]. An increase in temperature is a potential solution to improve the mineralization level achieved with the same dose of H_2O_2, which greatly reduces the cost of the reaction [107]. The first catalyst systems tested were Fenton homogeneous phase systems, and have been successfully applied in the oxidation of various compounds of recalcitrant nature. Homogenous catalysis has the disadvantage of the difficulty of separating the catalyst from the stream of products after the reaction. Therefore, it becomes necessary to use the recovery operations of the catalyst, which means an increase in operating costs. An alternative solution to this problem is encapsulation of the catalyst in a porous solid, with characteristics comparable to those of homogeneous catalysts. Solid catalysts are preferred, since they can be recovered by simple separation operations and can be reused in the treatment process. The metal oxides can also be recovered from the support [139], [140]. Solid catalysts must meet some requirements, such as high activity in terms of contaminants removal, marginal leaching of the active cation, stability in a wide range of pH and temperature, and a high conversion of hydrogen peroxide with minimal decomposition. For practical applications, these materials must be available at a reasonable cost and their separation should be accomplished by elementary steps in a potential industrial application [141].

Fenton process and ozone treatment have been widely used in many applications and installations for treating effluents of industrial mills, in both processes the degree of mineralization achieved is highly dependent on the initial concentration of recalcitrant compounds. In general, these systems are limited to the partial oxidation of organic matter, and need to be supplemented with other AOP techniques in order to achieve the final level required. This leads to complex processes increasing the treatment costs. The nature of the organic pollutants also has a marked influence when comparing costs of Fenton and ozonation processes, the latter seems to be the most costly AOP operation [142].

To solve the determinant of production of H_2O_2 in situ and continuously, so as to achieve greater efficiency in the oxidation reactions, new methods have been developed, as photo-assisted methods with a high level of UV radiation [143], and electro-chemical processes such as electro-Fenton [144], [145]. From an energy standpoint, the application of ozone based systems seem to be more efficient for the production of radicals, considering that ozone/UV produces H_2O_2 in water, which generates more radicals, increasing the degree of mineralization.

Table 3.   Increased efficiency of COD removal by the sequence AOP- biological treatments

Effluent	Initial COD [mgL^{-1}]	COD Reduction [%]			AOP used	Ref.
		Bio	AOP	AOP/Bio		
Leachate from a landfill	2320	64	-	70	UV/H$_2$O$_2$	[44]
Leachate from a landfill	2320	64	-	65	H$_2$O$_2$	[44]
Drinking water	20	-	-	40	O$_3$	[76]
Drinking water	20	-	-	62	H$_2$O$_2$/ O$_3$	[76]
Textile	408	-	36	65	UV/Fenton	[149]
Pharmaceutical	800	-	33	95	UV/Fenton	[150]
Industrial	500	-	34	84	UV/Fenton	[151]
Surfactant	1500	-	78	94	Fenton	[152]
Pulp bleaching plant	1586	20	21	40	O$_3$	[82]

The high operating costs associated to AOP based on H$_2$O$_2$ are highly dependent on the cost of this reactive, whereas the generation of UV radiation associated in the UV/AOP is always a small percentage of the total cost [146]. The oxidation potential of the hydroxyl radical (E$_0$ = 2.80V) is much larger than that of the ozone (E$_0$ = 2.07 V), therefore, the combination of ozone and UV radiation and / or H$_2$O$_2$ produce hydroxyl, superoxide and perhydroxyl radicals, generating processes which synergistically accelerate the removal of organic material [147].

As there is a growing worldwide concern for the development of alternative technologies for water reuse, AOPs are considered a highly competitive technology for water treatment as they remove all organic pollutants not treatable by conventional techniques. Nevertheless, chemical oxidation for complete mineralization is usually expensive, so its combination with a biological treatment reduces operating costs [123]. Even when the mineralization of all compounds is nearly complete, AOPs need to be combined with a biodegradation process to eliminate all the organic content of a given wastewater [148]. An increased efficiency is achieved hence using the sequence: AOP- biological treatment (see Table 3).

An increased efficiency of removal of organic matter is achieved by the sequence AOP- biological treatments. It was found that the biological degradation of biodegradable compounds produced by UV/H$_2$O$_2$ has a higher overall efficiency for recalcitrant compounds removal than the attainable by biological treatment followed by the same AOP [44] [153].

Acceptable levels of reduction of recalcitrant compounds were also obtained by ozone treatment as pretreatment, because the ozonation produces the breakage of large molecules, increased the system biodegradability [154]. For the economic optimization of the overall process it is necessary to limit the intensity and / or duration of the chemical treatment. Therefore, the determination of the biodegradability of the mixture of intermediate products generated during the advanced oxidation treatment is required to ensure that these combinations of strategies will reduce the overall costs of treating biodegradable effluents [155].

To find the optimal operating conditions of the combined process, it is necessary to calculate the individual biological and chemical oxidation efficiencies. This task involves profound knowledge of both processes. Several analytical parameters must be monitored during each step of the treatment line. Chemical parameters normally measured are: COD, some specific pollutants concentrations, and inorganic species generated by the complete degradation of contaminants during the AOP treatment. Toxicity analyses and biodegradability tests are also important. In the biological system itself the measurement of anions and cations is essential since nutrients are vital to the microorganism populations in the activated sludge, and monitoring the nitrogen species provides much information related to nitrification and denitrification. This series of analytical parameters satisfies the engineering needs for the design of the combined system [156]. The efficiency of the combined process normally requires the separate optimization of both chemical and biological stages. An additional difficulty for the efficient operation of a large-scale plant, is that the chemical oxidant must not come in contact with the biological culture. Low concentrations of hydrogen peroxide are not a problem but high concentrations cause an adverse effect on the microorganisms. The reaction time of chemical oxidation is one of the most important factors to be taken into account. When the treatment is too long, the effluent is chemically overdegraded and the metabolic value of the highly oxidized products is minimal for the microorganisms. This also causes that large doses of oxidant are spent in the degradation of easily biodegradable intermediates, reducing the efficiency of the overall system [123].

4. Conclusions

The pulp and paper industry is a complex activity which involves many different processes and products. Pollution of water bodies is of great concern because it is an industry that generates large volumes of waste water per ton of pulp or

paper produced, depending on the nature of the raw material, the final product and the extent of reused water.

Chemimechanical and semichemical cellulosic pulps manufacturing processes, due to their high yield, have no reactive recovery systems based on combustion of the dissolved organic matter, as indeed occurs in pulping processes such as the chemical Kraft process, and if the pulps are bleached with chlorine compounds, the effluent may have organochlorine substances.

Pollutants in these industrial effluents are highly colored, mainly due to the presence of chromophoric compounds from wood extractives, lignin derivatives and organochlorine compounds, all recalcitrant. Recalcitrant compounds are known as non-biodegradable and persist in the environment. This resistance to be degraded may be because they are not recognized as a substrate by the organisms in biological treatments; they are highly stable, that is, chemically inert due to substitutions with halogen, nitro, and sulfonate groups. They are insoluble in water, being highly toxic or either originating highly toxic degradation compounds. All these features make the biological treatment not sufficient for the removal of these compounds, so have been developed unconventional and technologically advanced treatment systems.

It is clear that advanced oxidation processes are technically applicable for the removal of recalcitrant compounds from effluents of pulp and paper mills. The merit of this technology is to improve biodegradability, reduce toxicity, enhance color removal and disposal of organic compounds, increasing the possibility of discharge those wastewaters into the receiving bodies without causing any damage. Due to the differences between the effluents from the various processes and operations of these industries, some oxidative processes must be combined to improve the efficiency of removal, though it can mean an increase in operating costs.

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