The application of advanced oxidation technologies to the treatment of effluents

from the pulp and paper industry. A review

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Abstract

Paper industry is adopting zero liquid effluent technologies to reduce fresh water use and meet environmental regulations, which implies water circuits closure and the progressive accumulation of pollutants that must be removed before water re-use and final wastewater discharge. The traditional water treatment technologies that are used in paper mills (such as dissolve air flotation or biological treatment) are not able to remove recalcitrant contaminants. Therefore, advanced water treatment technologies, such as advanced oxidation processes (AOPs), are being included in industrial wastewater treatment chains aiming to either improve water biodegradability or its final quality. A deep review of the current state of the art regarding the use of AOPs for the treatment of the organic load of effluents from the paper industry is herein addressed considering mature and emerging treatments for a sustainable water use in this sector. Wastewater composition, which is highly dependent of the raw materials being used in the mills, the selected AOP itself, and its combination with other technologies, will determine the viability of the treatment. In general, all AOPs have been reported to achieve good organics removal efficiencies (COD removal >40%; and about an extra 20% if AOPs are combined with biological stages). Particularly, ozonation has been the most extensively reported and successfully implemented AOP at an industrial scale for effluent treatment or reuse within pulp and paper mills; although Fenton processes (photo-Fenton particularly) have actually addressed better oxidative results (COD removal ≈65-75%) at lab scale, but still need further development at large scale.

1. Introduction

Sustainable water use is a current concern within the pulp and paper industry, and great efforts are being made to minimize water consumption, as well as to reduce the environmental impact of final effluents. Therefore, global water use has been reduced from 600 m^3/T in 1974 to 4-100 m^3/T in modern paper mills, which has resulted in the progressive accumulation of pollutants in process water that must be removed to meet the quality standards required for water to be re-used or discharged (Ordóñez *et al.* 2014).

Pulp and paper mills generate a wide variety of pollutants to their effluents, depending on the implemented type of pulping process and the posterior pulp treatment (Pokhrel and Viraraghavan 2004). The main compounds present in virgin fiber pulp effluents are hemicelluloses, pectin, lipophilic extractives (such as resin acids), lignans, lignin-related substances, carbohydrates, and carboxylic acids (e.g. acetic and formic acids) in small quantities (Gullichsen and Fogelholm 1999; Sundholm 1999). In addition, chemical pulping processes have been reported to generate more than 40% low biodegradable organics within the total organic matter of the effluent (Dahlman *et al.* 1995); and particularly, sulphite processes also produce low biodegradable sulfonic compounds as by-products (Amat *et al.* 2004; Gregor *et al.* 1997).

On the other hand, effluents from recovered paper mills are different. The pH is not usually as strongly basic as for a kraft process, and more starch-related products (rather than lignin ones) can be found (Amat *et al.* 2005a), resulting that these effluents are more biodegradable (Merayo *et al.* 2013; Thompson *et al.* 2001). In addition, it is also important to consider that the papermaking operation with recycled fibers may introduce different chemical compounds in the effluent, such as EDTA, which is very difficult to degrade by biological technologies (Sundholm 1999). Other potential

contaminants that may be generated in the papermaking process are different process and product additives, such as fillers, whiteners, dyes, defoamers, dispersion agents, surfactants, biocides, and slimicides (Lacorte *et al.* 2003).

The concentrations of all these diverse compounds change along the different stages defined in the papermaking process. During pulping, most of the contaminants are released. During bleaching, residual lignin is removed to enhance brightness (Wang *et al.* 2004), and different chlorinated organic compounds can be generated in low proportions in Elemental Chlorine Free processes (Balcioglu *et al.* 2003; Yeber *et al.* 2007); whereas bleaching with alkaline hydrogen peroxide causes an additional load of 5-15 $Kg \cdot T^{-1}$ BOD_7 and 15-40 $kg \cdot T^{-1}$ COD, decreases hemicelluloses content, and increases the presence of pectin, lignin and aliphatic carboxylic acids. Alkalinity strongly influences the dissolution of hemicelluloses and pectin, and the release of dissolved and colloidal material (Sundholm 1999; Miranda and Blanco 2010).

Soluble biodegradable organic compounds may efficiently be removed by combinations of anaerobic and aerobic processes (Ordóñez *et al.* 2010), but these treatments do not prevent the accumulation of the non-biodegradable organic chemical fraction (Ahmad *et al.* 2007; Habets and Knelissen 1997), such as high molecular weight organics (>1000 Da) (Yeber *et al.* 2007), lignin and lignin-derived compounds (Chang *et al.* 2004; Dahlman *et al.* 1995; Eriksson and Kolar 1985; Thompson *et al.* 2001), toxic chlorinated organics (Balcioglu *et al.* 2007), and pollutants with sulfonic groups (Beltrán *et al.* 2000; Masuyama *et al.* 2000), among others. These chemicals usually produce alterations in the activity of biological reactors (Habets and Knelissen 1997). Furthermore, biological treatment may fail to remove color from pulp mill effluents (Balcioglu *et al.* 2007).

Therefore, the treatment strategy to reduce negative impacts from water circuits closure aims to remove high molecular weight (HMW) compounds, as well as some low molecular weight (LMW) recalcitrant organic matter (Bijan and Mohseni 2005). Considering biological treatment is not able to remove bio-recalcitrant compounds (Balcioglu *et al.* 2003; Bijan and Mohseni 2004), new trends are focused on incorporating other processes like advanced oxidation ones (AOPs) (Balabaniç *et al.* 2012; Balcioglu *et al.* 2003; Bijan and Mohseni 2004; Hermosilla *et al.* 2012). Particularly, Balabaniç *et al.* (2012) reported the removal of selected endocrine-disruptors from a recycled paper mill. Whereas the combination of biological treatments (anaerobic and aerobic) achieved about an 80% removal of different phtalates, photo-Fenton treatment achieved a 100% removal. In general, AOPs can be applied to industrial wastewater as a polishing step integrated with conventional chemical and/or biological processes in order to increase the overall treatment effectiveness (Alvares *et al.* 2001; Balcioglu *et al.* 2003; Legrini *et al.* 1993; Merayo *et al.* 2013; Oeller *et al.* 1997; Tanaka and Ichikawa 1993).

AOPs are based in the formation of hydroxyl radicals in sufficient quantity to effect the chemical transformation of contaminants (Glaze *et al.* 1987). It is known that hydroxyl radicals are almost twice as reactive as chlorine, and its oxidation potential is close to that of fluorine (E = 2.32 V/NHE at pH=7) (Bigda 1995). Highly reactive hydroxyl radical usually initiates the oxidative destruction of organic substances (R) present in wastewater by the following processes (Huang *et al.* 1993):

a) OH· addition reaction:

$$OH· + R \rightarrow ROH· \rightarrow \text{hydroxylated products} \qquad K \approx 10^7\text{-}10^{10} \text{ M}^{-1}\text{s}^{-1} \qquad (1)$$

b) Hydrogen atom abstraction:

$$OH· + R \rightarrow R· + H_2O \rightarrow \text{oxidized products} \qquad K \approx 10^7\text{-}10^{10} \text{ M}^{-1}\text{s}^{-1} \qquad (2)$$

Organic free radicals (R·) are formed as transient intermediates and are further oxidized by other intermediates to form stable, oxidized products (Huang *et al.* 1993).

The oxidation of phenolic compounds occurs more rapidly than non-phenolics one (Antunes *et al.* 2004). In the presence of electron-rich aromatic moieties, OH· preferentially reacts by addition (Antunes *et al.* 2004; Huang *et al.* 1993; Vieira and Steenken 1987). Phenoxyl radicals rapidly react with $O_2^{\bullet-}$ to produce aromatic ring-opening precursors of CO_2 (Antunes *et al.* 2004). On the other hand, aliphatic carboxylic acids are very stable, and their degradation rates by OH· are really low in the absence of UV light (Hermosilla *et al.* 2009b).

The ability of hydroxyl radical to break down the molecular structure of complex organic structures into simpler compounds has long been proven (Bigda 1995), and it has been shown successful for the partial oxidation of non-biodegradable organics such as lignin or chlorinated organics; therefore contributing to increase the biodegradability of the effluent as well (Balcioglu *et al.* 2003; Balcioglu *et al.* 2007; Bijan and Mohseni 2004; Bijan and Mohseni 2005; Bijan and Mohseni 2008; Chang *et al.* 2004; Mansilla *et al.* 1997; Marco *et al.* 1997; Mounteer *et al.* 2007; Oeller *et al.* 1997; Salokannel *et al.* 2007; Yeber *et al.* 1999a; Yeber *et al.* 1999b). The full oxidation of organic compounds is however non-economically feasible because the use of large amounts of energy and chemicals would be necessary for achieving a complete mineralization (Bijan and Mohseni 2005).

The standalone use of AOPs for the treatment of pulp and paper mill effluents would mainly be limited by the fact they usually imply a high electrical energy demand or an excessive consumption of chemical reagents (Bauer and Fallmann 1997). Therefore, they will only be economically attractive if they are combined with other wastewater treatments (Mobius and Cordestolle 1997; Sarria *et al.* 2002). Moreover, the

use of AOPs as pre-treatment depends on wastewater composition. That is, effluents with high concentrations of hydroxyl radical scavengers (such as bicarbonate ions), or with a high presence of aliphatic carboxylic acids, which are difficult to be oxidized, will result in AOPs achieving lower degradation rates (Balcioglu and Cecen 1999; Barndõk et al. 2012; Gogate and Pandit 2004a; Gogate and Pandit 2004b).

In short, it is important to highlight that the application of AOPs within the pulp and paper industry has to be adapted to each particular case considering the influence of wastewater composition, the efficiency of the process itself, and the development of adequate procedures for the use of these technologies in mills with a very high degree of circuits closure, as well as the assessment of cost-effectiveness figures. A joint review of the application of AOPs to water treatment in the pulp and paper industrial sector is reported next.

2. Ozone oxidation processes

Ozone can oxidize other compounds in two different ways: directly reacting with dissolved substances; or indirectly, by hydroxyl radicals that are produced in its decomposition process (Esplugas et al. 2002). Due to the short half-life of ozone, continuous ozonation is required to keep the reaction going on. This is one of its major drawbacks, considering the high cost of generating ozone (Catalkaya and Kargi 2007; Kreetachat et al. 2007). Furthermore, the stability of ozone is also affected by the presence of salts (Barndõk et al. 2012), pH (alkaline solutions accelerate its decomposition generating hydroxyl radicals), and temperature (Bijan and Mohseni; Catalkaya and Kargi 2007); and process efficiency is highly dependent on an efficient gas liquid mass transfer, which is quite difficult to achieve due to the low solubility of ozone in aqueous solutions (Kreetachat et al. 2007).

Nevertheless, ozonation has successfully been used as a good method to oxidize chemicals present in wastewaters from pulp and paper mills, such as eugenol, cathecol, vainillin, guaiacol, syringaldehyde, phenol, chlorophenol, trichlorophenol, and cinnamic acid derivatives (Amat *et al.* 1999; Amat *et al.* 2005b; Fontanier *et al.* 2005a; Miranda *et al.* 2001). Particularly, Fontanier *et al.* (2005) reported the behavior of most of these organics in response to ozone treatment and described how the oxidation of phenol, chlorophenol and trichlorophenol takes place in one stage attributable to aromatic ring opening reactions; whether catechol, vanillin, guaiacol and syringaldehyde are oxidized in two stages due to the generation of intermediates that are more resistant to ozone attack. Oxidation proceeds by electrophilic attack, and then the reaction is favored when substituents with a donor effect are present. For example, trichlorophenol is highly reactive because chlorine atoms are weakly deactivating substituents and OH group is a very activating one, so these combining effects favor the electrophilic attack of ozone to the two free positions in the aromatic ring (Fontanier *et al.* 2005b).

On the other hand, the carboxylic acids that are formed by opening the aromatic ring have expectedly been reported to be very resistant to oxidation by ozone (Amat *et al.* 2003; Amat *et al.* 2005b; Bailey 1982; Balcioglu *et al.* 2007; Fontanier *et al.* 2005a; Hoigne and Bader 1983; Kreetachat *et al.* 2007), and they are usually responsible for TOC abatement limitation (Hoigne and Bader 1983); although they are generally highly biodegradable.

In addition, the ozone oxidation of resin acids has also been addressed relatively effective (Korhonen and Tuhkanen 2000; Laari *et al.* 2000; Ledakowicz *et al.* 2006; Roy-Arcand and Archibald 1996); whereas starch oxidation products showed lower degradation rates than lignin derivatives ones, probably due to the absence of carbon-carbon double bonds (Amat *et al.* 2005b; Langlais *et al.* 1991) (Figure 1). Furthermore,

why *p*-toluenesulfonic acid showed a slower degradation rate than other lignin derivatives was explained by the strong deactivating effect of its sulfonic group (Amat *et al.* 2004). In short, the composition of the pulp and paper industrial wastewater, which is mediated by the papermaking process itself, including raw materials and chemicals being used, is clearly determining the final oxidation treatment efficiency.

Particularly, the success of ozonation applied to real wastewater from pulp and paper mills, whether biologically pre-treated or not, and effluents from bleaching stages, has been mainly attributed to the effective degradation of toxic lignin products and chlorophenolic compounds (Amat *et al.* 2005b; Balcioglu *et al.* 2007; Bierbaum *et al.* 2012; Bijan and Mohseni 2004; Bijan and Mohseni 2005; Catalkaya and Kargi 2007; Fontanier *et al.* 2005b; Fontanier *et al.* 2006; Mansilla *et al.* 1997; Oeller *et al.* 1997; Rodríguez *et al.* 1998; Roy-Arcand and Archibald 1996; Salokannel *et al.* 2007; Sevimli 2005; Wang *et al.* 2004; Yeber *et al.* 1999a; Yeber *et al.* 1999b). As it has additionally been reported in several other essays, ozonation usually increases the biodegradability of paper mill effluents as well (Amat *et al.* 2005a; Balcioglu *et al.* 2007; Bijan and Mohseni 2004; Bijan and Mohseni 2005; Fontanier *et al.* 2006; Helble *et al.* 1999; Mansilla *et al.* 1997; Nakamura *et al.* 1997; Oeller *et al.* 1997; Roy-Arcand and Archibald 1996; Salokannel *et al.* 2007); mainly because of the successful degradation of certain toxic compounds and the promoted changes in molecular weight fractions from HMW to LMW (Amat *et al.* 2005a; Balcioglu *et al.* 2007; Bauman and Lutz 1974; Fontanier *et al.* 2006; Hostachy *et al.* 1997; Mansilla *et al.* 1997). In fact, Amat *et al.* (2003) also reported that there is an optimum ozone dosage which allows achieving the maximum increase in biodegradability and the highest efficiency of an ozonation process. Further ozonation would have to progress oxidizing LMW carboxylic acids, but they did not show an enhanced biodegradability after this

treatment. Summing up, the ozonation of paper mill effluents aiming to increase biodegradability would only be advisable at a BOD_5/COD ratio < 0.2 (Oeller *et al.* 1997).

Color has particularly been reported to be removed very easily because its main responsible is the presence of lignin compounds, which double and triple bonds are easily oxidized by ozone (Bijan and Mohseni 2004; El-Din and Smith 2002; Joss *et al.* 2007; Kreetachat *et al.* 2007; Prat *et al.* 1989; Salokannel *et al.* 2007). In addition, and as it has just been pointed out, dechlorination of organochloride compounds is very effective; 60 minutes of reaction time have been reported enough to finish the breakdown of all organochlorides present in effluents from bleaching stages (chlorination, extraction and hypochlorite) of a pulp mill (Balcioglu *et al.* 2007). In summary, the results reported by different authors in terms of COD, TOC, color, and AOX removals, are very variable probably due to the diverse nature of the organics contained in the different treated effluents, whether they were biologically pre-treated or not, the mill of origin, or the diverse ozone feeding rates used in the treatments, although the average value resulted ≈40% (Figure 2). Particularly, Fontanier *et al.* (2005b) reported that some oxidized products by ozonation were transferred from the liquid to the solid phase in the presence of calcium salts, and its precipitation was subsequently produced. As a result, a 31% TOC removal was attributed to this phenomenon (Table 1).

Regarding the conditions under which ozonation was performed, several authors have reported that ozone resulted more effective in basic media (Amat *et al.* 2004; Amat *et al.* 2005b; Bijan and Mohseni 2005; Sevimli 2005; Wang *et al.* 2004), just as it was expected due to the more effective generation of hydroxyl radicals, which is a better oxidizing agent than molecular ozone (Bijan and Mohseni 2005; Glaze *et al.* 1987);

although working under basic conditions also implies bearing with the presence of possible scavengers like carbonate or bicarbonate (Barndõk et al. 2012; Bijan and Mohseni 2005). Putting it all together, no significant different treatment effectiveness was found between pH = 9 and 11 (Bijan and Mohseni 2005), but a significant lower treatment efficiency was addressed when pH was adjusted to neutral (Wang et al. 2004). Besides, Catalkaya and Kargi (2007) found a better degradation rate at pH = 9 than at 11, and also addressed that pH must be at least as low as 7 to perform an enhanced oxidation. Correspondingly, Medeiros et al. (2008) also showed higher color and HMW fraction removals and biodegradability increase at pH = 7 than at 12. More recently, Merayo et al. (2013) have reported non-significant differences between the ozone treatment of recycled paper mill effluents performed at pH = 7 and 12; and an even higher ozonation efficiency at pH = 7 for kraft pulp mill effluents. Considering all together, working at the typical pH values of neutral-basic pulp and paper mill effluents (pH = 7-9) addressed the great advantage of avoiding pH control mechanisms (Kreetachat et al. 2007; Oeller et al. 1997; Salokannel et al. 2007). Nevertheless, slight pH variations may occur during the oxidation reaction due to the formation of small acid by-products (Balcioglu et al. 2007; Merayo et al. 2013) or the generation of carbonate along the mineralization process (Oeller et al. 1997).

Regarding the temperature at which the process is performed, Salokannel et al. (2007) did not find differences from 21 to 35 ºC, although ozone transfer efficiency from gas to water was slightly lower at higher temperatures, implying an insignificant effect on reaction time. Accordingly, Bijan and Mohseni (2004) did not found significant differences in the ozonation efficiency of paper mill effluents from 20 to 60 ºC. Finally, Oeller et al. (1997) have also reported that increasing temperature did not provide any appreciable COD removal enhancement, although DOC removal resulted a

10-15% higher at 40 ºC and extended reaction times (> 90 minutes) than at 25 ºC, which furthermore implied consuming a higher O_3 amount as well.

Several authors have reported different insights considering the setup of an optimal ozone feeding rate. Initially, Bauman and Lutz (1974) and Nebel *et al.* (1974) proposed that the achieved oxidation does depend on the ozone feeding concentration in their early reports. On the other hand, Catalkaya and Kargi (2007) did not find color and TOC removals to be affected by ozone feeding rate working with effluents from paper mills, although AOX removal increased at higher ozone feeding rates. In fact, according to Salokannel *et al.* (2007), purification results are not expected to be influenced by the feeding gas ozone concentration; they rather depend on the ozone dose that is applied to water, whereas the feeding gas ozone concentration and its mass transfer rate to the solution have a straight effect on the reaction time required to reach the desired ozone dose in water. Correspondingly, reaction rate is clearly dependent on ozone availability (Amat *et al.* 2004) and reaction time (Amat *et al.* 2003). Furthermore, in an enlightening work, Kreetachat *et al.* (2007) measured mass transfer to water when applying different ozone feeding rates, reporting that the volumetric mass transfer coefficient increases from 0.22 to 0.55 min^{-1} when the ozone feeding rate increases from 1 to 4 $L \cdot min^{-1}$, so the oxidation rate increases at a higher feeding rate because the driving force transferring ozone to the solution is greater.

Nevertheless, and as it has already been pointed out, ozone consumption rate will decrease during ozonation due to the progressive reaction with organic matter, so this decrease depends on the nature of the compounds present in the solution; that is, proportional to the amount of easily oxidized compounds (Fontanier *et al.* 2005b; Salokannel *et al.* 2007; Merayo *et al.* 2013). Finally, Bierbaum and Oeller (2009) implemented on-line control systems for the continuous ozonation treatment of

biologically treated effluents from recycled paper mills, showing that a controlled ozone production is useful and necessary, ensuring the stable operation of subsequent stages. Controlling ozone on-line provided a 20% cost saving per year, resulting in an 8 month investment return for this type of systems.

In general, wastewater composition in terms of COD, TOC, AOX, and pH is insufficient to foresee the optimum operation conditions of ozone treatment because they would not be equivalent in different types of water since the structures of the organic compounds present in each one also significantly determine its oxidation success. Therefore, it is recommended to perform systematic laboratory tests with the scope of meeting the required target purification values in each case (Oeller *et al.* 1997).

Finally, besides the actual industrial application of ozone oxidation for bleaching, this technology has also been included as a post-biological treatment alternative for the bio-recalcitrant organic load persisting in effluents of pulp and paper mills aiming to meet the quality standards for discharge (BREF 2013); which has already been addressed successful at large-scale application (Schmidt and Lange 2000). In addition, ozonation has also been successfully applied at an industrial scale to reuse paper mill effluents (Oeller and Offermanns 2002)

2.1. Ozone oxidation plus biological treatment

The oxidation by ozone as a standalone technology may actually be considered as unfeasible for pulp and paper mill effluents, not offering sufficient removal and mineralization of organics (Bijan and Mohseni 2008) due to their usually high volume and a potential high content of biodegradable compounds in the solution after first ozonation stages. Furthermore, the oxidation of these effluents by ozone implies implementing large reactors and an excessive energy consumption; which may partially

be overcome, even making ozonation economically feasible, using ozone oxidation to achieve the partial oxidation of the organic load enhancing the biodegradability of pulp and paper mill effluents (Alvares *et al.* 2001; Baig and Liechti 2001; Bijan and Mohseni 2004; Bijan and Mohseni 2005; Bijan and Mohseni 2008; Helble *et al.* 1999; Nakamura *et al.* 2004).

In fact, Bijan and Mohseni (2005) reported that whether a standalone biological or ozone treatment can reduce a 30% of the TOC mineralizing compounds of different nature, their combination improved TOC removal about a 20%. Considering all together the results found in the literature regarding the application of AOPs to pre or post biologically treated pulp and paper mill wastewater, an average 20-25% COD removal enhancement is also addressed (Figure 3). Although biological post-treatment was more effective, differences to biological pre-AOP treatment were not statistically significant.

Other very interesting treatment alternative would consider first applying a biological or membrane treatment to separate the HMW fraction; therefore, the unnecessary oxidation of the LMW organic fraction is avoided. The concentrate from the membranes or the effluents from the biological treatment might then be ozonized, after which its biodegradability would be expected to improve highly back. Finally, a consequent more efficient second bio-treatment stage would be performed aiming to remove turbidity, color and COD (Bijan and Mohseni 2008; Manttari *et al.* 2008; Schlichter *et al.* 2003). Both combinations, Bio-O_3-Bio and NF-O_3-Bio, have been reported to result in similar final wastewater quality and ozone demand (Bijan and Mohseni 2008), that is, ≈40-50% mineralization, ≈60% COD removal, and an 80% color removal (Table 2); being ozone consumption 10 times lower than when ozonation without complementary pre- and post-treatments were performed. A more selective

oxidation of HMW compounds and a more effective utilization of ozone were mainly addressed to drive such better results (Bijan and Mohseni 2008).

Besides, comparing both pre-treatments under real conditions, it results that membranes would produce lower rejection water volumes, so the ozone contactor may be reduced about a 50% in industry because the HMW fraction stream just constitutes the 45% of the total effluent (Bijan and Mohseni 2008). On the other hand, whether the integrated treatment with MBR and ozonation, whether the Bio-O_3-Bio system, both provided a considerable increase in COD reduction (Gommers *et al.* 2007; Merayo *et al.* 2013), but ozone use in the second alternative was more efficient than in the first one because the MBR effluent was made of components that resulted more difficult to be chemically oxidized than in the case of using a continuous activated sludge (Gommers *et al.* 2007).

In addition, the use of bio-filters in combination with ozone has also been assessed, and results have shown that the combination of ozone with a subsequent bio-filter treatment required a lower amount of ozone to be supplied in the oxidation stage, as well as it would be ecologically preferable, reaching more than a 80% total COD removal (Helble *et al.* 1999; Mobius and Helble 2004). Moreover, the combination with a subsequent new ozonation stage (O_3+bio-filter+O_3+bio-filter) improved the removal of the COD in more than an extra 10% reducing the need of ozone, and therefore the cost of the overall treatment (Baig and Liechti 2001).

Finally, Balcioglu *et al.* (2007) considered improving algal treatment with ozone pre-treatment. Overall efficiency mainly resulted enhanced in terms of color removal, but also significantly in COD and UV_{280}. Furthermore, the resident time of algal treatment was reduced from 8 to 5 days.

2.2. Combination of ozone and H₂O₂ in an oxidation treatment (peroxone)

The combination of ozone and hydrogen peroxide (O_3/H_2O_2) has also been proposed as a promising alternative to remove refractory organic chemicals (Masten and Davies 1994). According to Gogate and Pandit (2004), and Mounteer *et al.* (2007), H_2O_2 produces faster ozone degradation. In fact, a millimolar concentration of HO_2^- (the conjugate base of H_2O_2) initiates the decomposition of ozone also producing hydroxyl radical much more rapidly than hydroxide ion does (Catalkaya and Kargi 2007) as it is described by the following reactions (Glaze 1987):

$$H_2O_2 + H_2O \rightarrow HO_2^- + H_3O^+ \tag{3}$$

$$HO_2^- + O_3 \rightarrow OH^\bullet + O_2^- + O_2 \tag{4}$$

In addition, ozone decomposition rate has been reported to increase at higher pH values because H_2O_2 dissociation into HO_2^- is favored (Catalkaya and Kargi 2007); so pH = 11 was addressed to be the most suitable value to perform this treatment. Besides, it may be more adequate to perform the treatment at the normal pH values of the effluents from basic pulp and paper mills because the benefits of raising the pH may not compensate the cost of implementing and managing the required pH control system (Salokannel *et al.* 2007).

Although this combination may theoretically be more efficient than standalone ozone, results within the pulp and paper industry (Tables 1 and 2) did not always address this improvement when H_2O_2 was added to enhance ozone treatment. Particularly, Sevimli (2005) and Balabaniç *et al.* (2012) reported a 20% COD removal improvement when this treatment combination was applied to effluents from a biologically treated corrugated board factory and a recycled paper mill. In turn, Ko *et al.* (2009) reported an increase of color removal, but no effect on the reduction of the COD, when they treated diluted weak black liquor from a hardwood kraft pulp mill. In

addition, Catalkaya and Kargi (2007) showed that peroxone treatment did not significantly improve the removal of both color and TOC (0.2% and 10%, respectively) from a biologically treated pulp mill effluent in comparison to the standalone use of ozone (Figure 2) adding 5 mM H_2O_2 at pH=11.

In fact, Mounteer et $al.$ (2007) reported that the ozone dose had a greater effect on BOD behavior and on removing COD than the peroxide dose; but, the presence of H_2O_2 nevertheless had some beneficial effect increasing the average oxidation state. Finally, Salokannel et $al.$ (2007) also reported that H_2O_2 did not add a noticeable effect on the removal of COD from a biologically treated effluent from a pulp and paper mill; probably because the reactions between molecular ozone and organic compounds competed with O_3/H_2O_2 reactions. Moreover, the improvement of biodegradability was also reported lower using O_3/H_2O_2 than standalone O_3 because the additional generation of radicals also degraded some biodegradable molecules.

According to these results, ozonation without the addition of H_2O_2 may also be considered a more reasonable treatment than the peroxone option from an economic point of view (Salokannel et $al.$ 2007); although taking into account those trials reporting a significant treatment enhancement, it may depend on the characteristics of each effluent. Therefore a singular cost analysis should support the choice in any case.

2.3. Ozone/UV

In this treatment combination, the supplied UV energy interacts with O_3 as described in the following reaction (Beltrán et $al.$ 1998; Esplugas et $al.$ 2002; Guittonneau et $al.$ 1990):

$$O_3 + H_2O \xrightarrow{h\nu} 2 \cdot OH\cdot + O_2 \tag{5}$$

But not all photo-assisted processes require the same light quality in terms of wavelength and energy to reach an optimal performance. Specifically, the direct photolysis of O_3 (and H_2O_2 as well) requires short-wavelength photons (<310 nm) (Hoffmann *et al.* 1995).

Particularly, the O_3/UV treatment combination showed a significant synergetic effect applied to starch degradation products. That is, COD removal increased from 3 to 24% when ozone treatment was photo-assisted at pH=6 (Amat *et al.* 2005b).In fact, these authors previously addressed that this synergetic treatment efficiency may only occur under acidic pH because ozone itself decomposes to OH· radicals under basic conditions, and irradiation would therefore be unnecessary (Amat *et al.* 2004). In addition, Ledakowicz *et al.* (2006) also reported that this treatment improved the removal of the COD from resin acids; results being particularly better at higher temperature (80 ºC).

Otherwise, non-significant differences in COD removal were addressed when this treatment was applied to actual pulp and paper industry effluents (Tables 1 and 2) due to its high turbidity; although the introduction of an ozone stream into the UV-photolysis system resulted in a significant improvement of both decolorization and dechlorination of paper mills effluents (Yeber *et al.* 1999b; Ledakowicz *et al.* 2006; Wang *et al.*).

In addition, O_3 consumption has been reported to be higher in the O_3/UV process than when O_3 was used standalone, resulting that a 90% additional O_3 was used to remove the COD (Oeller *et al.* 1997). Therefore, it was recommended to consider O_3 supply and UV radiation in any case and separately compare their results to its combination treatment in a single reactor chamber. In fact, Amat *et al.* (2005b) found a lower biodegradation improvement applying this treatment to an effluent from a

cardboard mill than when it was treated with standalone ozone alone because of its higher aggressiveness producing more oxidized compounds; whereas Mansilla *et al.* (1997) and Wang *et al.* (2005) found similar results for both treatments applied to effluents from kraft pulp industry and chlorophenols, respectively.

Disparate results may be explained in terms of differences in the nature of the organic compounds contained in the treated solution. Molecular ozone is hardly able to attack highly deactivated aromatic rings (i.e. sulfonic compounds; (Amat *et al.* 2004) or highly oxidized LMW aliphatic carboxylic acids when it is the predominating oxidizing agent without applying irradiation; but it decomposes to produce hydroxyl radical (OH·) when UV irradiation assists the process, which is a more powerful oxidation agent than ozone itself (Glaze *et al.* 1987). Therefore, more energy incises in the C-C bonds of organic molecules, which will be expected to be more easily oxidized. But for compounds that are actually more easily oxidizable, such as cinnamic acid derivatives (Amat *et al.* 1999; Miranda *et al.* 2001), the synergistic effect between ozone and UV light is very low because they have more activated aromatic rings exposed to degradation, so molecular ozone is already able to attack them as efficiently as OH· does, and adding UV irradiance to the treatment producing the decomposition of ozone into OH· shows a very limited effect (Amat *et al.* 2004).

2.4. Catalytic ozonation

In the application of this treatment, ozone may react according to two possible pathways, corresponding to a direct reaction and the catalyzed process itself. Catalytic ozonation mainly provides the same advantages than the conventional one, but it significantly enhances organic matter removal and requires a much lower ozone dose (Fontanier *et al.* 2005b). Particularly, surface catalysis (heterogeneous) involves five

consecutive steps which influence on the overall rate of the chemical conversion: (1) diffusion of the reagents towards the catalyst; (2) interaction of the reagents with the catalyst (adsorption); (3) reaction among the adsorbed reagents determining the products; (4) desorption of the products from the surface of the catalyst towards the medium; and (5) diffusion of the products away from the catalyst (Fontanier *et al.* 2006).

The almost complete mineralization of seven model compounds (phenol, chlorophenol, trichlorophenol, guaiacol, vanillin, catechol, and syringaldehyde) has been achieved using a catalyst containing cobalt as the active metal deposited on a mineral catalytic support (TOCCATAs-catalyzed ozonation; (Fontanier *et al.* 2005b), which are chemicals that have indeed also been reported to be easily oxidized by ozone. Furthermore, acetic acid resulted to be the most difficult final oxidation product to remove, such as it has also been addressed when applying Fenton, photo-Fenton, and electro-Fenton processes to solutions containing different chemical moieties (Hermosilla *et al.* 2009b).

In addition, this treatment produced higher TOC removal figures than direct ozonation when applied to different effluents from paper mills (Fontanier *et al.* 2006). Pilot-scale trials reported a maximum removal of the 74% of the TOC and the 72% of the COD applying this treatment to different effluents of pulp mills; as well as the transformation of high molecular weight compounds into lower molecular weight ones was also addressed. Furthermore, a strong difference between the results of the application of this treatment to biologically treated effluents coming from mills using virgin or recycled fibers was clearly shown in this essay. When a biologically treated effluent from a recycled paper mill was treated, lower removal efficiency was achieved

because the original wastewater composition was intrinsically more biodegradable (Table 2).

Another treatment alternative was proposed by Balcioglu *et al.* (2007) aiming to purify bleach effluents from a pulp mill using O_3 and granulated activated carbon (GAC) as catalyst. In this treatment, supplementary OH· radicals were formed thanks to the initiating role shown by activated carbon (Jans and Hoigne 1998). This system led to a COD removal improvement of the 23% with respect to direct ozonation; whereas it was just a 15% in comparison to standalone GAC. Higher AOX and color removals were also achieved. In addition, better COD and color removals were also reported treating diluted weak black liquor from a kraft pulp mill with ozone in the presence of activated carbon (Ko *et al.* 2009). This enhancement was primarily attributed to the regeneration of occupied sites on activated carbon. Moreover, the degradation of high molecular weight compounds was also reported higher than for simple ozonation (Balcioglu *et al.* 2007). Although both processes, ozonation and catalyzed ozonation, enhanced toxicity removal, the treatment of bleach effluents combining O_3 and GAC significantly reduced the reaction time that was required to produce a non-toxic effluent. In fact, oxidation is more aggressive in catalyzed ozonation treatments than in standalone ozonation, so more oxidized compounds can be formed as treatment time runs on, and these may increase the toxicity of the effluent (Balcioglu *et al.* 2007).

In addition, the homogeneous catalytic ozonation of bleaching wastewater from a kraft pulp and paper mill increased COD removal up to about a 50-55% by the addition of 5 mM Fe^{2+} or Mn^{2+}; whereas it just resulted a 25% using standalone ozone (Balcioglu and Moral 2008). On the other hand, the treatment of the same wastewater with ozone combined with GAC resulted in a 63% COD removal (Table 2).

Finally, Mansilla *et al.* (1997) reported the capacity of the electron withdrawing ability of ozone to promote the generation of holes onto a catalyst surface. They applied an ozone photocatalytic treatment to effluents from a kraft pulp mill using ZnO as catalyst, achieving a 30% COD removal improvement in comparison to the application of standalone ozone. Complementarily, Yeber *et al.* (1999) reported that chloride ions were released to the solution, reaching maximum presence values after one minute of reaction time, when the treatment was performed with TiO_2; whereas for an O_3/UV/ZnO system, they reported this maximum chloride content after 15 minutes, thus showing a much slower efficiency on removing organochloride compounds.

3. UV Processes

An UV process is based on supplying energy to chemical compounds as radiation, which is absorbed by reactant molecules that are promoted to excited states and may further promote new reactions along treatment (Esplugas *et al.* 2002; Legrini *et al.* 1993). In general, UV alone is not considered as an effective treatment when applied standalone in comparison to other AOPs (e.g. ozone (Amat *et al.* 2005b) or TiO_2/UV (Chang *et al.* 2004) (Table 3); although it may be more effective when combined with H_2O_2 (Ahmed *et al.* 2009), salts of particular metals (Fe), or ozone (see tables 2 and 3). Nevertheless, Catalkaya and Kargi (2007) determined that its best treatment efficiency would be achieved at pH = 3 when it is going to be applied to biologically pre-treated effluents from wood industry.

In particular, it has been demonstrated that radiation with a wavelength lower than 400 nm is able to photolize H_2O_2 molecules (Esplugas *et al.* 2002; Legrini *et al.* 1993). As a result, the addition of H_2O_2 to an UV treating system has been reported to significantly improve both color and TOC removals in comparison to a standalone UV

treatment; even when low H_2O_2 concentrations were supplied (Catalkaya and Kargi 2007). On the other hand, Wang *et al.* (2004) assessed potential dechlorination of a bleaching kraft pulp mill effluent, finally reporting that the applied UV treatment did not achieve any significant removal (nor even color); and although the addition of H_2O_2 led to the removal of color, dechlorination did not further result improved. In addition, several authors have addressed the improvement of the process when it was performed at a basic pH, better if close to 11 (Ahmed *et al.* 2009; Catalkaya and Kargi 2007; Prat *et al.* 1988).

Nonetheless, even though COD and color reductions are improved in comparison to when H_2O_2 is used alone (Ahmed *et al.* 2009; Prat *et al.* 1988), the application of an H_2O_2/UV system is not generally economically competitive to other alternative processes because the achieved treatment improvement does not compensate the cost of implementing such technology (Prat *et al.* 1988). Particularly, although the color removal that would be achieved by the mere addition of H_2O_2 may be acceptable ($\approx$30%) (Catalkaya and Kargi 2007; Joss *et al.* 2007), it has not enough power to induce COD and TOC removals (<5%; (Catalkaya and Kargi 2007; Joss *et al.* 2007; Pérez *et al.* 2001), as it is reported in table 3.

4. Semi-conductor photocatalytic processes

These treatments imply the irradiation of a semiconductor (e.g. TiO_2, ZnO) with UV light at a wavelength shorter than 390 nm (Hoffmann *et al.* 1995; Yeber *et al.* 2000). The photoexcitation that is produced by UV light with an energy greater than the band gap is able to promote an electron from the valence band to the conduction band creating an electronic vacancy or "hole" (h^+) at the valence band edge; a process that can be simply represented by equation (6) for TiO_2, the most widely used

semiconductor material in these processes (Antunes *et al.* 2004; Fujishim and Honda 1972).

$$TiO_2 \xrightarrow{2\ hv} TiO_2\ (2e^-, 2p^+) \tag{6}$$

In order to perform a productive photocatalysis, electron-hole pair recombination must be suppressed (Antunes *et al.* 2004), which may be achieved by trapping either the photogenerated electron or the corresponding hole. Since the position of the valence band is very high for TiO_2 (3.1 V/SCE) (Fox 1989), the photogenerated hole will be able to oxidize a wide variety of organic substrates (S) to the corresponding radical cations ($S^{\cdot+}$), as it is expressed in the following equation (Antunes *et al.* 2004):

$$TiO_2(h^+) + S \rightarrow TiO_2 + S^{\cdot+} \tag{7}$$

On the other hand, the photogenerated electron may instead be trapped by suitable acceptors (electron scavengers), being O_2 the most widely used one, forming the superoxide radical anion $O_2^{\cdot-}$ (Antunes *et al.* 2004; Fox 1989), as described by the next reaction:

$$TiO_2(e^-) + A \rightarrow TiO_2 + A^{\cdot-} \tag{8}$$

It has been pointed out that TiO_2 is a more efficient catalyst than ZnO, respectively generating a 55% and a 31% TOC removals when mineralizing the organic matter of alkaline extractions from the bleaching sequence of a kraft pulp industry (Yeber *et al.* 2000) (Table 4). Better results with TiO_2 have also been reported by Kansal *et al.* (2008) treating acid effluents from a kraft/soda process that uses agricultural residues as raw material; whereas ZnO produced a higher COD removal in basic effluents. In addition, TiO_2 also resulted more efficient than ZnO when it was applied immobilized on glass (Yeber *et al.* 1999a). Finally, these essays also addressed that photocatalytic treatments performed with a supported catalyst resulted to be as efficient as when added in suspension. Although the supported type required longer

reaction time to produce the same results (Yeber *et al.* 1999a; Yeber *et al.* 2000), it also allows the possibility of performing the treatment under flow conditions, thus avoiding the annoying catalyst recovering step that is required when the catalyst is added in suspension (Yeber *et al.* 2000), which otherwise represents a good advantage to take into account.

Catalyst doping has also been proposed in several essays to improve the efficiency of the process. Particularly, Mansilla *et al.* (1994) reported the use of a ZnO catalyst doped with Ag or Pt. The first one showed little effect on color and COD removals, whereas the second one induced modifications in the kinetic profile of color reduction (Table 4). In addition, Gouvea *et al.* (2000) reported the semiconductor-assisted photochemical degradation of lignin, dye, and kraft effluent using an Ag-doped ZnO catalyst. Results addressed that lignin color progressively decreased up to a 50% after 15 minutes of treatment; whereas it was almost total (99%) after 60 minutes.

The efficiency of the TiO_2-photocatalytic process, and therefore the required reaction time to maximize it, are influenced by the dosage of TiO_2 itself (Chang *et al.* 2004; Tanaka *et al.* 1999); that is, the degradation of organics is improved until an excessive catalyst dosage causes a shadow effect interfering with the transmission of UV light so the generation of electron-hole pairs cannot effectively occur (Catalkaya and Kargi 2008; Chang *et al.* 2004). Particularly, an optimum dosage of 10 $g \cdot L^{-1}$ of TiO_2 has been reported for the treatment of lignin powder, resulting in the 50% reduction of the color within the first 10 minutes of reaction (Chang *et al.* 2004); whereas the removal efficiencies of both color and DOC reached about a 90% when the process was extended up to 960 minutes.

In addition, although Catalkaya and Kargi (2008) reported good removal figures of organics (i.e. 80% TOC removal) by applying this treatment at basic pH to a

biologically pretreated pulp and paper mill effluent, using 0.75 g·L^{-1} of TiO$_2$ at pH = 11 during 60 minutes (Table 4); working at a neutral pH produced better treatment efficiencies purifying effluents in a newsprint paper mill (Merayo *et al.* 2013), as well as it also yielded an almost complete decolorization of a kraft pulp mill effluent (Gouvea *et al.* 2000). A lower competition of anions and cations for the reactive sites of TiO$_2$ particles may be responsible for treatment improvement at neutral pH values. On the other hand, a 64% color removal was reported at pH = 7 for lignin decomposition, whereas a 99% was achieved at pH = 3 (Chang *et al.* 2004). Correspondingly, Boroski *et al.* (2008) and Rodrigues *et al.* (2008) also reported the highest efficiency of this process at pH = 3 (Table 4), which was attributed to the positive charge that TiO$_2$ surface acquire in acid solutions, which favors the adsorption of anionic compounds to be prioritized resulting in a great decolorization of the effluent (Yeber *et al.* 2007).

A rapid decrease of toxicity has also been reported for several effluents from the pulp and paper industry (Catalkaya and Kargi 2008; Chang *et al.* 2004; Pérez *et al.* 2001; Reyes *et al.* 1998; Yeber *et al.* 2000). Furthermore, COD was particularly reported to be very efficiently removed ($\approx$ 90%) from a bleaching effluent of a non-recovered paper mill by TiO$_2$ photocatalysis (Toor *et al.* 2007), and from an agro-residue-based soda bleaching effluent by both TiO$_2$ (COD removal $\approx$ 90%) and ZnO (COD removal $\approx$ 95%) photocatalytic treatments (Kansal *et al.* 2008) (Table 4). Virgin fiber was used in the pulping process, so its content in lignin, starch and resin acids surely contributed to a certain extent to these very successful results (Figure 1).

Finally, photocatalysis might be considered as an interesting alternative for pre- or post- biological treatment stages, as it has also previously been pointed out for ozonation (Merayo *et al.* 2013). For example, the relative quantity of HMW compounds considerably decreased (> 30%) in a kraft bleaching effluent that was subjected to

supported photocatalytic treatments producing a higher content of LMW species in the solution (Yeber *et al.* 2000). In fact, the application of photocatalysis as post-biological treatment achieved a 75% color removal in the treatment of black liquor, which is 15 times higher than the resulting decolorization after a standalone photochemical process; as well as mineralization was enhanced up to a 140% with respect to the previous biological stage (Moraes *et al.* 2007). In addition, a 45% mineralization enhancement was also reported in this essay for the pre-biological treatment of kraft effluent by photocatalysis (Moraes *et al.* 2006) (Table 4).

4.1. Solar Photocatalysis

This process is based on the use of sunlight to provide the UV radiation that is required to be absorbed by the catalyst to perform the treatment. For example, Amat *et al.* (2005a) assessed its application to the treatment of effluents from board industry (recycle fibers) reporting good COD removal percentages, that is, about a 40% at pre-industrial level and a 50% in laboratory trials (Table 4); as well as Kansal *et al.* (2008) addressed the solar photocatalytic treatment of bleaching effluent, reporting better results when using ZnO as catalyst than TiO_2, which is in contrast to the results previously reported using other UV light sources. Furthermore, the achieved chemical degradation resulted faster than when using other UV light sources.

Otherwise, Amat *et al.* (2005) reported that COD removal resulted lower than when applying a solar photo-Fenton treatment (Tables 4 and 5); which agrees with the essay performed by Gomathi and Kanmani (2006). In both essays, the degradation of organics was mainly driven towards the pollutants that are more reluctant to biological degradation. In addition, better results were addressed for derivatives from lignin than for non-aromatic compounds. That is, whereas the treatment of eugenol by solar

photocatalysis resulted in a 60% COD removal, a 30% was just reached treating guaiacol. Furthermore, 27% COD removal was addressed for *p*-toluenesulfonic acidic solutions; and only aliphatic LMW carboxylic acids (e.g. maleic, oxalic, and formic acids) were found as by-products of the process. Finally, the application of this treatment to acidic fractions resulting from starch degradation led to similar COD removal figures (≈ 20%) to those addressed by ozone/UV and photo-Fenton processes. As it has already been pointed out, these compounds are more reluctant to be treated by AOPs because of the inherent lower reactivity of C-C bonds in comparison to C=C ones (Amat *et al.* 2005a).

The combination of solar photocatalysis and biological treatment has also recently been assessed for effluents from chlorination and the alkaline extraction of soda pulp bleaching stages in an agro-residue-based pulp and paper mill using ZnO as catalyst (Dhir *et al.* 2012). In summary, this treatment achieved a 53% COD removal treating the chlorinated effluent, and a 43% when it was applied to the alkaline-extracted one; whereas the overall treatment efficiency reached a 92% COD removal when solar ZnO-photocatalysis was applied to the chlorinated effluent as the pre-treatment of a biological process, and it resulted 95% when it was combined as the post-treatment of the biological degradation of the alkaline extracted effluent (Table 4)

4.2. UV/TiO$_2$/H$_2$O$_2$

Several essays have considered the addition of hydrogen peroxide to the UV/TiO$_2$-photocatalytic treatment in order to assess the potential generation of hydroxyl radicals as an additional oxidizing agent. All these trials reported COD removal improvements in comparison to a regular UV/TiO$_2$ treatment (Catalkaya and Kargi 2008; Chang *et al.* 2004; Kumar *et al.* ; Muñoz *et al.* 2006; Pérez *et al.* 2001; Rodrigues *et al.* 2008),

particularly when performed at a pH value close to neutral. Two possible roles have been proposed for the action of H_2O_2 (Pérez *et al.* 2001): (a) being an alternative electron acceptor to oxygen at the conductance band, or (b) accepting electrons from the superoxide anion; as expressed by the following equations:

(a) $e^-_{CB} + H_2O_2 \rightarrow OH\cdot + OH^-$ (9)

(b) $O_2^{\bullet-} + H_2O_2 \rightarrow OH\cdot + OH^- + O_2$ (10)
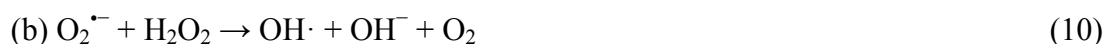
Particularly, this treatment led to a 50% COD removal after 6 h of irradiation when it was applied to an ECF effluent of a pulp mill, and a 50% TOC removal was finally achieved after 7 h of treatment (Pérez *et al.* 2001); Table 4). Therefore, COD removal can be mainly attributed to organic matter mineralization. On the other hand, Rodrigues *et al.* (2008) reported that the addition of H_2O_2 to an UV/TiO$_2$ treatment did not significantly improve degradation rate, but increased the velocity of the photo-process in the treatment of cellulose and paper industry effluents; although Boroski *et al.* (2008) did report a higher increase of the degradation results produced by the photocatalytic process adding H_2O_2 along the treatment of the same type of effluent (Table 4). In addition, the better performance of this treatment was also addressed by Kumar *et al.* (2011), who reported a 10% increase of the COD removal when H_2O_2 was added to the treatment of a non-recovered paper mill effluent by TiO$_2$-photocatalysis (Table 4).

Furthermore, Balcioglu *et al.* (2003) reported a 40% COD removal (Table 4) when treating kraft bleaching effluents by this treatment; as well as chloride release and an increase of the BOD$_5$/COD ratio were also addressed. Additionally, Catalkaya and Kargi (2008) achieved an 84% TOC removal applying this treatment to pre-biologically treated effluents from the pulp and paper industry (Table 4); and Mounteer *et al.* (2007) further reported the increase of organic matter content in the treated effluent after

performing this type of treatment, which might have been caused by colloidal matter solubilization during the oxidative process. In short, about an average 10% COD removal enhancement could be expected when the photocatalytic treatment of pulp and paper mill effluents is assisted by the addition of H_2O_2 (Figure 2).

4.3. UV/TiO$_2$/O$_2$

In this aeroxide process, oxygen is used as an efficient electron trap preventing electrons to return back to photo-generated holes. Mansilla *et al.* (1997) addressed the application of this treatment to effluents from kraft pulp industry reporting a 50% COD removal; whereas Yeber *et al.* (1999b) assessed a 50% toxicity abatement in cellulose mill effluents from bleaching sequences (Table 4). In addition, this essay also showed a slight better treatment efficiency when TiO_2 was used as catalyst in the O_2-assisted photocatalytic treatment of these effluents in comparison to using ZnO as catalyst, or in combination with O_3 (Tables 2 and 4). In fact, better mineralization rates were obtained using TiO_2 photocatalytic systems rather than applying ZnO catalyzed ones.

Furthermore, Yeber *et al.* (2007) reported the removal of 70% of the COD, 50% TOC, 94% color, and 50% toxicity, when applying this treatment to effluents from the first extraction step of ECF bleaching pulp (Table 4). Finally, applying either UV/TiO$_2$/O$_2$ or UV/ZnO/O$_2$ processes to an effluent from a bleaching sequence, Yeber *et al.* (1999b) also reported the release of chloride ions to the solution, which maximum content was detected after five minutes of treatment.

4.4. UV/TiO$_2$/Cu (II)

Biodegradation efficiency might also be improved using metallic ions as electron acceptors, as proposed by Yeber *et al.* (2007) in the same essay the aeroxide treatment

just described was also assessed. In short, it was confirmed that copper (II) efficiently acted as an electron acceptor when photocatalytic treatment was applied to an ECF bleaching pulp effluent to which this metallic ion was added. Therefore, this should be considered a very interesting treatment alternative for effluents that are contaminated with both organic matter and metal ions because the use of additional oxygen is avoided (Yeber *et al.* 2007). The removal of 70% of the COD, 50% TOC, and 50% toxicity was also achieved performing this photocatalytic treatment type (Table 4).

5. Fenton processes

Fenton process is based on the electron transfer between H_2O_2 and Fe^{2+}, which acts as an homogenous catalyst, to produce hydroxyl radical (OH·), which is able to powerfully degrade organic compounds, as it is expressed by the following equation (Harber and Weiss 1934):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH· \qquad\qquad K_1 = 70.0\ M^{-1}·s^{-1} \qquad (11)$$

The highly reactive hydroxyl radical that is produced along the Fenton process initiate the oxidative destruction of organic substances typically present in wastewater according to equations 1 and 2 (Huang *et al.* 1993). The iron cycle implying Fe^{2+} and Fe^{3+} forms plays the catalyst role according to the following reactions (Pignatello *et al.* 2006):

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO·_2 + H^+ \qquad\qquad K_2 <<< K_1 \qquad (12)$$

$$H_2O_2 + OH· \rightarrow HO·_2 + H_2O \qquad\qquad K_3 = 3.3·10^7\ M^{-1}·s^{-1} \qquad (13)$$

$$Fe^{2+} + OH· \rightarrow Fe^{3+} + OH^- \qquad\qquad K_4 = 3.2·10^8\ M^{-1}·s^{-1} \qquad (14)$$

$$Fe^{3+} + HO·_2 \rightarrow Fe^{2+} + O_2H^+ \qquad\qquad K_5 < 2.0·10^3\ M^{-1}·s^{-1} \qquad (15)$$

$$Fe^{2+} + HO·_2 + H^+ \rightarrow Fe^{3+} + H_2O_2 \qquad\qquad K_6 = 1.20·10^6\ M^{-1}·s^{-1} \qquad (16)$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \qquad\qquad K_7 = 8.3 \cdot 10^5 \ M^{-1} \cdot s^{-1} \qquad (17)$$

$$HO_2^{\cdot} + H_2O_2 \rightarrow OH^{\cdot} + H_2O + O_2 \qquad\qquad K_8 = 3.0 \ M^{-1} \cdot s^{-1} \qquad (18)$$

Although it has been addressed that the optimal pH value to perform this treatment is about 3.0 (e.g. Tambosi *et al.* 2006; Kazmi and Thul 2007) it has also been indicated that it was really better performed at a pH value ranging from 5.0 to 6.0 due to the final coagulation of iron hydroxides, which further favors COD and color removals (Catalkaya and Kargi 2007; Tambosi *et al.* 2006). In fact, performing this treatment at more basic initial pH implies avoiding pH-control operation and cost, and the process itself tends to produce acids that lower the pH to more efficient acidic values anyway. Regarding this chance, good treatment efficiencies have already been addressed performing this treatment under natural initial neutral pH conditions (Hermosilla *et al.* 2012), although the best removal results were always achieved at pH = 2.8.

In general, Fenton processes have produced better overall results treating pulp and paper mill effluents than other AOPs-based treatment technologies (Figure 2). Particularly, a 95% COD removal was reported for the Fenton treatment of synthetic black liquor wastewater optimizing the treatment by central composite experimental design (Torrades *et al.* 2011). Similarly, the treatment of reverse osmosis concentrate flowing out a specific pilot treatment train implemented in a recycled paper mill, consisting of anaerobic and aerobic biological stages followed by ultrafiltration and reverse osmosis membrane treatments, was also tested and optimized by surface response methodology by Hermosilla *et al.* (2012), and an 80% COD removal was achieved at the best resulting treatment conditions (Table 5).

In addition, Sevimli (2005) reported that color was effectively eliminated by this treatment method from pulp industry effluents that were biologically pre-treated; as well as it was proven the superiority of this process to more effectively remove refractory

organics (COD removal = 83%; Table 5) than O_3 (COD removal = 43%; Table 1) and O_3/H_2O_2 (COD removal = 64%; Table 2) processes. In addition, it is also a more economic AOPs-based treatment alternative (Hermosilla *et al.* 2012). Correspondingly, Catalkaya and Kargi (2007) reported the removal of an 85% of the color and an 88% of the TOC; whereas Kazmi and Thul (2007) achieved a 98% color removal and a 62% COD reduction; both applying Fenton treatment to biologically pre-treated pulp and paper mill effluents (Table 5).

Nevertheless, despite this treatment process is generally more oxidative than other alternatives non-considering the assistance of radiation as well, Amat *et al.* (2005a) only addressed a 3% COD removal for the treatment of acid fractions from starch degradation, which was attributed to the inherent organic structure of these compounds. Furthermore, Pirkanniemi *et al.* (2007) tested Fenton treatment for the particular removal of EDTA from ECF bleaching effluent, concluding that it could be used as an effective pre-treatment prior to its biological treatment.

Finally, Tambosi *et al.* (2006) assessed the applicability of a so-called Fenton-like reaction, consisting in initiating the Fenton process with Fe (III) instead of Fe (II), to treat a paper mill wastewater. Maximum COD removals ranging from 30 to 50% were reported depending on the supplied hydrogen peroxide and Fe^{3+} dosages, and nearly 100% of color and aromatic compounds were removed as well (Table 5). Despite addressing these good results, the partially oxidized composition of the treated wastewater showed a higher acute toxicity to *Artemia salina* than the untreated effluent.
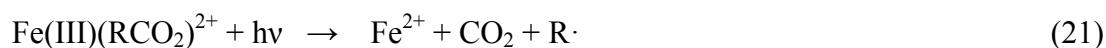
5.1. Photo-Fenton

The use of UV light in combination with Fenton's reagent, that is, the so-called photo-Fenton process, is able to re-generate ferrous iron reducing ferric ions and producing

additional hydroxyl radical content by photolysis according to the following equation (Faust and Hoigne 1990; Kavitha and Palanivelu 2004; Kim and Vogelpohl 1998):

$$Fe(III)OH^{2+} + h\nu \rightarrow Fe^{2+} + OH\cdot \tag{20}$$

Besides, the photo-decarboxylation of ferric carboxylates is also produced as expressed by the following equations (Kavitha and Palanivelu 2004; Safarzadeh-Amiri *et al.* 1996):

$$Fe(III)(RCO_2)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R\cdot \tag{21}$$

$$R\cdot + O_2 \rightarrow RO\cdot_2 \rightarrow Products \tag{22}$$

As a result, the amount of catalytic iron that would be required to produce the same treatment results, and the volume of sludge consequently generated, could be strongly reduced; as well as some additional organic compounds (carboxylates) that are very difficult to treat by AOPs may otherwise be effectively treated by this methodology (Hermosilla *et al.* 2009a; Hermosilla *et al.* 2009b). Consequently, the photo-Fenton alternative has generally been shown to be more efficient in the degradation of effluent components than its dark version (Karimi *et al.* 2010), and improves both the total quantity and the rate of TOC abatement in comparison to the UV/H_2O_2 system (Catalkaya and Kargi 2007; Hermosilla *et al.* 2009b; Hermosilla *et al.* 2012).

Considering those factors affecting the process, the influence of irradiation wavelength on the treatment depends on the catalyst that would be used. Whereas photons with a wavelength close to 400 nm are required to successfully perform a standard photo-Fenton process using ferrous iron as catalyst; the absorption of photons is preferred at 550 nm in Fenton-like processes that are based on Fe(III)/H_2O_2 mixtures (Pignatello *et al.* 1999; Sun and Pignatello 1993).

In addition, the temperature dependence of this process has also been assessed addressing the result of an improved reaction rate when temperature was raised from 25 to 40 ºC (Pérez *et al.* 2002b). Therefore, temperature seems to be assisting alternative ways of H_2O_2 cleavage, OH· formation, or Fe (II) recovery. On the other hand, the same persistent organic fraction (TOC = 50 ppm) remained in solution from 40 to 70 ºC; and bubbling O_2 through the solutions neither improved the results of this treatment (Pérez *et al.* 2002b).

Furthermore, although Catalkaya and Kargi (2007) considered an initial pH=5-6 to be better to perform Fenton treatment in wastewater from pulp and paper industry, and that Zahrim *et al*. (2007) only found slight differences performing the treatment at initial pH values between 3 and 5, it is important highlighting negligible amounts of iron hydroxides are expected to be generated in a photo-Fenton process, and pH will always evolve towards the optimal more acid value along the process (e.g. Tambosi *et al.* 2006). In fact, faster TOC removal rates have been shown at pH=2.8 (Hermosilla *et al.* 2009a; Pérez *et al.* 2002b). Besides, either a strong acidic media (pH=1.5), or under neutral-basic conditions (pH=8), slowed down the process mainly because of the instability that hydrogen peroxide and iron species showed in the solution (Hermosilla *et al.* 2012).

And finally, it is important to take into account in processes that involve both iron presence and UV light irradiation that the quantum yield of light absorption by Fe(III) directly depends on the specific absorbing iron species. $Fe(OH)^{2+}(H_2O)_5$ is the predominant species at pH=2-3, and it holds one of the largest light absorption coefficients and quantum yields for OH· production along with Fe (II) regeneration, ranging from 280 to 370 nm (Benkelberg and Warneck 1995; Pérez *et al.* 2002b).

Regarding the particular performance of this treatment within the paper industry, the removal of 85% of the TOC, 82% color, and 93% AOX content was achieved (Table 5) adding 50 mM of H_2O_2 and 2.5 mM of Fe(II) and applying 5 minutes of UV irradiation to a pulp mill effluent (Catalkaya and Kargi 2007). In addition, Pérez *et al.* (2002) reported a TOC reduction of about 60%, and the total removal of LMW chlorinated compounds (Table 5), after 30 min of UV irradiation assisting a Fenton treatment of 450 ppm of Fe(II) and 7500 ppm of H_2O_2 being applied to purify an effluent from the chlorinated step of the bleaching sequence of a kraft pulp mill.

Complementarily, Justino *et al.* (2011) assessed the assistance of the photo-Fenton treatment with fungi (*Rhizopus oryzae* and *Pleurotus sajor caju*), and an enzyme (laccase) aiming to remove individual phenols from a bleached kraft pulp and paper mill final effluent that had previously undergone secondary treatment. The complete removal of phenols was addressed when *Rhizopus oryzae* and photo-Fenton oxidation were combined (Table 5) whereas with *P. sajor caju* and laccase just achieved a 60-85% removal. In line with these results, Hermosilla *et al.* (2012) also reported the photo-Fenton treatment as being able to totally remove the organic load present in the concentrate from a reverse osmosis installed in a recycled paper mill (Table 5).

Finally, ultrasonic irradiation and a Fenton-like treatment just provided a 12% COD removal when they were applied to bleaching effluents from pulp and paper mills (Table 5); and although the photo-Fenton oxidation treatment using Fe (III) degraded up to the 84-93% of some model compounds of wood extractives, it only reached to removed 20% of the COD after 30 minutes of treatment (Eskelinen *et al.* 2010). These poor results removing COD were probably caused by the inherent neutral pH value that is characteristic of this wastewater (pH=6.9), which has recently been reported as non-

optimal to perform this process, and it has also been proved to be of greater relevance than for performing dark Fenton (Hermosilla *et al.* 2012).

6.2. Solar photo-Fenton

Photo-Fenton processes can alternatively be driven by low-energy photons in the visible range of the spectrum (Pérez *et al.* 2002b; Safarzadeh-Amiri *et al.* 1996). As a result, photo-Fenton processes may be implemented at a significantly reduced cost when performed using solar irradiation (Pérez *et al.* 2002b). As it has already been pointed out, the optimal treatment would be performed at pH=2.8, which is related to iron speciation in the solution (Hermosilla *et al.* 2009b; Pérez *et al.* 2002a; Torrades *et al.* 2003). Besides, a good TOC removal (> 60%) has also been achieved treating bleaching effluent at an initial pH value of 6, adding the advantage of avoiding the extra operation and cost associated to initial pH adjustment (Xu *et al.* 2007); as well as better treatment results were reported at 50ºC than at a lower treatment temperature in this essay. Correspondingly, Torrades *et al.* (2003) also reported a 35% TOC removal increase when solar photo-Fenton treatment was applied to a kraft pulp mill effluent at a right temperature interval ranging from 30 to 45-60 ºC.

In particular, approximately a 60 and a 30% COD removals were obtained applying this treatment to solutions containing eugenol and guaiacol (lignin derivatives), respectively (Amat *et al.* 2005a). These authors also effectively treated *p*-toluenesulfonic solutions by solar photo Fenton, achieving a 47% degradation of this compound. In addition, a 40% of the residual sulphur was determined as sulphate, that is, the final solution enhanced its biodegradability. Furthermore, they reported a 24% COD removal after 7 hours of solar irradiation in the treatment of a simulation of the acidic fraction from starch degradation (sodium acetate 2.5 g·L^{-1}, sodium butyrate 2.5

g·L^{-1} and glucose 2.5 g·L^{-1}); whereas only a 3% COD removal was achieved by the dark process.

Considering the specific application of solar photo-Fenton to pulp and paper effluents (Table 5), Torrades *et al.* (2003) particularly addressed a 60% TOC removal and the total elimination of LMW chlorinated compounds that were initially present in kraft bleaching effluents applying 30 min of irradiation using 450 ppm of Fe(II) and 7500 ppm of H_2O_2. Moreover, Xu *et al.* (2007) also reported an almost 70% TOC removal when treating a recycled pulp and paper mill effluent by solar photo-Fenton for 3 hours. Additionally, Amat *et al.* (2005) achieved a 23-50% COD removal in board industry effluents (recycled fibers) depending on the composition of the sample, which better explained the reported differences in wastewater treatment efficiency rather than concentration.

Finally, very good particular COD removal results (90% after a 2h-process) have been reported in the treatment of biologically pre-treated pulp and paper mill wastewater. This improvement may be attributed to the previous removal of biodegradable material in the biological stages of the treatment train; whereas directly treating the raw wastewater mixture of contaminants would have reduced the efficiency of the solar photo-Fenton process because certain oxidative power would have been lost trying to degrade biodegradable, but recalcitrant to oxidation, organic compounds.

6. Electro-oxidation processes

Electrochemical oxidation is based on the direct degradation of organic compounds on the electrodes, the generation of hydroxyl and other oxidative radicals by wastewater electrolysis, and the action of other by-products generated during the process. Current density applied during treatment, electrode material, reaction time, and the

characteristics of the wastewater to be treated are the main factors affecting this treatment process. Perng *et al.* (2008) particularly assessed the influence of pH reporting better results at higher values; that is, the treatment at pH = 9 (hydraulic retention time = 57 s, electrode gap = 15 mm, and current density = 287 A·m^{-2}) of an effluent from a paper mill producing corrugating medium resulted in a 28% COD removal and a 94% color removal (Table 5).

In particular, the electro-oxidation treatment of kraft bagasse bleaching effluent applying a current density of 0.87 A·dm^{-2} during 1.75 h reported a 53% COD removal (Antony and Natesan 2012); whereas a 63% reduction of the COD was achieved in a cellulose pulp mill effluent that was treated applying 22.5 A·dm^{-2} during 180 minutes (Buzzini *et al.* 2006) (Table 5).

Furthermore, the combination of electro-oxidation with a post-biological treatment stage of the same kraft bagasse bleaching effluent increased the overall COD removal up to an 87% (Antony and Natesan 2012). The synergistic effect of these combined treatments was attributed to the produced increase of the biodegradability of the effluent after the electro-oxidation step. Moreover, the combination of electro-coagulation (1 A·dm^2 during 34.4 minutes), electro-oxidation (1.5 A·dm^2 during 90.5 minutes), and biological process (521 minutes) applied to the same wastewater addressed a 95% COD removal; and the operating cost resulted lower indeed (Antony and Natesan 2012).

In addition, the treatment of model compounds from the paper industry even addressed better results. For example, the electrochemical oxidation of lignosulfonate achieved an 80% TOC removal (Domínguez-Ramos *et al.* 2008). Moreover, the treatment of lignin obtained from Saiccor's acid bisulphite-based pulping process

resulted in the production of vanillin, which would be a byproduct of interesting commercial value (Moodley *et al.* 2011).

Finally, the combination of Fenton process with electrochemical oxidation (namely, electro-Fenton treatment) is a further interesting alternative. Its application to a biologically-treated newsprint paper industry effluent addressed a 95% color removal and a 90% COD reduction (Selvabharathi and Kanmani 2010) (Table 5). As previously reported for other Fenton processes, performing the treatment at higher pH values decreased the efficiency because of the precipitation of $Fe(OH)_3$ (Selvabharathi and Kanmani 2010).

7. Oxone^{TM} (Peroxymonosulfate salt; $2KHSO_5:KHSO_4:K_2SO_4$)

Joss *et al.* (2007) assessed the treatment performance of this commercial salt aiming decolorization of an alkaline stage effluent from a kraft pulp mill. Oxone^{TM} mainly resulted effective during the initial phases of the treatment. A 5 $g \cdot L^{-1}$ Oxone^{TM} treatment produced a 79% color removal, a 14% COD reduction, and a negligible TOC abatement (Table 5). The adjustment of the pH was not necessary because this salt performs treatment over a wide range of values.

8. A first approximation to the cost of AOPs applied to the treatment of pulp and paper mill effluents

Although AOPs are generally considered to be more expensive than conventional biological or physicochemical treatment alternatives that are more extensively used in paper mills, they have actually been assessed with success as an advanced treatment aiming to accomplish specific objectives that may not otherwise be achieved. The successful industrial implementation of these treatments depends on the fine selection of

the most economical operational conditions that allow the achievement of the treatment objective.

Several authors have already assessed the cost of AOPs at laboratory, pilot, or industrial scale, but there are not general available figures to consider because the cost of these treatments strongly depends on the selected AOP and each specific application. Particularly, Bierbaum *et al.* (2014) established the cost for the ozone treatment of biologically pre-treated paper mill effluents in 2.90 € per kg of removed COD, which in their particular case implied 0.2 €/m^3 (including an additional bio-filter). Moreover, they assessed that the additional use of H_2O_2 will increase the cost in an extra 0.2 €/m^3. Finally, the cost for a Fenton treatment aiming the removal of trace compounds in the same effluents was assessed in the range of 0.45 to 7.50 €/m^3 depending on chemicals use and sludge disposal; whereas the cost of an UV+H_2O_2 treatment was estimated in about 1 €/m^3.

Furthermore, it has been reported that the cost of ozonation in pulp and paper mills can be reduced from 0.23 to 0.14 \$/m^3 using an ozone system equipped with an on-line controlled ozone supply (Bierbaum and Öeller 2009). In addition, the higher operational cost of an ozone oxidation process can be significantly reduced from 4.5 to 2.34 M€/year implementing its combination with a subsequent bio-filtration stage (Karat 2013). Nevertheless, the industrial application of ozone requires a more accurate economic analysis because its overall cost may be significantly reduced operating at full scale and/or reusing the ozonized effluent within the mill (Bierbaum *et al.* 2014; Bierbaum *et al.* 2012; Öeller and Offermanns 2002).

Complementarily, the operational cost of several AOPs applied to degrade different compounds up to achieve an 85% COD removal was estimated in Cañizares *et al.* (2009). Although treatment cost depends on the considered compound, ozone was

assessed as much more expensive than electrochemical oxidation and Fenton process in all the cases. Considering the oxygen-equivalent chemical-oxidation capacity in order to properly compare these processes, Fenton's cost resulted to be 0.7-3.0 €/kg of equivalent O_2, whereas electrochemical oxidation addressed 2.4-4.0 €/kg of equivalent O_2, and ozonation raised its cost up to 8.5-10 €/kg of equivalent O_2. In fact, Fenton processes (photo-Fenton particularly) were also considered by Hermosilla *et al.* (2012) as the cheapest alternatives for the treatment of RO retentate from a paper mill.

In particular, the operational cost of different modifications of the photo-Fenton process was assessed by Durán *et al.* (2012) for the removal of 4.5 g of TOC from 1 m^3 of industrial wastewater. Solar photo-Fenton using ferrioxalate addressed the lowest operational cost (0.045 €/g TOC), whereas conventional photo-Fenton treatment resulted the most expensive one (0.31 €/g TOC). As a result, the operational cost of the solar photo-Fenton treatment of industrial wastewater was assessed in 3.6 to 6 €/m^3. The application of this treatment at industrial scale in pulp and paper mills still awaits further development and report.

In short, considering the estimated average operational cost of conventional treatment plants (0.45 €/m^3, ranging from 0.05 to 2.35 €/m^3; Jung *et al.* 2011) and actual treatment cost figures for the alternative use of AOPs, it results that the use of the latter may just be justified by targeting specific treatment objectives such as meeting very specific quality standards set by the legislation in force for discharge, the treatment of trace compounds, or the production of water of enough quality to be reused back in the mill again.

Conclusions

AOPs are a promising alternative to develop new treatment strategies in the paper industry aiming to either improve water reuse or fulfill the legislation in force regarding wastewater discharge. In fact, several AOPs-based treatment possibilities have already been assessed successful for pulp and paper industry wastewater at a laboratory scale in many cases. In particular, ozonation has received further attention due to the possibility of using already available facilities for this treatment in some mills previously devoting them for bleaching.

The composition of wastewater is one of the main factors affecting the final efficiency of the application of AOPs-based treatments to effluents from the pulp and paper industry; particularly resulting more efficient when lignin compounds are highly present in wastewater from virgin fiber mills.

Considering together all the results that have been reported for the application of AOPs to effluents of the pulp and paper industry it comes out that standalone ozonation achieved the worst treatment efficiency figures (COD removal $\approx$ 40%). Fenton processes addressed the best ones (COD removal $\approx$ 70%), and photocatalysis showed an intermediate performance (COD removal $\approx$ 50%).

Furthermore, it has especially been addressed that the combination of AOPs with biological stages generally enhances overall treatment efficiency and reduces its cost. Although differences were not assessed significant, using AOPs as a post-biological treatment has specifically been reported as a more efficient alternative.

In short, the use of AOPs within pulp and paper mills is conditioned by the nature of wastewater composition, the efficiency of the process itself, and its potential combination with other treatment technologies to newly implement, or already existing within the facilities of the mill; as well as the assessment of final economic figures.

Acknowledgments

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Table 1. Ozone oxidation treatment results for paper industry effluents.

Effluent type	Removal (%)	COD	TOC	Color	AOX	DBO5/COD improvement	Reference
Cardboard industry, recycled paper		38					(Amat *et al.* 2005b)
CEH bleaching effluent, wood		23		74	46	Yes	(Balcioglu *et al.* 2007)
Kraft bleach effluent, wood		25				Yes	(Balcioglu and Moral 2008)
Biologically treated		35				Yes	(Bierbaum *et al.* 2012)
Biologically treated		40					(Bierbaum *et al.* 2014)
Biologically treated, recycled		51					(Bierbaum and Oeller 2009)
Alkaline bleach effluent, wood				70		Yes	(Bijan and Mohseni 2004)
Kraft bleach effluent, wood		21	20	70		Yes	(Bijan and Mohseni 2005)
Kraft ECF effluent, wood		17	5			Yes	(Bijan and Mohseni 2008)
Biologically treated, wood			29	91	62		(Catalkaya and Kargi 2007)
Kraft effluent biologically treated, wood		22	15	86	44		(El-Din and Smith 2002)
Biologically treated, wood		97	[a]98	100			(Fontanier *et al.* 2005b)
Biologically treated, wood		52	39				(Fontanier *et al.* 2006)
Biologically treated, recycled		36	19				(Fontanier *et al.* 2006)
Biologically treated bleached sulphate pulp, wood		76	51				(Fontanier *et al.* 2006)
Biologically treated		40					(Gommers *et al.* 2007)
Final discharge		55					(Hostachy *et al.* 1997)
Kraft Eop effluent, wood		18	14	74		No	(Joss *et al.* 2007)
Kraft weak black liquor, hardwood		58		85			(Ko *et al.* 2009)
Wood			24	85			(Kreetachat *et al.* 2007)
Kraft bleach, wood		20		30		Yes	(Mansilla *et al.* 1997)
Biologically treated mechanical pulp mill and board mill effluent, mixture		20		65		Yes	(Manttari *et al.* 2008)
Alkaline bleach effluent, wood		16	0	62			(Medeiros *et al.* 2008)
Kraft E1 effluent, wood			5	27			(Moraes *et al.* 2006)
Diluted black liquor, wood			0	14			(Moraes *et al.* 2006)
Kraft bleach effluent, wood		4	7	8	10		(Morais *et al.* 2008)
Kraft bleach effluent, wood			[b]47				(Muñoz *et al.* 2006)
Biologically treated, recycled (75%) and wood (25%)		80	[b]47				(Oeller *et al.* 1997)
Partly biologically treated, recycled		20	[b]22				(Oeller *et al.* 1997)
Biologically treated, recycled		85	[b]31				(Oeller *et al.* 1997)
Biologically treated, wood		82	[b]64				(Oeller *et al.* 1997)
Biologically treated, recycled		53	[b]18				(Oeller *et al.* 1997)
Partly biologically treated, recycled		41	[b]18				(Oeller *et al.* 1997)
Biologically pretreated, wood		12	[b]9	50	25	Yes	(Salokannel *et al.* 2007)
Biologically pretreated, wood		18	[b]9	85	25	Yes	(Salokannel *et al.* 2007)
Biologically treated, recycled		43		91			(Sevimli 2005)
ECF bleach effluent, birch wood		40					(Tuhkanen *et al.* 1997)

ECF bleach effluent, pine wood	23		(Tuhkanen *et al.* 1997)
Kraft ECF effluent, wood		72	Yes	(Yeber *et al.* 1999b)
Newsprint, recycled	40		(Merayo *et al.* 2013)
Kraft effluent, wood	57		(Merayo *et al.* 2013)
Newsprint biologically treated, recycled	38		(Balabaniç *et al.* 2012)

[a] 31 % TOC removal due to precipitation.
[b] DOC

Table 2. The combination of ozone oxidation with other treatment technologies within the pulp and paper industry.

e	Treatment	Removal (%)	COD	TOC	Color	AOX	DBO$_5$/COD improvement	Refere
eated, woodfree	O$_3$+biofilter		53				Yes	(Baig and Lied
eated, woodfree	O$_3$+biofilter+O$_3$+biofilter		80				Yes	(Baig and Lied
g, wood	O$_3$ + algal		90		99	87		(Balcioglu et a
ch, wood	O$_3$ + Bio			50				(Bijan and Mol
	O$_3$ + Bio		57	40				(Bijan and Mol
	Bio + O$_3$ + Bio		58	50	80			(Bijan and Mol
	NF + O$_3$ + Bio		65	40	80			(Bijan and Mol
eated, woodfree	O$_3$+biofilter		81					(Helble et al. 1
eated, recycled	O$_3$+biofilter		57					(Helble et al. 1
cycled	Bio + O$_3$		90					(Merayo et al.
cycled	O$_3$ + Bio		81					(Merayo et al.
y, wood	O$_3$+biofilter		60					(Mobius and H
y, wood	O$_3$+biofilter+O$_3$+biofilter		85					(Mobius and H
	O$_3$ + Bio		58					(Yeber et al. 1
	O$_3$/UV + Bio		63					(Yeber et al. 1
	O$_3$/UV/TiO$_2$ + Bio		70					(Yeber et al. 1
	O$_3$/UV/ZnO + Bio		62					(Yeber et al. 1
logically treated, recycled	O$_3$/H$_2$O$_2$		59					(Balabaniç et a
eated, wood	O$_3$/H$_2$O$_2$			31	81	95		(Catalkaya and
ack liquor, hardwood	O$_3$/H$_2$O$_2$		50		90			(Ko et al. 2009
	O$_3$/H$_2$O$_2$		20	5	67		Yes	(Mounteer et a
eated, wood	O$_3$/H$_2$O$_2$		10		82	35	Yes	(Salokannel e
eated, paper mill	O$_3$/H$_2$O$_2$				90	35	Yes	(Salokannel e
eated, recycled	O$_3$/H$_2$O$_2$		64		97			(Sevimli 2005)
dustry, recycled paper	O$_3$/UV		42					(Amat et al. 20
nventional bleaching, wood	O$_3$/UV		20		40		Yes	(Mansilla et al.
effluent, wood	O$_3$/UV			[a]68				(Muñoz et al. 2
eated, 90% recycled, 10% TMP	O$_3$/UV		14	[a]5				(Oeller et al. 1
EPDD), wood	O$_3$/UV				72			(Wang et al. 20
	O$_3$/UV			76			Yes	(Yeber et al. 1
nventional bleaching, wood	O$_3$/UV/ZnO		52		40		Yes	(Mansilla et al.
EPDD), wood	O$_3$/UV/H$_2$O$_2$				76			(Wang et al. 20
	O$_3$/UV/ZnO		44	70			Yes	(Yeber et al. 1
	O$_3$/UV/TiO$_2$		51	72			Yes	(Yeber et al. 1
g, wood	O$_3$/Active carbon		46		87	80	Yes	(Balcioglu et a
effluent, wood	O$_3$/Active carbon		63				Yes	(Balcioglu and
effluent, wood	O$_3$/Fe^{2+}		52				Yes	(Balcioglu and
effluent, wood	O$_3$/Mn^{2+}		53				Yes	(Balcioglu and
eated, wood	Catalytic ozonation		84	84	100			(Fontanier et a
eated, wood	Catalytic O$_3$, continuous mode		75	61	95			(Fontanier et a
eated, wood	Catalytic ozonation		67	74				(Fontanier et a
eated, recycled	Catalytic ozonation		53	35				(Fontanier et a
eated, bleached sulphate pulp, wood	Catalytic ozonation		72	73				(Fontanier et a
ack liquor, hardwood	O$_3$/Active carbon		60		88			(Ko et al. 2009
ack liquor, hardwood	O$_3$/Active carbon/H$_2$O$_2$		65		95			(Ko et al. 2009

[a]DOC

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Table 3. Hydrogen peroxide and UV treatments applied to effluents from the pulp and paper industry.

	Treatment	Removal (%)	COD	TOC	Color	AOX	Reference
d paper mill, wood	H_2O_2		10				(Ahmed *et al.* 2009)
ally treated, wood	H_2O_2			5	24	34	(Catalkaya and Karg
p effluent, wood	H_2O_2		1	0	31		(Joss *et al.* 2007)
d paper mill, wood	UV		0.3				(Ahmed *et al.* 2009)
ally treated, wood	UV			4	7	17	(Catalkaya and Karg
EPDD) effluent, wood	UV				6		(Wang *et al.* 2004)
d paper mill, wood	UV/H_2O_2		92	90			(Ahmed *et al.* 2009)
ally treated, wood	UV/H_2O_2			11	41	19	(Catalkaya and Karg
ally treated, wood	UV/H_2O_2			45			(Catalkaya and Karg
F filtrate, wood	UV/H_2O_2		0	0	30		(Mounteer *et al.* 2007
ted-flocculated bleaching effluent, wood	UV/H_2O_2		37				(Rodrigues *et al.* 200
ch effluent, wood	UV/H_2O_2					100	(Ugurlu and Karaoglu
EPDD) effluent, wood	UV/H_2O_2				67		(Wang *et al.* 2004)

Table 4. Photocatalytic treatments application to effluents from the pulp and paper industry.

	Treatment	Removal (%)	COD	TOC	Color	AOX	DBO$_5$/COD improvement	Ref
cally treated, recycled	TiO$_2$/UV		39					(Balabaniç e
ed, wood	TiO$_2$/UV			80				(Catalkaya a
newsprint, recycled	TiO$_2$/UV		35	30				(Hermosilla e
n effluent, agricultural residual	TiO$_2$/UV		88					(Kansal et al
hill effluent, hardwood	TiO$_2$/UV		54		84			(Kumar et al.
ed	TiO$_2$/UV		20					(Merayo et a
ent, wood	TiO$_2$/UV			[a]15				(Muñoz et al
wood	TiO$_2$/UV		89					(Toor et al. 2
t, wood	TiO$_2$/UV		16			71		(Pérez et al.
ulated bleaching effluent, wood	TiO$_2$/UV		40					(Rodrigues e
ed soda bleaching effluent	ZnO/UV		55					(Dhir et al. 20
n effluent, agricultural residual	ZnO/UV		94					(Kansal et al
or, wood	ZnO/UV		57		80			(Mansilla et a
wood	ZnO/UV			15	54			(Moraes et a
or, wood	ZnO/UV			0	5			(Moraes et a
t, wood	TiO$_2$/UV/H$_2$O$_2$ supported				40			(Mounteer e
raction conventional bleaching,	TiO$_2$/UV/O$_2$ supported		58	55		90		(Yeber et al.
t, wood	TiO$_2$/UV/O$_2$ supported + Bio		70				Yes	(Yeber et al.
raction conventional bleaching,	TiO$_2$/UV supported		58	55		90		(Yeber et al.
raction conventional bleaching,	ZnO/UV supported		58	31		90		(Yeber et al.
raction conventional bleaching,	ZnO/UV/O$_2$ supported		58	31		90		(Yeber et al.
t, wood	ZnO/UV/O$_2$ supported		44				Yes	(Yeber et al.
or, wood	Pt-ZnO/UV		57		80			(Mansilla et a
od	Ag-ZnO/UV			15	99			(Gouvea et a
ed soda bleaching effluent	ZnO/solar UV + Bio		93	89				(Dhir et al. 20
ed soda bleaching effluent	Bio + ZnO/solar UV		86					(Dhir et al. 20
ed	Solar TiO$_2$ + Bio		83					(Merayo et a
ed	Bio + solar TiO$_2$		82					(Merayo et a
wood	ZnO/UV + Bio			62				(Moraes et a
or, wood	ZnO/UV + Bio			36				(Moraes et a
t, wood	ZnO/UV/O$_2$ + Bio		64					(Yeber et al.
ecycled	TiO$_2$/solar UV		40					(Amat et al. 2
ed effluent	TiO$_2$/solar UV		83					(Gomathi and
n effluent, agricultural residual	TiO$_2$/solar UV		61					(Kansal et al
ed soda bleaching effluent	ZnO/solar UV		53					(Dhir et al. 20
n effluent, agricultural residual	ZnO/solar UV		74					(Kansal et al
wood	TiO$_2$/UV/H$_2$O$_2$		40				Yes	(Balcioglu et
wood	TiO$_2$/UV/H$_2$O$_2$		51				Yes	(Balcioglu et
d-flotated bleaching effluent,	TiO$_2$/UV/H$_2$O$_2$		64				Yes	(Boroski et a
ed, wood	TiO$_2$/UV/H$_2$O$_2$			84				(Catalkaya a
hill effluent, hardwood	TiO$_2$/UV/H$_2$O$_2$		65		89			(Kumar et al.

Effluent	Treatment	COD	TOC	Color	AOX	Biodegradability	Reference
ent, wood	TiO₂/UV/H₂O₂		[a]22				(Muñoz et al...
t, wood	TiO₂/UV/H₂O₂	50	50	90			(Pérez et al...
ulated bleaching effluent, wood	TiO₂/UV/H₂O₂	55					(Rodrigues e...
ent, wood	TiO₂/UV/H₂O₂			91			(Ugurlu and...
raction conventional bleaching,	TiO₂/UV/O₂	50			40	Yes	(Mansilla et a...
t, wood	TiO₂/UV/O₂	53	72			Yes	(Yeber et al...
t, wood	TiO₂/UV/O₂ + Bio	67					(Yeber et al...
on effluent ECF, wood	TiO₂/UV/O₂	70	50	94		Yes	(Yeber et al...
raction conventional bleaching,	ZnO/UV/O₂	57			42	Yes	(Mansilla et a...
t, wood	ZnO/UV/O₂	51	70			Yes	(Yeber et al...
on effluent ECF, wood	TiO₂/UV/Cu	70		94		Yes	(Yeber et al...

[a] DOC

Table 5. Fenton processes and Oxone™ treatment results for effluents from the pulp and paper industry.

	Treatment	Removal (%)	COD	TOC	Color	AOX	Phenols	Reference
cally treated, recycled	Fenton		75					(Balabaniç et al. 20...
ed, wood	Fenton			88	85	89		(Catalkaya and Kar...
newsprint, recycled	Fenton		80					(Hermosilla et al. 2...
pulp effluent, wood	Fenton				20			(Karimi et al. 2010)
o effluent, wood	Fenton				62			(Karimi et al. 2010)
ed, pulp and paper mill	Fenton		62		98			(Kazmi and Thul 20...
step, wood	Fenton			40	>90			(Pérez et al. 2002b...
ed, recycled	Fenton		83		95			(Sevimli 2005)
paper mill	Fenton-like		50		100			(Tambosi et al. 200...
paper mill	Fenton-like pilot scale		52	90	98			(Tambosi et al. 200...
ed, wood	photo-Fenton			85	82	93		(Catalkaya and Kar...
wood	photo-Fenton		20					(Eskelinen et al. 20...
newsprint, recycled	photo-Fenton		100					(Hermosilla et al. 2...
ed kraft ECF effluent, wood	photo-Fenton						100	(Justino et al. 2011...
pulp effluent, wood	photo-Fenton				41			(Karimi et al. 2010)
o effluent, wood	photo-Fenton				65			(Karimi et al. 2010)
ent, wood	photo-Fenton			[a]30				(Muñoz et al. 2006)
ent, wood	photo-Fenton		67		91			(Pereira et al. 2009...
ent, wood	photo-Fenton		85		81			(Pereira et al. 2009...
step, wood	photo-Fenton			60	>90			(Pérez et al. 2002b...
cally treated, recycled	photo-Fenton		96					(Balabaniç et al. 20...
ed, wood	Photo-Fenton		[b]87					(Zahrim et al. 2007...
wood	Fenton-like + ultrasonic		12					(Eskelinen et al. 20...
ent, wood	photo-Fenton/TiO₂			30				(Muñoz et al. 2006)
ecycled	solar photo-Fenton		50					(Amat et al. 2005a)
ed effluent	solar photo-Fenton		90					(Gomathi and Kanr...
ffluent (22% ClO₂ substitution),	solar photo-Fenton			60				(Torrades et al. 200...
t (H₂O₂), wood	solar photo-Fenton			70				(Xu et al. 2007)
eaching effluent	Electro-oxidation		53					(Antony and Natesa...
ed, cellulose	Electro-oxidation		63	38	96			(Buzzini et al. 2006...

um mill effluent, recycled	Electro-oxidation	28		94	(Perng *et al.* 2008)
eaching effluent	Electro-oxidation + bio	87			(Antony and Nates...)
eaching effluent	Electro-coagulation+ electro-oxidation+bio	95			(Antony and Nates...)
ed effluent	Electro-Fenton	90		95	(Selvabharathi and...)
t, wood	Oxone[TM c]	14	0	79	(Joss *et al.* 2007)

[a] DOC

[b] BOD_3

[c] Peroxymonosulfate salt

Figure 1. COD removal by AOPs in the pulp and paper industry considering the type of fiber (recycled or virgin fiber - wood), and comparison to the treatment of resin acids (resin), starch degradation products (starch), and lignin. Letters (a, b) identify different statistically significant groups by Tukey's test, P < 0.05).
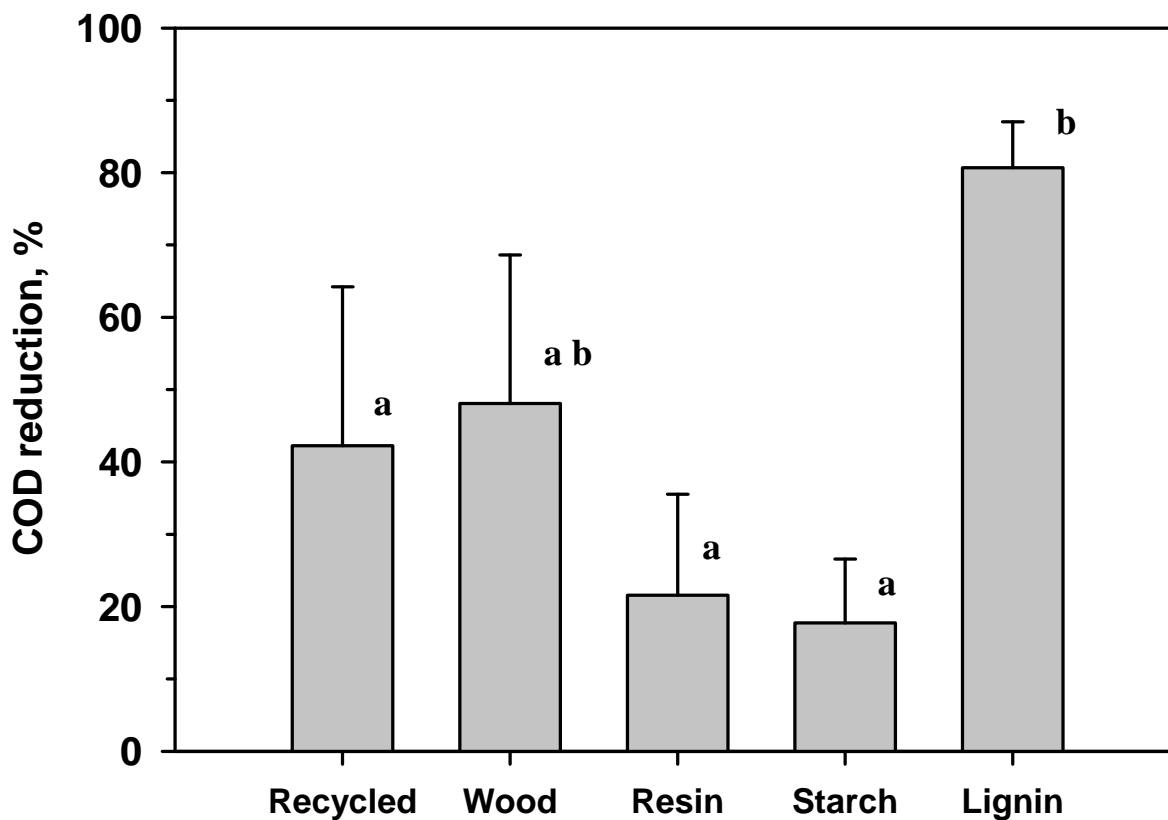
Figure 2. COD removal by AOPs in the pulp and paper industry (Ozone+ includes all treatment combinations with ozone. TiO_2+ includes non-supported $TiO_2/UV/H_2O_2$ treatments. Letters (a, b) label different statistically significant groups identified by Tukey's test, $P < 0.05$).
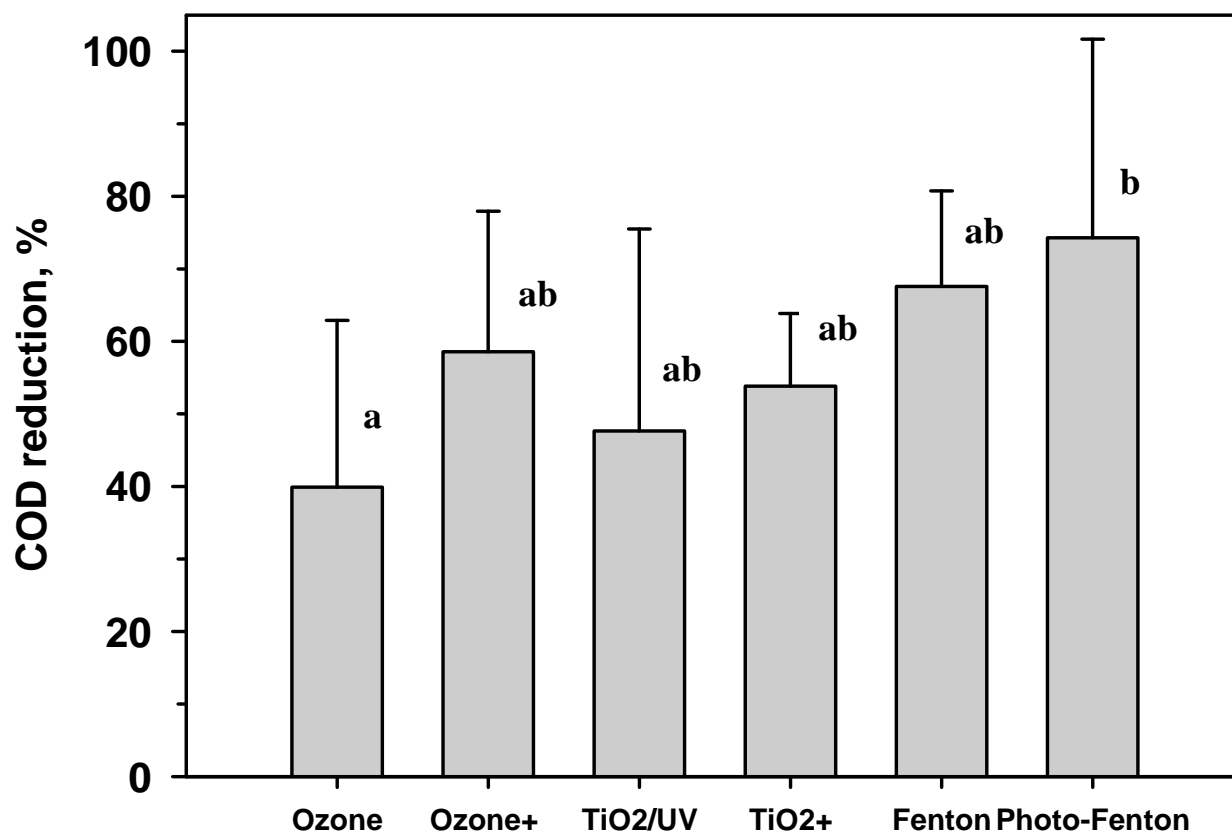
Figure 3. COD removal by AOPs combined with biological treatment (Letters (a,b) identify statistically significant groups by Tukey's test, $P < 0.05$).