

The application of advanced oxidation technologies to the treatment of effluents from the pulp and paper industry: a review

Daphne Hermosilla · Noemí Merayo · Antonio Gascó · Ángeles Blanco

Received: 8 May 2014 / Accepted: 24 August 2014 / Published online: 5 September 2014
© Springer-Verlag Berlin Heidelberg 2014

Abstract The paper industry is adopting zero liquid effluent technologies to reduce freshwater use and meet environmental regulations, which implies closure of water circuits and the progressive accumulation of pollutants that must be removed before water reuse and final wastewater discharge. The traditional water treatment technologies that are used in paper mills (such as dissolved 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 comprehensive 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 on 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 organic 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 \approx 65–75 %) at a lab scale, but still need further development at a large scale.

Keywords Advanced oxidation processes · Biodegradability · Electrooxidation · Fenton · Ozone · Paper industry · Photocatalysis · Wastewater treatment chains

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 m³/t in 1974 to 4–100 m³/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 reused 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, sulfite 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

Responsible editor: Philippe Garrigues

D. Hermosilla (✉) · N. Merayo · Á. Blanco
Department of Chemical Engineering, Complutense University of Madrid, Ciudad Universitaria s/n, 28040 Madrid, Spain
e-mail: dhermosi@ucm.es

A. Gascó
School of Biology, IE University, Cardenal Zúñiga 12,
40003 Segovia, Spain

process, and more starch-related products (rather than lignin ones) can be found (Amat et al. 2005a), resulting in these effluents being 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 t⁻¹ biochemical oxygen demand (BOD)₇ and 15–40 kg 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 nonbiodegradable organic chemical fraction (Ahmad et al. 2007; Habets and Knelissen 1997), such as high molecular weight organics (>1,000 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 circuit 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 biorecalcitrant 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 phthalates, 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; Öeller 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:



(b) Hydrogen atom abstraction:



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 nonphenolics (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). Phenoxy radicals rapidly react with O₂^{•-} to produce aromatic ring opening precursors of CO₂ (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 nonbiodegradable organics such as lignin or chlorinated organics, therefore contributing to increase the biodegradability of the effluent as well (Balcioglu et al. 2003, 2007; Bijan and Mohseni 2004, 2005, 2008; Chang et al. 2004; Mansilla et al. 1997; Marco et al. 1997; Mounteer et al. 2007; Öeller et al. 1997;

Salokannel et al. 2007; Yeber et al. 1999a, b). The full oxidation of organic compounds is however noneconomically feasible because the use of large amounts of energy and chemicals would be necessary for achieving a complete mineralization (Bijan and Mohseni 2005).

The stand-alone 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 pretreatment 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; Barndök et al. 2012; Gogate and Pandit 2004a, b).

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 circuit closure, as well as the assessment of cost-effective figures. A joint review of the application of AOPs to water treatment in the pulp and paper industrial sector is reported next.

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 (Barndök et al. 2012), pH (alkaline solutions accelerate its decomposition generating hydroxyl radicals), and temperature (Bijan and Mohseni 2004; 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, 2005b; Fontanier et al. 2005a; Miranda et al. 2001).

Particularly, Fontanier et al. (2005b) 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, 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 total organic carbon (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 effectively (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, probably due to the absence of carbon-carbon double bonds (Amat et al. 2005b; Langlais et al. 1991) (Fig. 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

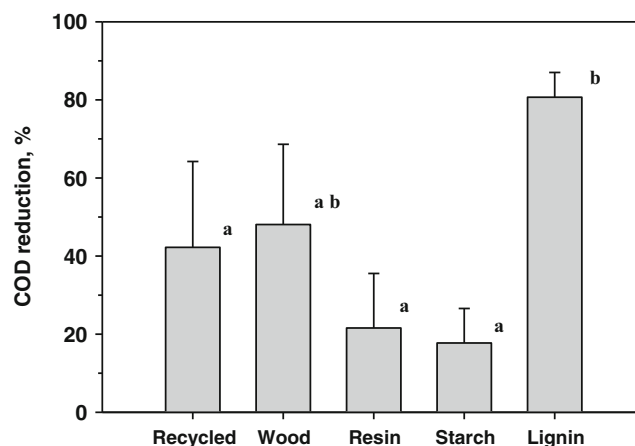


Fig. 1 COD removal by AOPs in the pulp and paper industry considering the type of fiber (recycled or virgin fiber—wood), and comparison to the treatment of resin acids (resin), starch degradation products (starch), and lignin. Letters (a, b) identify different statistically significant groups by Tukey's test, $P < 0.05$

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 pretreated 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, 2005; Catalkaya and Kargi 2007; Fontanier et al. 2005b, 2006; Mansilla et al. 1997; Öeller 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, b). As it has additionally been reported in several other studies, ozonation usually increases the biodegradability of paper mill effluents as well (Amat et al. 2005a; Balcioglu et al. 2007; Bijan and Mohseni 2004, 2005; Fontanier et al. 2006; Helble et al. 1999; Mansilla et al. 1997; Nakamura et al. 1997; Öeller 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 BOD₅/COD ratio < 0.2 (Öeller 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 min of reaction time has 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 chemical oxygen demand (COD), TOC, color, and absorbable organic halide (AOX) removals are very variable probably due to the diverse nature of the organics contained in the different treated effluents, whether they were biologically pretreated or not, the mill of origin, or the diverse ozone feeding rates used in the treatments, although the average value resulted ≈ 40 % (Fig. 2). Particularly, Fontanier et al.

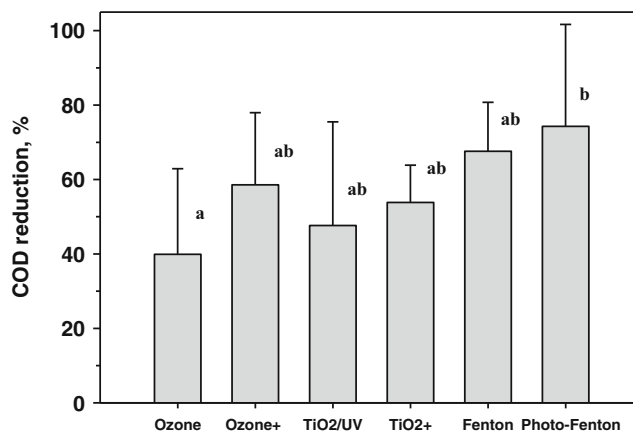


Fig. 2 COD removal by AOPs in the pulp and paper industry. Ozone+ includes all treatment combinations with ozone. TiO₂+ includes nonsupported TiO₂/UV/H₂O₂ treatments. Letters (a, b) label different statistically significant groups identified by Tukey’s test, *P* < 0.05

(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 to be more effective in basic media (Amat et al. 2004, 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 the 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 (Barndök 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 showed 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 nonsignificant 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; Öeller 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.

Table 1 Ozone oxidation treatment results for paper industry effluents

Effluent type removal (%)	COD	TOC	Color	AOX	DBO ₅ /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 Öeller (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	98 ^a	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 sulfate 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		47 ^b				Muñoz et al. (2006)
Biologically treated, recycled (75 %) and wood (25 %)	80	47 ^b				Öeller et al. (1997)
Partly biologically treated, recycled	20	22 ^b				Öeller et al. (1997)
Biologically treated, recycled	85	31 ^b				Öeller et al. (1997)
Biologically treated, wood	82	64 ^b				Öeller et al. (1997)
Biologically treated, recycled	53	18 ^b				Öeller et al. (1997)
Partly biologically treated, recycled	41	18 ^b				Öeller et al. (1997)
Biologically pretreated, wood	12	9 ^b	50	25	Yes	Salokannel et al. (2007)
Biologically pretreated, wood	18	9 ^b	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					Balabanıç et al. (2012)

^a Thirty-one percent TOC removal due to precipitation^b DOC

2013) or the generation of carbonate along the mineralization process (Öeller et al. 1997).

Regarding the temperature at which the process is performed, Salokannel et al. (2007) did not find differences from 21 to 35 °C, 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 find significant differences in the ozonation efficiency of paper mill effluents from 20 to 60 °C. Finally, Öeller et al. (1997) have also reported that increasing temperature did not provide any appreciable COD removal enhancement, although dissolved organic carbon (DOC) removal was 10–15 % higher at 40 °C and had extended reaction times (>90 min) than at 25 °C, which furthermore implied consuming a higher O₃ 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 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 Öeller (2009) implemented online 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 online 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 (Öeller et al. 1997).

Finally, besides the actual industrial application of ozone oxidation for bleaching, this technology has also been included as a postbiological treatment alternative for the biorecalcitrant 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 successfully at a large-scale application (Schmidt and Lange 2000). In addition, ozonation has also been successfully applied at an industrial scale to reuse paper mill effluents (Öeller and Offermanns 2002).

Ozone oxidation plus biological treatment

The oxidation by ozone as a stand-alone 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, 2005, 2008; Helble et al. 1999; Nakamura et al. 2004).

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

Another very interesting treatment alternative would be to 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

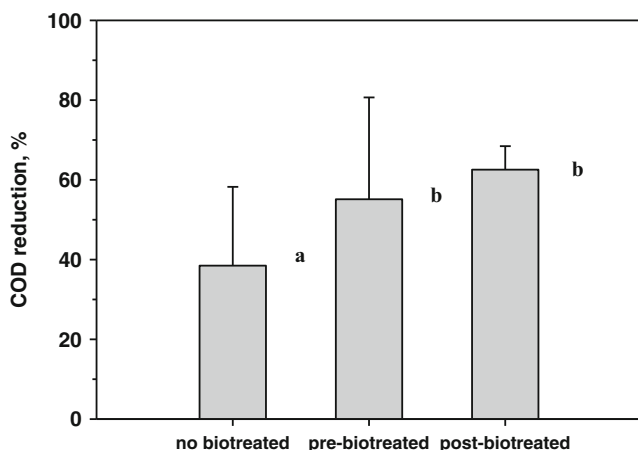


Fig. 3 COD removal by AOPs combined with biological treatment. Letters (a, b) identify statistically significant groups by Tukey's test, $P < 0.05$

biodegradability would be expected to improve highly. Finally, a consequent, more efficient second biotreatment 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), with ozone consumption ten times lower than when ozonation without complementary pre- and posttreatments, 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 pretreatments under real conditions, it results that membranes would produce lower rejection water volumes, so the ozone contactor may be reduced by about 50 % in the industry because the HMW fraction stream just constitutes 45 % of the total effluent (Bijan and Mohseni 2008). On the other hand, regarding the integrated treatment with MBR and ozonation and 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 were more difficult to be chemically oxidized than in the case of using a continuous activated sludge (Gommers et al. 2007).

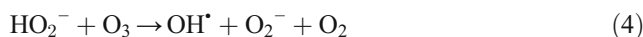
In addition, the use of biofilters in combination with ozone has also been assessed, and results have shown that the combination of ozone with a subsequent biofilter treatment required a lower amount of ozone to be supplied in the oxidation stage, as well as it would be ecologically preferable, reaching more than 80 % total COD removal (Helble et al. 1999; Mobius and Helble 2004). Moreover, the combination with a subsequent new ozonation stage (O_3 + biofilter + O_3 + biofilter) 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 pretreatment. Overall efficiency was mainly enhanced in terms of color removal and also significantly in COD and UV_{280} . Furthermore, the resident time of algal treatment was reduced from 8 to 5 days.

Combination of ozone and H_2O_2 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 (2004a) and Mounter 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 described by the following reactions (Glaze 1987):



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 stand-alone 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 stand-alone use of ozone (Fig. 2) adding 5 mM H_2O_2 at pH=11.

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

Effluent type	Treatment removal (%)	COD	TOC	Color	AOX	DBO ₅ /COD improvement	Reference
Biologically treated, woodfree	O ₃ + biofilter	53				Yes	Baig and Liechti (2001)
Biologically treated, woodfree	O ₃ + biofilter + O ₃ + biofilter	80				Yes	Baig and Liechti (2001)
CEH bleaching, wood	O ₃ + algal	90		99	87		Balcioglu et al. (2007)
Alkaline bleach, wood	O ₃ + bio		50				Bijan and Mohseni (2005)
ECF, wood	O ₃ + bio	57	40				Bijan and Mohseni (2008)
ECF, wood	Bio + O ₃ + bio	58	50	80			Bijan and Mohseni (2008)
ECF, wood	NF + O ₃ + bio	65	40	80			Bijan and Mohseni (2008)
Biologically treated, woodfree	O ₃ + biofilter	81					Helble et al. (1999)
Biologically treated, recycled	O ₃ + biofilter	57					Helble et al. (1999)
Newsprint, recycled	Bio + O ₃	90					Merayo et al. (2013)
Newsprint, recycled	O ₃ + bio	81					Merayo et al. (2013)
Paper industry, wood	O ₃ + biofilter	60					Mobius and Helble (2004)
Paper industry, wood	O ₃ + biofilter + O ₃ + biofilter	85					Mobius and Helble (2004)
ECF, wood	O ₃ + bio	58					Yeber et al. (1999b)
ECF, wood	O ₃ /UV + bio	63					Yeber et al. (1999b)
ECF, wood	O ₃ /UV/TiO ₂ + bio	70					Yeber et al. (1999b)
ECF, wood	O ₃ /UV/ZnO + bio	62					Yeber et al. (1999b)
Newsprint biologically treated, recycled	O ₃ /H ₂ O ₂	59					Balabanić et al. (2012)
Biologically treated, wood	O ₃ /H ₂ O ₂		31	81	95		Catalkaya and Kargi (2007)
Kraft weak black liquor, hardwood	O ₃ /H ₂ O ₂	50		90			Ko et al. (2009)
ECF, wood	O ₃ /H ₂ O ₂	20	5	67		Yes	Mounteer et al. (2007)
Biologically treated, wood	O ₃ /H ₂ O ₂	10		82	35	Yes	Salokannel et al. (2007)
Biologically treated, paper mill	O ₃ /H ₂ O ₂			90	35	Yes	Salokannel et al. (2007)
Biologically treated, recycled	O ₃ /H ₂ O ₂	64		97			Sevimli (2005)
Cardboard industry, recycled paper	O ₃ /UV	42					Amat et al. (2005b)
Kraft pulp, conventional bleaching, wood	O ₃ /UV	20		40		Yes	Mansilla et al. (1997)
Kraft bleach effluent, wood	O ₃ /UV		68 ^a				Muñoz et al. (2006)
Biologically treated, 90 % recycled, 10 % TMP	O ₃ /UV	14	5 ^a				Öeller et al. (1997)
Bleaching (CEPDD), wood	O ₃ /UV			72			Wang et al. (2004)
ECF, wood	O ₃ /UV		76			Yes	Yeber et al. (1999b)
Kraft pulp, conventional bleaching, wood	O ₃ /UV/ZnO	52		40		Yes	Mansilla et al. (1997)
Bleaching (CEPDD), wood	O ₃ /UV/H ₂ O ₂			76			Wang et al. (2004)
ECF, wood	O ₃ /UV/ZnO	44	70			Yes	Yeber et al. (1999b)
ECF, wood	O ₃ /UV/TiO ₂	51	72			Yes	Yeber et al. (1999b)
CEH bleaching, wood	O ₃ /active carbon	46		87	80	Yes	Balcioglu et al. (2007)
Kraft bleach effluent, wood	O ₃ /active carbon	63				Yes	Balcioglu and Moral (2008)
Kraft bleach effluent, wood	O ₃ /Fe ²⁺	52				Yes	Balcioglu and Moral (2008)
Kraft bleach effluent, wood	O ₃ /Mn ²⁺	53				Yes	Balcioglu and Moral (2008)
Biologically treated, wood	Catalytic ozonation	84	84	100			Fontanier et al. (2005b)
Biologically treated, wood	Catalytic O ₃ , continuous mode	75	61	95			Fontanier et al. (2005b)
Biologically treated, wood	Catalytic ozonation	67	74				Fontanier et al. (2006)
Biologically treated, recycled	Catalytic ozonation	53	35				Fontanier et al. (2006)
Biologically treated, bleached sulfate pulp, wood	Catalytic ozonation	72	73				Fontanier et al. (2006)
Kraft weak black liquor, hardwood	O ₃ /active carbon	60		88			Ko et al. (2009)
Kraft weak black liquor, hardwood	O ₃ /active carbon/H ₂ O ₂	65		95			Ko et al. (2009)

^a DOC

In fact, Mounter 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 H₂O₂ nevertheless had some beneficial effect increasing the average oxidation state. Finally, Salokannel et al. (2007) also reported that H₂O₂ 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 the molecular ozone and organic compounds competed with O₃/H₂O₂ reactions. Moreover, the improvement of biodegradability was also reported to be lower using O₃/H₂O₂ than stand-alone O₃ because the additional generation of radicals also degraded some biodegradable molecules.

According to these results, ozonation without the addition of H₂O₂ 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.

Ozone/UV

In this treatment combination, the supplied UV energy interacts with O₃ as described in the following reaction (Beltrán et al. 1998; Esplugas et al. 2002; Guittonneau et al. 1990):



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 O₃ (and H₂O₂ as well) requires short-wavelength photons (<310 nm) (Hoffmann et al. 1995).

Particularly, the O₃/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, with results being particularly better at higher temperature (80 °C).

Otherwise, nonsignificant 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. 2004).

In addition, O₃ consumption has been reported to be higher in the O₃/UV process than when O₃ was used as a stand-alone, resulting in a 90 % additional O₃ used to remove the COD (Öeller et al. 1997). Therefore, it was recommended to consider O₃ 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 stand-alone 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, there were more energy incisives 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).

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 as 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 the overall rate of the chemical conversion: (1) diffusion of the reagents toward 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 toward 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 the 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, and 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 74 % of the TOC and 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 study. 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 $OH\cdot$ 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 23 % with respect to direct ozonation, whereas it was just 15 % in comparison to stand-alone 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 nontoxic effluent. In fact, oxidation is more aggressive in catalyzed ozonation treatments than in stand-alone 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 50–55 % by the

addition of 5 mM Fe^{2+} or Mn^{2+} , whereas it just resulted to 25 % using stand-alone 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 stand-alone ozone. Complementarily, Yeber et al. (1999b) reported that chloride ions were released to the solution, reaching maximum presence values after 1 min 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 min, thus showing a much slower efficiency on removing organochloride compounds.

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 stand-alone 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 applied to biologically pretreated effluents from the wood industry.

In particular, it has been demonstrated that radiation with a wavelength lower than 400 nm is able to photolyze 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 stand-alone 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 improve the result. 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).

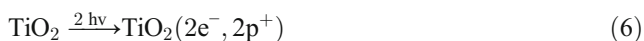
Table 3 Hydrogen peroxide and UV treatments applied to effluents from the pulp and paper industry

Effluent	Treatment removal (%)	COD	TOC	Color	AOX	Reference
Pulp and paper mill, wood	H ₂ O ₂	10				Ahmed et al. (2009)
Biologically treated, wood	H ₂ O ₂		5	24	34	Catalkaya and Kargi (2007)
Kraft Eop effluent, wood	H ₂ O ₂	1	0	31		Joss et al. (2007)
Pulp and paper mill, wood	UV	0.3				Ahmed et al. (2009)
Biologically treated, wood	UV		4	7	17	Catalkaya and Kargi (2007)
Kraft (CEPDD) effluent, wood	UV			6		Wang et al. (2004)
Pulp and paper mill, wood	UV/H ₂ O ₂	92	90			Ahmed et al. (2009)
Biologically treated, wood	UV/H ₂ O ₂		11	41	19	Catalkaya and Kargi (2007)
Biologically treated, wood	UV/H ₂ O ₂		45			Catalkaya and Kargi (2008)
Kraft ECF filtrate, wood	UV/H ₂ O ₂	0	0	30		Mounteer et al. (2007)
Coagulated-flocculated bleaching effluent, wood	UV/H ₂ O ₂	37				Rodrigues et al. (2008)
Kraft bleach effluent, wood	UV/H ₂ O ₂				100	Ugurly and Karaoglu (2009)
Kraft (CEPDD) effluent, wood	UV/H ₂ O ₂			67		Wang et al. (2004)

Nonetheless, even though COD and color reductions are improved in comparison to when H₂O₂ is used alone (Ahmed et al. 2009; Prat et al. 1988), the application of an H₂O₂/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 H₂O₂ may be acceptable ($\approx 30\%$) (Catalkaya and Kargi 2007; Joss et al. 2007), it does not have enough power to induce COD and TOC removals ($< 5\%$; Catalkaya and Kargi 2007; Joss et al. 2007; Pérez et al. 2001), as reported in Table 3.

Semiconductor photocatalytic processes

These treatments imply the irradiation of a semiconductor (e.g., TiO₂, 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 Eq. (6) for TiO₂, the most widely used semiconductor material in these processes (Antunes et al. 2004; Fujishim and Honda 1972).



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 TiO₂ (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⁺), as it is expressed in the following equation (Antunes et al. 2004):



On the other hand, the photogenerated electron may instead be trapped by suitable acceptors (electron scavengers), with O₂ the most widely used one, forming the superoxide radical anion O₂^{•-} (Antunes et al. 2004; Fox 1989), as described by the next reaction:



It has been pointed out that TiO₂ is a more efficient catalyst than ZnO, respectively generating 55 and 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 TiO₂ 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, TiO₂ also was more efficient than ZnO when it was applied immobilized on glass (Yeber et al. 1999a). Finally, these studies 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, 2000), it also allows the possibility of performing the treatment under flow conditions, thus avoiding the annoying catalyst recovering step that is required

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

Effluent	Treatment removal (%)	COD	TOC	Color	AOX	DBO ₅ /COD improvement	Reference
Newsprint biologically treated, recycled	TiO ₂ /UV	39					Balabanıç et al. (2012)
Biologically treated, wood	TiO ₂ /UV		80				Catalkaya and Kargı (2008)
RO concentrate newsprint, recycled	TiO ₂ /UV	35	30				Hermosilla et al. (2012)
Kraft/soda bleach effluent, agricultural residual materials	TiO ₂ /UV	88					Kansal et al. (2008)
Pulp and paper mill effluent, hardwood	TiO ₂ /UV	54		84			Kumar et al. (2011)
Newsprint, recycled	TiO ₂ /UV	20					Merayo et al. (2013)
Kraft bleach effluent, wood	TiO ₂ /UV		15 ^a				Muñoz et al. (2006)
Bleach effluent, wood	TiO ₂ /UV	89					Toor et al. (2007)
Kraft ECF effluent, wood	TiO ₂ /UV	16			71		Pérez et al. (2001)
Coagulated-flocculated bleaching effluent, wood	TiO ₂ /UV	40					Rodrigues et al. (2008)
Agro-residue-based soda bleaching effluent	ZnO/UV	55					Dhir et al. (2012)
Kraft/soda bleach effluent, agricultural residual materials	ZnO/UV	94					Kansal et al. (2008)
Diluted black liquor, wood	ZnO/UV	57		80			Mansilla et al. (1994)
Kraft E1 effluent, wood	ZnO/UV		15	54			Moraes et al. (2006)
Diluted black liquor, wood	ZnO/UV		0	5			Moraes et al. (2006)
Kraft ECF effluent, wood	TiO ₂ /UV/H ₂ O ₂ supported			40			Mounteer et al. (2007)
Kraft alkaline extraction conventional bleaching, wood	TiO ₂ /UV/O ₂ supported	58	55		90		Yeber et al. (1999a)
Kraft ECF effluent, wood	TiO ₂ /UV/O ₂ supported + Bio	70				Yes	Yeber et al. (1999a)
Kraft alkaline extraction conventional bleaching, wood	TiO ₂ /UV supported	58	55		90		Yeber et al. (2000)
Kraft alkaline extraction conventional bleaching, wood	ZnO/UV supported	58	31		90		Yeber et al. (2000)
Kraft alkaline extraction conventional bleaching, wood	ZnO/UV/O ₂ supported	58	31		90		Yeber et al. (1999a)
Kraft ECF effluent, wood	ZnO/UV/O ₂ supported	44				Yes	Yeber et al. (1999a)
Diluted black liquor, wood	Pt-ZnO/UV	57		80			Mansilla et al. (1994)
Kraft effluent, wood	Ag-ZnO/UV		15	99			Gouvea et al. (2000)
Agro-residue-based soda bleaching effluent	ZnO/solar UV + Bio	93	89				Dhir et al. (2012)
Agro-residue-based soda bleaching effluent	Bio + ZnO/solar UV	86					Dhir et al. (2012)
Newsprint, recycled	Solar TiO ₂ + Bio	83					Merayo et al. (2013)
Newsprint, recycled	Bio + solar TiO ₂	82					Merayo et al. (2013)
Kraft E1 effluent, wood	ZnO/UV + Bio		62				Moraes et al. (2006)
Diluted black liquor, wood	ZnO/UV + Bio		36				Moraes et al. (2006)
Kraft ECF effluent, wood	ZnO/UV/O ₂ + Bio	64					Yeber et al. (1999b)
Board industry, recycled	TiO ₂ /solar UV	40					Amat et al. (2005a)
Biologically treated effluent	TiO ₂ /solar UV	83					Gomathi and Kanmani (2006)
Kraft/soda bleach effluent, agricultural residual materials	TiO ₂ /solar UV	61					Kansal et al. (2008)
Agro-residue-based soda bleaching effluent	ZnO/solar UV	53					Dhir et al. (2012)
Kraft/soda bleach effluent, agricultural residual materials	ZnO/solar UV	74					Kansal et al. (2008)
Kraft bleaching, wood	TiO ₂ /UV/H ₂ O ₂	40				Yes	Balcioglu et al. (2003)
Kraft bleaching, wood	TiO ₂ /UV/H ₂ O ₂	51				Yes	Balcioglu et al. (2003)
Electrocoagulated-floated bleaching effluent, wood	TiO ₂ /UV/H ₂ O ₂	64				Yes	Boroski et al. (2008)

Table 4 (continued)

Effluent	Treatment removal (%)	COD	TOC	Color	AOX	DBO ₅ /COD improvement	Reference
Biologically treated, wood	TiO ₂ /UV/H ₂ O ₂		84				Catalkaya and Kargi (2008)
Pulp and paper mill effluent, hardwood	TiO ₂ /UV/H ₂ O ₂	65		89			Kumar et al. (2011)
Kraft bleach effluent, wood	TiO ₂ /UV/H ₂ O ₂		22 ^a				Muñoz et al. (2006)
Kraft ECF effluent, wood	TiO ₂ /UV/H ₂ O ₂	50	50		90		Pérez et al. (2001)
Coagulated-flocculated bleaching effluent, wood	TiO ₂ /UV/H ₂ O ₂	55					Rodrigues et al. (2008)
Kraft bleach effluent, wood	TiO ₂ /UV/H ₂ O ₂				91		Ugurly and Karaoglu (2009)
Kraft alkaline extraction conventional bleaching, wood	TiO ₂ /UV/O ₂	50		40		Yes	Mansilla et al. (1997)
Kraft ECF effluent, wood	TiO ₂ /UV/O ₂	53	72			Yes	Yeber et al. (1999b)
Kraft ECF effluent, wood	TiO ₂ /UV/O ₂ + Bio	67					Yeber et al. (1999b)
Kraft first extraction effluent ECF, wood	TiO ₂ /UV/O ₂	70	50	94		Yes	Yeber et al. (2007)
Kraft alkaline extraction conventional bleaching, wood	ZnO/UV/O ₂	57		42		Yes	Mansilla et al. (1997)
Kraft ECF effluent, wood	ZnO/UV/O ₂	51	70			Yes	Yeber et al. (1999b)
Kraft first extraction effluent ECF, wood	TiO ₂ /UV/Cu	70		94		Yes	Yeber et al. (2007)

^a DOC

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 studies 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 showed that lignin color progressively decreased up to 50 % after 15 min of treatment, whereas it was almost total (99 %) after 60 min.

The efficiency of the TiO₂-photocatalytic process and, therefore, the required reaction time to maximize it are influenced by the dosage of TiO₂ 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 L⁻¹ of TiO₂ has been reported for the treatment of lignin powder, resulting in a 50 % reduction of the color within the first 10 min of reaction (Chang et al. 2004), whereas the removal efficiencies of both color and DOC reached about 90 % when the process was extended up to 960 min.

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 TiO₂ at pH=11 during 60 min (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 TiO₂ 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 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 the TiO₂ surface acquires 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 (~90 %) from a bleaching effluent of a nonrecovered paper mill by TiO₂ photocatalysis (Toor et al. 2007) and from an agro-residue-based soda bleaching effluent by both TiO₂ (COD removal~90 %) and ZnO (COD removal~95 %) photocatalytic treatments (Kansal et al. 2008) (Table 4). Virgin fiber was used in the pulping process, so its lignin, starch, and resin acid contents surely contributed to a certain extent to these very successful results (Fig. 1).

Finally, photocatalysis might be considered as an interesting alternative for pre- or postbiological 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 postbiological treatment achieved a 75 % color removal in the treatment of black liquor, which is 15 times higher than the resulting decolorization after a stand-alone photochemical process, and 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 study for the prebiological treatment of kraft effluent by photocatalysis (Moraes et al. 2006) (Table 4).

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 40 % at the preindustrial level and 50 % in laboratory trials (Table 4), and Kansal et al. (2008) addressed the solar photocatalytic treatment of bleaching effluent, reporting better results when using ZnO as catalyst than TiO₂, which is in contrast to the results previously reported using other UV light sources. Furthermore, the achieved chemical degradation was faster than when using other UV light sources.

In contrast, Amat et al. (2005a) reported that COD removal was lower than when applying a solar photo-Fenton treatment (Tables 4 and 5), which agrees with the study performed by Gomathi and Kanmani (2006). In both studies, the degradation of organics was mainly driven toward the pollutants that are more reluctant to biological degradation. In addition, better results were addressed for derivatives from lignin than for nonaromatic compounds. That is, whereas the treatment of eugenol by solar photocatalysis resulted in a 60 % COD removal, 30 % was just reached when 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 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 pretreatment of a biological process, and it resulted to 95 % when it was combined as the posttreatment of the biological degradation of the alkaline-extracted effluent (Table 4).

UV/TiO₂/H₂O₂

Several studies have considered the addition of hydrogen peroxide to the UV/TiO₂-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/TiO₂ treatment (Catakaya and Kargi 2008; Chang et al. 2004; Kumar et al. 2011; 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 H₂O₂ (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:



Particularly, this treatment led to a 50 % COD removal after 6 h of irradiation when it was applied to an elemental chlorine-free (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 H₂O₂ to an UV/TiO₂ treatment did not significantly improve degradation rate, but increased the velocity of the photoprocess 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 H₂O₂ 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 %

Table 5 Fenton processes and OxoneTM treatment results for effluents from the pulp and paper industry

Effluent	Treatment removal (%)	COD	TOC	Color	AOX	Phenols	Reference
Newsprint biologically treated, recycled	Fenton	75					Balabaniç et al. (2012)
Biologically treated, wood	Fenton		88	85	89		Catalkaya and Kargi (2007)
RO concentrate newsprint, recycled	Fenton	80					Hermosilla et al. (2012)
Chemimechanical pulp effluent, wood	Fenton			20			Karimi et al. (2010)
Soda bagasse pulp effluent, wood	Fenton			62			Karimi et al. (2010)
Biologically treated, pulp and paper mill	Fenton	62		98			Kazmi and Thul (2007)
Kraft chlorination step, wood	Fenton		40	>90			Pérez et al. (2002b)
Biologically treated, recycled	Fenton	83		95			Sevimli (2005)
Equalization tank paper mill	Fenton-like	50		100			Tambosi et al. (2006)
Equalization tank paper mill	Fenton-like pilot scale	52	90	98			Tambosi et al. (2006)
Biologically treated, wood	Photo-Fenton		85	82	93		Catalkaya and Kargi (2007)
Bleach effluent, wood	Photo-Fenton	20					Eskelinen et al. (2010)
RO concentrate newsprint, recycled	Photo-Fenton	100					Hermosilla et al. (2012)
Biologically treated kraft ECF effluent, wood	Photo-Fenton					100	Justino et al. (2011)
Chemimechanical pulp effluent, wood	Photo-Fenton			41			Karimi et al. (2010)
Soda bagasse pulp effluent, wood	Photo-Fenton			65			Karimi et al. (2010)
Kraft bleach effluent, wood	Photo-Fenton		30 ^a				Muñoz et al. (2006)
Kraft bleach effluent, wood	Photo-Fenton	67		91			Pereira et al. (2009)
Kraft bleach effluent, wood	Photo-Fenton	85		81			Pereira et al. (2009)
Kraft chlorination step, wood	Photo-Fenton		60	>90			Pérez et al. (2002b)
Newsprint biologically treated, recycled	Photo-Fenton	96					Balabaniç et al. (2010)
Biologically treated, wood	Photo-Fenton	87 ^b					Zahrim et al. (2007)
Bleach effluent, wood	Fenton-like + ultrasonic	12					Eskelinen et al. (2010)
Kraft bleach effluent, wood	Photo-Fenton/TiO ₂		30				Muñoz et al. (2006)
Board industry, recycled	Solar photo-Fenton	50					Amat et al. (2005a)
Biologically treated effluent	Solar photo-Fenton	90					Gomathi and Kanmani (2006)
Kraft bleaching effluent (22 % ClO ₂ substitution), wood	Solar photo-Fenton		60				Torrades et al. (2003)
Bleaching effluent (H ₂ O ₂), wood	Solar photo-Fenton		70				Xu et al. (2007)
Kraft bagasse bleaching effluent	Electrooxidation	53					Antony and Natesan (2012)
Biologically treated, cellulose	Electrooxidation	63	38	96			Buzzini et al. (2006)
Corrugating medium mill effluent, recycled	Electrooxidation	28		94			Perng et al. (2008)
Kraft bagasse bleaching effluent	Electrooxidation + bio	87					Antony and Natesan (2012)
Kraft bagasse bleaching effluent	Electrocoagulation + electrooxidation + bio	95					Antony and Natesan (2012)
Biologically treated effluent	Electro-Fenton	90		95			Selvabharathi and Kanmani (2010)
Kraft EOP effluent, wood	Oxone ^{TMc}	14	0	79			Joss et al. (2007)

^a DOC^b BOD₃^c Peroxymonosulfate salt

increase of the COD removal when H₂O₂ was added to the treatment of a nonrecovered paper mill effluent by TiO₂ photocatalysis (Table 4).

Furthermore, Balcioglu et al. (2003) reported a 40 % COD removal (Table 4) when treating kraft bleaching effluents by this treatment, and chloride release and an increase of the

BOD₅/COD ratio were also addressed. Additionally, Catalkaya and Kargi (2008) achieved an 84 % TOC removal applying this treatment to prebiologically 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 H₂O₂ (Fig. 2).

UV/TiO₂/O₂

In this aerioxide process, oxygen is used as an efficient electron trap preventing electrons to return back to the photogenerated 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 study also showed a slight better treatment efficiency when TiO₂ was used as catalyst in the O₂-assisted photocatalytic treatment of these effluents in comparison to using ZnO as catalyst, or in combination with O₃ (Tables 2 and 4). In fact, better mineralization rates were obtained using TiO₂ photocatalytic systems rather than applying ZnO-catalyzed ones.

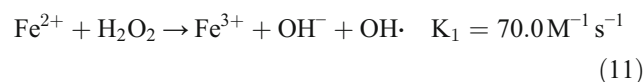
Furthermore, Yeber et al. (2007) reported the removal of 70 % of the COD, 50 % TOC, 94 % color, and 50 % toxicity, when applying this treatment to effluents from the first extraction step of ECF bleaching pulp (Table 4). Finally, applying either UV/TiO₂/O₂ or UV/ZnO/O₂ processes to an effluent from a bleaching sequence, Yeber et al. (1999b) also reported the release of chloride ions to the solution, whose maximum content was detected after 5 min of treatment.

UV/TiO₂/Cu (II)

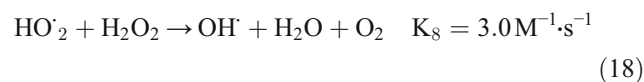
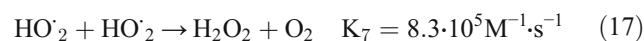
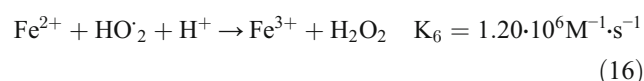
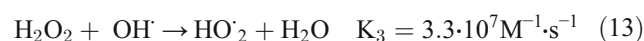
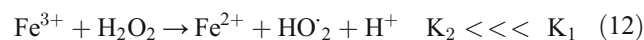
Biodegradation efficiency might also be improved using metallic ions as electron acceptors, as proposed by Yeber et al. (2007) in the same study the aerioxide treatment just described was also assessed. In short, it was confirmed that copper (II) efficiently acted as an electron acceptor when photocatalytic 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 COD, 50 % TOC, and 50 % toxicity was also achieved performing this photocatalytic treatment type (Table 4).

Fenton processes

The Fenton process is based on the electron transfer between H₂O₂ and Fe²⁺, which acts as a homogenous catalyst, to produce hydroxyl radical (OH·), which is able to powerfully degrade organic compounds, as expressed by the following equation (Harber and Weiss 1934):



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 Eqs. 1 and 2 (Huang et al. 1993). The iron cycle implying Fe²⁺ and Fe³⁺ forms plays the catalyst role according to the following reactions (Pignatello et al. 2006):



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 AOP-based treatment technologies (Fig. 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 pretreated, and the superiority of this process to more effectively remove refractory organics (COD removal=83 %; Table 5) than O₃ (COD removal=43 %; Table 1) and O₃/H₂O₂ (COD removal=64 %; Table 2) processes has been proven. In addition, it is also a more economic AOP-based treatment alternative (Hermosilla et al. 2012). Correspondingly, Catalkaya and Kargi (2007) reported the removal of 85 % of the color and 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 pretreated pulp and paper mill effluents (Table 5).

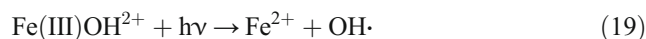
Nevertheless, despite this treatment process being generally more oxidative than other alternatives considering the assistance of radiation as well, Amat et al. (2005a) only addressed a 3 % COD removal for the treatment of acid fractions from starch degradation, which was attributed to the inherent organic 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 pretreatment 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 Fe³⁺ dosages, and nearly 100 % of color and

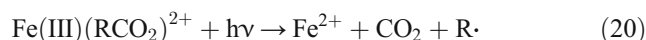
aromatic compounds were removed as well (Table 5). Despite addressing these good results, the partially oxidized composition of the treated wastewater showed a higher acute toxicity to *Artemia salina* than the untreated effluent.

Photo-Fenton

The use of UV light in combination with Fenton's reagent, that is, the so-called photo-Fenton process, is able to regenerate 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):



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



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, and 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, b). 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/H₂O₂ system (Catalkaya and Kargi 2007; Hermosilla et al. 2009b, 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)/H₂O₂ 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 °C (Pérez et al. 2002b). Therefore, temperature seems to be assisting alternative ways of H₂O₂ 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 °C, and bubbling O₂ 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 the 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 to highlight that negligible amounts of iron hydroxides are expected to be generated in a photo-Fenton process, and pH will always evolve toward 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).

Finally, it is important to take into account in the 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⁺(H₂O)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 H₂O₂ and 2.5 mM of Fe (II) and applying 5 min of UV irradiation to a pulp mill effluent (Catalkaya and Kargi 2007). In addition, Pérez et al. (2002b) 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 7,500 ppm of H₂O₂ 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 *R. oryzae* and photo-Fenton oxidation were combined (Table 5), whereas with *P. sajor caju* and laccase, just 60–85 % removal was achieved. 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 84–93 % of some model compounds of wood extractives, it only reached 20 % removal of the COD after 30 min 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 nonoptimal to perform this process, and it has also been proven to be of greater relevance than performing dark Fenton (Hermosilla et al. 2012).

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), and better treatment results were reported at 50 °C than at a lower treatment temperature in this study. 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 °C.

In particular, approximately 60 and 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, 40 % of the residual sulfur was determined as sulfate, that is, the final solution enhanced its biodegradability. Furthermore, they reported a 24 % COD removal after 7 h 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 7,500 ppm of H₂O₂.

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 h. Additionally, Amat et al. (2005a) 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 2 h process) have been reported in the treatment of biologically pretreated 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.

Electrooxidation 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 electrooxidation 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 min (Buzzini et al. 2006) (Table 5).

Furthermore, the combination of electrooxidation with a postbiological treatment stage of the same kraft bagasse bleaching effluent increased the overall COD removal up to 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 electrooxidation step. Moreover, the combination of electrocoagulation (1 A dm⁻² during 34.4 min), electrooxidation (1.5 A dm⁻² during 90.5 min), and biological process (521 min) applied to the same wastewater addressed a

95 % COD removal, and the operating cost was lower indeed (Antony and Natesan 2012).

In addition, the treatment of model compounds from the paper industry even had 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 bisulfite-based pulping process resulted in the production of vanillin, which would be a by-product of interesting commercial value (Moodley et al. 2011).

Finally, the combination of Fenton process with electrochemical oxidation (namely, electro-Fenton treatment) is another 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).

Oxone™ (peroxymonosulfate salt; 2KHSO₅·KHSO₄:K₂SO₄)

Joss et al. (2007) assessed the treatment performance of this commercial salt aiming at the decolorization of an alkaline stage effluent from a kraft pulp mill. Oxone™ was mainly effective during the initial phases of the treatment. A 5 g L⁻¹ Oxone™ 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.

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 no 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 pretreated paper mill effluents in 2.90€ per kg of removed COD, which

in their particular case implied $0.2\text{€}/\text{m}^3$ (including an additional biofilter). Moreover, they assessed that the additional use of H_2O_2 will increase the cost in an extra $0.2\text{€}/\text{m}^3$. 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 $7.50\text{€}/\text{m}^3$ depending on the chemicals used and sludge disposal, whereas the cost of an UV + H_2O_2 treatment was estimated to be about $1\text{€}/\text{m}^3$.

Furthermore, it has been reported that the cost of ozonation in pulp and paper mills can be reduced from 0.23 to $0.14\text{€}/\text{m}^3$ using an ozone system equipped with an online 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 $2.34\text{ M€}/\text{year}$ implementing its combination with a subsequent biofiltration 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. 2012, 2014; Öeller and Offermanns 2002).

Complementarily, the operational cost of several AOPs applied to degrade different compounds 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 – $3.0\text{€}/\text{kg}$ of equivalent O_2 , whereas electrochemical oxidation addressed 2.4 – $4.0\text{€}/\text{kg}$ of equivalent O_2 , and ozonation raised its cost up to 8.5 – $10\text{€}/\text{kg}$ 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 ($0.045\text{€}/\text{g}$ TOC), whereas conventional photo-Fenton treatment was the most expensive one ($0.31\text{€}/\text{g}$ TOC). As a result, the operational cost of the solar photo-Fenton treatment of industrial wastewater was assessed to be 3.6 to $6\text{€}/\text{m}^3$. The application of this treatment at an 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 ($0.45\text{€}/\text{m}^3$, ranging from 0.05 to $2.35\text{€}/\text{m}^3$; Jung et al. 2011) and the actual treatment cost figures for the alternative use of AOPs, it can be inferred 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 AOP-based treatment possibilities have already been assessed successfully 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 AOP-based treatments to effluents from the pulp and paper industry, particularly being 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 stand-alone 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 significantly, using AOPs as a postbiological 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 be newly implemented or already existing within the facilities of the mill, as well as the assessment of final economic figures.

Acknowledgments This research was developed in the frame of the projects “PROLIPAPEL” (P-2009/AMB/1480), funded by the Regional Government of Madrid; and “OXIPAPEL” (CIT-310000-2008-15), funded by the Ministry of Science & Innovation of Spain. N. Merayo's participation was sponsored by a Ph.D. grant from the Ministry of Economy & Competitiveness of Spain.

References

- Ahmad AL, Wong SS, Teng TT, Zuhairi A (2007) Optimization of coagulation-flocculation process for pulp and paper mill effluent by response surface methodological analysis. *J Hazard Mater* 145: 162–168

- Ahmed B, Mohamed H, Limem E, Nasr B (2009) Degradation and mineralization of organic pollutants contained in actual pulp and paper mill wastewaters by a UV/H₂O₂ process. *Ind Eng Chem Res* 48:3370–3379
- Alvares ABC, Diaper C, Parsons SA (2001) Partial oxidation by ozone to remove recalcitrance from wastewaters—a review. *Environ Technol* 22:409–427
- Amat AM, Arques A, Miranda MA (1999) p-Coumaric acid photodegradation with solar light, using 2,4,6-triphenylpyrylium salt as photosensitizer—a comparison with other oxidation methods. *Appl Catal B* 23:205–214
- Amat AM, Arques A, Beneyto H, García A, Miranda MA, Seguí S (2003) Ozonisation coupled with biological degradation for treatment of phenolic pollutants: a mechanistically based study. *Chemosphere* 53:79–86
- Amat AM, Arques A, López F, Seguí S, Miranda MA (2004) Abatement of industrial sulfonic pollutants by ozone and UV radiation. *Environ Eng Sci* 21:485–492
- Amat AM, Arques A, López F, Miranda MA (2005a) Solar photocatalysis to remove paper mill wastewater pollutants. *Sol Energy* 79:393–401
- Amat AM, Arques A, Miranda MA, López F (2005b) Use of ozone and/or UV in the treatment of effluents from board paper industry. *Chemosphere* 60:1111–1117
- Antony SP, Natesan B (2012) Optimization of integrated electro-bio process for bleaching effluent treatment. *Ind Eng Chem Res* 51:8211–8221
- Antunes CSA, Bietti M, Salamone M, Scione N (2004) Early stages in the TiO₂-photocatalyzed degradation of simple phenolic and non-phenolic lignin model compounds. *J Photochem Photobiol A* 163:453–462
- Baig S, Liechti PA (2001) Ozone treatment for biorefractory COD removal. *Water Sci Technol* 43:197–204
- Bailey PS (ed) (1982) *Ozonation in organic chemistry: nonolefinic compounds*. Academic, New York
- Balabanić D, Hermosilla D, Blanco A, Merayo N, Klemencić AK (2010) The possibility of removal of endocrine disruptors from paper mill waste waters using anaerobic and aerobic biological treatment, membrane bioreactor, ultra-filtration, reverse osmosis and advanced oxidation processes. In: Popov V, Brebbia CA (eds) *Environmental toxicology III*, vol 132. WIT Transactions on Ecology and the Environment. pp 33–44
- Balabanić D, Hermosilla D, Merayo N, Klemencić AK, Blanco A (2012) Comparison of different wastewater treatments for removal of selected endocrine-disruptors from paper mill wastewaters. *J Environ Sci Health A* 47:1350–1363
- Balcioglu IA, Cecen F (1999) Treatability of kraft pulp bleaching wastewater by biochemical and photocatalytic oxidation. *Water Sci Technol* 40:281–288
- Balcioglu IA, Moral CK (2008) Homogeneous and heterogeneous catalytic ozonation of pulp bleaching effluent. *J Adv Oxid Technol* 11:543–550
- Balcioglu IA, Alaton IA, Otker M, Bahar R, Bakar N, Ikiz M (2003) Application of advanced oxidation processes to different industrial wastewaters. *J Environ Sci Health A* 38:1587–1596
- Balcioglu IA, Tarlan E, Kivilcimdan C, Sacan MT (2007) Merits of ozonation and catalytic ozonation pre-treatment in the algal treatment of pulp and paper mill effluents. *J Environ Manag* 85:918–926
- Barndök H, Hermosilla D, Cortijo L, Negro C, Blanco A (2012) Assessing the effect of inorganic anions on TiO₂-photocatalysis and ozone oxidation treatment efficiencies. *J Adv Oxid Technol* 15:125–132
- Bauer R, Fallmann H (1997) The photo-Fenton oxidation—a cheap and efficient wastewater treatment method. *Res Chem Intermed* 23:341–354
- Bauman HD, Lutz LR (1974) Ozonation of a kraft mill effluent. *Tappi J* 57:116–119
- Beltrán FJ, Encinar JM, Alonso MA (1998) Nitroaromatic hydrocarbon ozonation in water. 1. Single ozonation. *Ind Eng Chem Res* 37:25–31
- Beltrán FJ, García-Araya JF, Alvarez PM (2000) Sodium dodecylbenzenesulfonate removal from water and wastewater. 1. Kinetics of decomposition by ozonation. *Ind Eng Chem Res* 39:2214–2220
- Benkelberg HJ, Warneck P (1995) Photodecomposition of iron (III) hydroxo and sulfato complexes in aqueous solution—wavelength dependence of OH[•] and SO₄^{•-} quantum yields. *J Phys Chem* 99:5214–5221
- Bierbaum S, Öeller HJ (2009) Cost savings in the ozone treatment of paper mill effluents achieved by a closed-loop ozone control system. *Ozone Sci Eng* 31:454–460
- Bierbaum S, Escabasse J-Y, Well A, Kompare B, Drev D, Krivograd Klemencic A (2012) Reducing fresh water consumption in paper industry by recycling AOP-treated effluents. *Fresenius Environ Bull* 8:2178–2184
- Bierbaum S, Öeller HJ, Kersten A, Krivograd Klemencic A (2014) Reduction of organic trace compounds and fresh water consumption by recovery of advanced oxidation processes treated industrial wastewater. *Water Sci Technol* 69(1):156–160
- Bigda RJ (1995) Consider Fenton's chemistry for wastewater treatment. *Chem Eng Prog* 91:62–66
- Bijan L, Mohseni M (2004) Using ozone to reduce recalcitrant compounds and to enhance biodegradability of pulp and paper effluents. *Water Sci Technol* 50:173–182
- Bijan L, Mohseni M (2005) Integrated ozone and biotreatment of pulp mill effluent and changes in biodegradability and molecular weight distribution of organic compounds. *Water Res* 39:3763–3772
- Bijan L, Mohseni M (2008) Novel membrane pretreatment to increase the efficiency of ozonation-biooxidation. *Environ Eng Sci* 25:229–237
- Boroski M, Rodrigues AC, García JC, Gerola AP, Nozaki J, Hioka N (2008) The effect of operational parameters on electrocoagulation-flotation process followed by photo-catalysis applied to the decontamination of water effluents from cellulose and paper factories. *J Hazard Mater* 160:135–141
- BREF (2013) *Integrated Pollution Prevention and Control (IPPC): reference document on best available techniques in the pulp and paper industry (final draft)*, European Commission
- Buzzini AP, Miwa DW, Motheo AJ, Pires EC (2006) Use of electrochemical oxidation process as post-treatment for the effluents of a UASB reactor treating cellulose pulp mill wastewater. *Water Sci Technol* 54:207–213
- Cañizares P, Paz R, Saez C, Rodrigo MA (2009) Costs of the electrochemical oxidation of wastewaters: a comparison with ozonation and Fenton oxidation processes. *J Environ Manage* 90:410–420
- Catalkaya EC, Kargi F (2007) Color, TOC and AOX removals from pulp mill effluent by advanced oxidation processes: a comparative study. *J Hazard Mater* 139:244–253
- Catalkaya EC, Kargi F (2008) Advanced oxidation treatment of pulp mill effluent for TOC and toxicity removals. *J Environ Manag* 87:396–404
- Chang CN, Ma YS, Fang GC, Chao AC, Tsai MC, Sung HF (2004) Decolorizing of lignin wastewater using the photochemical UV/TiO₂ process. *Chemosphere* 56:1011–1017
- Dahlman OB, Reimann AK, Strömberg LM, Mörck RE (1995) High molecular weight effluents materials from modern ECF and TCF bleaching. *Tappi J* 78:99–109
- Dhir A, Prakash NT, Sud D (2012) Coupling of solar-assisted advanced oxidative and biological treatment for degradation of agro-residue-based soda bleaching effluent. *Environ Sci Pollut Res* 19:3906–3913
- Domínguez-Ramos A, Aldaco R, Irabien A (2008) Electrochemical oxidation of lignosulfonate: total organic carbon oxidation kinetics. *Ind Eng Chem Res* 47:9848–9853

- Durán A, Monteagudo JM, San Martín I (2012) Photocatalytic treatment of an industrial effluent using artificial and solar UV radiation: an operational cost study on a pilot plant scale. *J Environ Manag* 98:1–4
- El-Din MG, Smith DW (2002) Ozonation of kraft pulp mill effluents: process dynamics. *J Environ Eng Sci* 1:45–57
- Eriksson KE, Kolar MC (1985) Microbial-degradation of chlorolignins. *Environ Sci Technol* 19:1086–1089
- Eskelinen K, Sarkka H, Kurniawan TA, Sillanpää MET (2010) Removal of recalcitrant contaminants from bleaching effluents in pulp and paper mills using ultrasonic irradiation and Fenton-like oxidation, electrochemical treatment, and/or chemical precipitation: a comparative study. *Desalination* 255:179–187
- Esplugas S, Gimenez J, Contreras S, Pascual E, Rodríguez M (2002) Comparison of different advanced oxidation processes for phenol degradation. *Water Res* 36:1034–1042
- Faust BC, Hoigne J (1990) Photolysis of Fe(III)-hydroxy complexes as sources of OH radicals in clouds, fog and rain. *Atmos Environ A* 24:79–89
- Fontanier V, Albet J, Baig S, Molinier J (2005a) Simulation of pulp mill wastewater recycling after tertiary treatment. *Environ Technol* 26:1335–1344
- Fontanier V, Baig S, Albet J, Molinier J (2005b) Comparison of conventional and catalytic ozonation for the treatment of pulp mill wastewater. *Environ Eng Sci* 22:127–137
- Fontanier V, Farines V, Albet J, Baig S, Molinier J (2006) Study of catalyzed ozonation for advanced treatment of pulp and paper mill effluents. *Water Res* 40:303–310
- Fox MA (1989) Mechanistic photocatalysis in organic synthesis. In: Serpone N, Pellizzetti E (eds) *Photocatalysis, fundamentals and Applications*. Wiley, New York, pp 421–455
- Fujishim A, Honda K (1972) Electrochemical photolysis of water at a semiconductor electrode. *Nature* 238:37–38
- Glaze WH (1987) Drinking-water treatment with ozone. *Environ Sci Technol* 21:224–230
- Glaze WH, Kang JW, Chapin DH (1987) The chemistry of water-treatment processes involving ozone, hydrogen-peroxide and ultraviolet-radiation. *Ozone Sci Eng* 9:335–352
- Gogate PR, Pandit AB (2004a) A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. *Adv Environ Res* 8:501–551
- Gogate PR, Pandit AB (2004b) A review of imperative technologies for wastewater treatment II: hybrid methods. *Adv Environ Res* 8:553–597
- Gomathi G, Kanmani S (2006) Tertiary treatment of pulp and paper industry wastewater by solar photocatalysis and photofenton. *J Inst Public Health Eng* 2006–07:5–10
- Gommers K, De Wever H, Brauns E, Peys K (2007) Recalcitrant COD degradation by an integrated system of ozonation and membrane bioreactor. *Water Sci Technol* 55:245–251
- Gouvea CAK, Wypych F, Moraes SG, Duran N, Peralta-Zamora P (2000) Semiconductor-assisted photodegradation of lignin, dye, and kraft effluent by Ag-doped ZnO. *Chemosphere* 40:427–432
- Gregor KH, Luft G, Yaderdjama F, Baur K (1997) Application of a wet peroxide oxidation system using *p*-toluenesulfonic acid as a model substance. In: Wesley W, Eckenfelder J, Roth A, Bower AR (eds) *Chemical oxidation. Technologies for the nineties*. CRC, Boca Raton, pp 175–196
- Guittonneau S, Delaet J, Duguet JP, Bonnel C, Dore M (1990) Oxidation of parachloronitrobenzene in dilute aqueous-solution by O₃+UV and H₂O₂+UV—a comparative study. *Ozone Sci Eng* 12:73–94
- Gullichsen J, Fogelholm C (1999) *Chemical pulping vol 6B. Papermaking science and technology*. Gummerus Printing, Helsinki
- Habets LHA, Knelissen HJ (1997) In line biological water regeneration in a zero discharge recycle paper mill. *Water Sci Technol* 35:41–48
- Harber F, Weiss JJ (1934) The catalytic decomposition of hydrogen peroxide by iron salts. *J Am Chem Soc* 45:338–351
- Helble A, Schlayer W, Liechti PA, Jenny R, Mobius CH (1999) Advanced effluent treatment in the pulp and paper industry with a combined process of ozonation and fixed bed biofilm reactors. *Water Sci Technol* 40:343–350
- Hermosilla D, Cortijo M, Huang CP (2009a) Optimizing the treatment of landfill leachate by conventional Fenton and photo-Fenton processes. *Sci Total Environ* 407:3473–3481
- Hermosilla D, Cortijo M, Huang CP (2009b) The role of iron on the degradation and mineralization of organic compounds using conventional Fenton and photo-Fenton processes. *Chem Eng J* 155:637–646
- Hermosilla D, Merayo N, Ordóñez R, Blanco A (2012) Optimization of conventional Fenton and ultraviolet-assisted oxidation processes for the treatment of reverse osmosis retentate from a paper mill. *Waste Manag* 32:1236–1243
- Hoffmann MR, Martin ST, Choi WY, Bahnemann DW (1995) Environmental applications of semiconductor photocatalysis. *Chem Rev* 95:69–96
- Hoigne J, Bader H (1983) Rate constants of reactions of ozone with organic and inorganic-compounds in water. 1. Non-dissociating organic-compounds. *Water Res* 17:173–183
- Hostachy JC, Lenon G, Pisicchio JL, Coste C, Legay C (1997) Reduction of pulp and paper mill pollution by ozone treatment. *Water Sci Technol* 35:261–268
- Huang CP, Dong C, Tang Z (1993) Advanced chemical oxidation: its present role and potential future in hazardous waste treatment. *Waste Manag* 13:361–377
- Jans U, Hoigne J (1998) Activated carbon and carbon black catalyzed transformation of aqueous ozone into OH-radicals. *Ozone Sci Eng* 20:67–90
- Joss EN, McGrouther KG, Slade AH (2007) Comparison of the efficacy of oxidative processes and flocculation for the removal of colour from Eop effluent. *Water Sci Technol* 55:57–64
- Jung H, Kappen J, Hesse A, Götz B (2011) Wasser- und Abwassersituation in der deutschen Papier- und Zellstoffindustrie—Ergebnisse der Wasserumfrage 2010 (Water and wastewater situation in German pulp and paper industry—results of water survey 2010). *Wochenbl Pap* 139(9):337–339
- Justino C, Marques AG, Rodrigues D, Silva L, Duarte AC, Rocha-Santos T, Freitas AC (2011) Evaluation of tertiary treatment by fungi, enzymatic and photo-Fenton oxidation on the removal of phenols from a kraft pulp mill effluent: a comparative study. *Biodegradation* 22:267–274
- Kansal SK, Singh M, Sud D (2008) Effluent quality at kraft/soda agro-based paper mills and its treatment using a heterogeneous photocatalytic system. *Desalination* 228:183–190
- Karat I (2013) Advanced oxidation processes for removal of COD from pulp and paper mill effluents—a technical, economical and environmental evaluation. Master of Science Thesis, Royal Institute of Technology, Stockholm
- Karimi S, Abdulkhani A, Karimi A, Ghazali AHB, Ahmadun FR (2010) The effect of combination enzymatic and advanced oxidation process treatments on the colour of pulp and paper mill effluent. *Environ Technol* 31:347–356
- Kavitha V, Palanivelu K (2004) The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol. *Chemosphere* 55:1235–1243
- Kazmi AA, Thul R (2007) Colour and COD removal from pulp and paper mill effluent by Fenton's oxidation. *J Environ Sci Eng* 49:189–194
- Kim SM, Vogelpohl A (1998) Degradation of organic pollutants by the photo-Fenton-process. *Chem Eng Technol* 21:187–191
- Ko C-H, Hsieh P-H, Chang M-W, Chern J-M, Chiang S-M, Tzeng C-J (2009) Kinetics of pulp mill effluent treatment by ozone-based processes. *J Hazard Mater* 168:875–881

- Korhonen S, Tuhkanen T (2000) Effects of ozone on resin acids in thermomechanical pulp and paper mill circulation waters. *Ozone Sci Eng* 22:575–584
- Kreetachat T, Damrongsri M, Punsuwon V, Vaithanomsat P, Chiemchaisri C, Chomsurin C (2007) Effects of ozonation process on lignin-derived compounds in pulp and paper mill effluents. *J Hazard Mater* 142:250–257
- Kumar P, Kumar S, Bhardwaj NK, Choudhary AK (2011) Optimization of process parameters for the photocatalytic treatment of paper mill wastewater. *Environ Eng Manag J* 10:595–601
- Laari A, Korhonen S, Kallas J, Tuhkanen T (2000) Selective removal of lipophilic wood extractives from paper mill water circulations by ozonation. *Ozone Sci Eng* 22:585–605
- Lacorte S, Latorre A, Barceló D, Rigol A, Malmqvist A, Welander T (2003) Organic compounds in paper-mill process waters and effluents. *Trends Anal Chem* 22:725–736
- Langlais B, Reckhow DA, Brink DR (eds) (1991) *Ozone in water treatment: application and engineering*. AWWA Research Foundation and Lewis Publishers, Boca Raton
- Ledakowicz S, Michniewicz M, Jagiella A, Stufka-Olczyk J, Martynelis M (2006) Elimination of resin acids by advanced oxidation processes and their impact on subsequent biodegradation. *Water Res* 40:3439–3446
- Legrini O, Oliveros E, Braun AM (1993) Photochemical processes for water-treatment. *Chem Rev* 93:671–698
- Mansilla HD, Villasenor J, Maturana G, Baeza J, Freer J, Durán N (1994) ZnO-catalyzed photodegradation of kraft black liquor. *J Photochem Photobiol A* 78:267–273
- Mansilla HD, Yeber MC, Freer J, Rodríguez J, Baeza J (1997) Homogeneous and heterogeneous advanced oxidation of a bleaching effluent from the pulp and paper industry. *Water Sci Technol* 35:273–278
- Manttari M, Kuosa M, Kallas J, Nystrom M (2008) Membrane filtration and ozone treatment of biologically treated effluents from the pulp and paper industry. *J Membr Sci* 309:112–119
- Marco A, Esplugas S, Saum G (1997) How and why to combine chemical and biological processes for wastewater treatment. *Water Sci Technol* 35:321–327
- Masten SJ, Davies SHR (1994) The use of ozonation to degrade organic contaminants in wastewaters. *Environ Sci Technol* 28:A180–A185
- Masuyama A, Endo C, Takeda S, Nojima M, Ono D, Takeda T (2000) Ozone-cleavable gemini surfactants. Their surface-active properties, ozonolysis, and biodegradability. *Langmuir* 16:368–373
- Medeiros DR, Pires EC, Mohseni M (2008) Impact of ozonation of alkaline bleach effluent and its impact on biodegradability and molecular weight distribution of organic compounds. *Papel* 69:49–59
- Merayo N, Hermosilla D, Blanco L, Cortijo L, Blanco A (2013) Assessing the application of advanced oxidation processes, and their combination with biological treatment, to effluents from pulp and paper industry. *J Hazard Mater* 262:420–427
- Miranda R, Blanco A (2010) Influence of pulping chemistry on the release of contaminants in recycled paper production. In: Dietz W, Bley-Christen L, Grenz R (eds) *PTS symposium of applied interface chemistry*, Munich
- Miranda MA, Amat AM, Arques A (2001) Abatement of the major contaminants present in olive oil industry wastewaters by different oxidation methods: ozone and/or UV radiation versus solar light. *Water Sci Technol* 44:325–330
- Mobius CH, Cordestolle M (1997) Enhanced biodegradability by oxidative and radiative wastewater treatment. *Water Sci Technol* 35:245–250
- Mobius CH, Helble A (2004) Combined ozonation and biofilm treatment for reuse of paper mill wastewaters. *Water Sci Technol* 49:319–323
- Moodley B, Mulholland DA, Brookes HC (2011) The electro-oxidation of lignin in Sappi Saiccor dissolving pulp mill effluent. *Water SA* 37:33–40
- Moraes SG, Duran N, Freire RS (2006) Remediation of Kraft E1 and black liquor effluents by biological and chemical processes. *Environ Chem Lett* 4:87–91
- Moraes PB, Pelegrino RRL, Bertazzoli R (2007) Degradation of Acid Blue 40 dye solution and dye house wastewater from textile industry by photo-assisted electrochemical process. *J Environ Sci Health A* 42:2131–2138
- Morais ADA, Mounter AH, Silveira DSA (2008) Improvement of eucalyptus bleached kraft pulp effluent treatment through combined ozone-biological treatment. *Tappi J* 7:26–32
- Mounter AH, Pereira RO, Morais AA, Ruas DB, Silveira DSA, Viana DB, Medeiros RC (2007) Advanced oxidation of bleached eucalypt kraft pulp mill effluent. *Water Sci Technol* 55:109–116
- Muñoz I, Rieradevall J, Torrades F, Peral J, Domenech X (2006) Environmental assessment of different advanced oxidation processes applied to a bleaching Kraft mill effluent. *Chemosphere* 62:9–16
- Nakamura Y, Sawada T, Kobayashi F, Godliving M (1997) Microbial treatment of kraft pulp wastewater pretreated with ozone. *Water Sci Technol* 35:277–282
- Nakamura Y, Daidai M, Kobayashi F (2004) Ozonolysis mechanism of lignin model compounds and microbial treatment of organic acids produced. *Water Sci Technol* 50:167–172
- Nebel C, Gottschling RD, O'Neill HJ (1974) Ozone: a new method to remove color in secondary effluents. *Pulp Pap* 48:142–145
- Öeller HJ, Demel I, Weinberger G (1997) Reduction in residual COD in biologically treated paper mill effluents by means of combined ozone and ozone/UV reactor stages. *Water Sci Technol* 35:269–276
- Öeller HJ, Offermanns U (2002) Successful start-up of the world's 1st ozone-based effluent recirculation system in a paper mill. In: NJD G (ed) *Proceedings of the international conference advances in ozone science and engineering: environmental processes and technological applications*, Hong Kong, 15–16 April 2002, p 365–372
- Ordóñez R, Hermosilla D, Pio IS, Blanco A (2010) Replacement of fresh water use by final effluent recovery in a highly optimized 100% recovered paper mill. *Water Sci Technol* 62:1694–1703
- Ordóñez R, Hermosilla D, Merayo N, Gascó A, Negro C, Blanco A (2014) Reviewing the application of multi-barrier membrane filtration technologies to reclaim municipal wastewater for industrial water use. *Sep Purif Rev* 43:263–310
- Pereira R, Antunes SC, Gonçalves AMM, Marques SM, Gonçalves F, Ferreira F, Freitas AC, Rocha-Santos TAP, Diniz MS, Castro L, Peres I, Duarte AC (2009) The effectiveness of a biological treatment with *Rhizopus oryzae* and of a photo-Fenton oxidation in the mitigation of toxicity of a bleached kraft pulp mill effluent. *Water Res* 43:2471–2480
- Pérez M, Torrades F, Peral J, Lizama C, Bravo C, Casas S, Freer J, Mansilla HD (2001) Multivariate approach to photocatalytic degradation of a cellulose bleaching effluent. *Appl Catal B* 33:89–96
- Pérez M, Torrades F, Domenech X, Peral J (2002a) Removal of organic contaminants in paper pulp effluents by AOPs: an economic study. *J Chem Technol Biotechnol* 77:525–532
- Pérez M, Torrades F, García-Hortal JA, Domenech X, Peral J (2002b) Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions. *Appl Catal B* 36:63–74
- Perng YS, Wang IC, Yu ST, Lin YF (2008) Application of an electro-oxidation treatment method to industrial paper mill effluents in the lab. *Taiwan J For Sci* 23:111–123
- Pignatello JJ, Liu D, Huston P (1999) Evidence for an additional oxidant in the photoassisted Fenton reaction. *Environ Sci Technol* 33:1832–1839
- Pignatello JJ, Oliveros E, MacKay A (2006) Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Crit Rev Environ Sci Technol* 36:1–84
- Pirkanniemi K, Metsdrinne S, Sillanpaa M (2007) Degradation of EDTA and novel complexing agents in pulp and paper mill process and waste waters by Fenton's reagent. *J Hazard Mater* 147:556–561

- Pokhrel D, Viraraghavan T (2004) Treatment of pulp and paper mill wastewater—a review. *Sci Total Environ* 333:37–58
- Prat C, Vicente M, Esplugas S (1988) Treatment of bleaching waters in the paper industry by hydrogen peroxide and ultraviolet radiation. *Water Res* 22:663–668
- Prat C, Vicente M, Esplugas S (1989) Ozonation of bleaching waters of the paper industry. *Water Res* 23:51–55
- Reyes J, Dezotti M, Mansilla H, Villasenor J, Esposito E, Duran N (1998) Biomass photochemistry-XXII: combined photochemical and biological process for treatment of Kraft E1 effluent. *Appl Catal B* 15: 211–219
- Rodrigues AC, Boroski M, Shimada NS, Garcia JC, Nozaki J, Hioka N (2008) Treatment of paper pulp and paper mill wastewater by coagulation-flocculation followed by heterogeneous photocatalysis. *J Photochem Photobiol A* 194:1–10
- Rodríguez J, Fuentes S, Freer J, Mansilla HD, Ferraz A, Baeza J (1998) Response to ozonation of different cellulose pulp bleaching effluents. *Environ Technol* 19:75–81
- Roy-Arcand L, Archibald F (1996) Selective removal of resin and fatty acids from mechanical pulp effluents by ozone. *Water Res* 30:1269–1279
- Safarzadeh-Amiri A, Bolton JR, Cater SR (1996) The use of iron in advanced oxidation processes. *J Adv Oxid Technol* 1:18–26
- Salokannel A, Heikkinen J, Kumpulainen M, Sillanpaa M, Turunen J (2007) Tertiary treatment of pulp and paper mill wastewaters by ozonation and O₃/H₂O₂ techniques. *Pap Puu* 89:348–351
- Sarria V, Parra S, Adler N, Peringer P, Benitez N, Pulgarin C (2002) Recent developments in the coupling of photoassisted and aerobic biological processes for the treatment of biorecalcitrant compounds. *Catal Today* 76:301–315
- Schlichter B, Mavrov V, Chmiel H (2003) Study of a hybrid process combining ozonation and membrane filtration—filtration of model solutions. *Desalination* 156:257–265
- Schmidt T, Lange S (2000) Treatment of paper mill effluent by the use of ozone and biological systems: large scale application at Lang paper, Ettringen (Germany). In: TAPPI 2000 Environmental Conference & Trade Fair Proceedings, Denver, 6–10 May 2000
- Selvbharathi G, Kanmani S (2010) Tertiary treatment of pulp and paper industrial wastewater by electro-Fenton process. *J Environ Sci Eng* 52:103–106
- Sevimli MF (2005) Post-treatment of pulp and paper industry wastewater by advanced oxidation processes. *Ozone Sci Eng* 27:37–43
- Sun YF, Pignatello JJ (1993) Photochemical-reactions involved in the total mineralization of 2,4D by Fe³⁺/H₂O₂/UV. *Environ Sci Technol* 27:1696
- Sundholm J (1999) Mechanical pulping. Papermaking science and technology. Gummerus Printing, Helsinki
- Tambosi JL, Di Domenico M, Schirmer WN, Jose HJ, Moreira R (2006) Treatment of paper and pulp wastewater and removal of odorous compounds by a Fenton-like process at the pilot scale. *J Chem Technol Biotechnol* 81:1426–1432
- Tanaka S, Ichikawa T (1993) Effects of photolytic pretreatment on biodegradation and detoxification of surfactants in anaerobic-digestion. *Water Sci Technol* 28:103–110
- Tanaka K, Calanag RCR, Hisanaga T (1999) Photocatalyzed degradation of lignin on TiO₂. *J Mol Catal A* 138:287–294
- Thompson G, Swain J, Kay M, Forster CF (2001) The treatment of pulp and paper mill effluent: a review. *Bioresour Technol* 77:275–286
- Toor AP, Singh V, Jotshi CK, Bajpai PK, Verma A (2007) Treatment of bleaching effluent from the pulp and paper industry by photocatalytic oxidation. *Tappi J* 6:9–13
- Torrades F, Pérez M, Mansilla HD, Peral J (2003) Experimental design of Fenton and photo-Fenton reactions for the treatment of cellulose bleaching effluents. *Chemosphere* 53:1211–1220
- Torrades F, Saiz S, García-Hortal JA (2011) Using central composite experimental design to optimize the degradation of black liquor by Fenton reagent. *Desalination* 268:97–102
- Tuhkanen T, Naukkarinen M, Blackburn S, Tanskanen H (1997) Ozonation of pulp mill effluent prior to activated sludge treatment. *Environ Technol* 18:1045–1051
- Ugurlu M, Karaoglu MH (2009) Removal of AOX, total nitrogen and chlorinated lignin from bleached Kraft mill effluents by UV oxidation in the presence of hydrogen peroxide utilizing TiO₂ as photocatalyst. *Environ Sci Pollut Res* 16:265–273
- Vieira A, Steenken S (1987) Pattern of OH radical reaction with N₆, N₆-dymethyladenosine—production of 3 isomeric OH adducts and their dehydration and ring-opening reactions. *J Am Chem Soc* 109:7441–7448
- Wang R, Chen CL, Gratzl JS (2004) Dechlorination and decolorization of chloro-organics, in pulp bleach plant E-1 effluents, by advanced oxidation processes. *Bioresour Technol* 94:267–274
- Wang R, Chen CL, Gratzl JS (2005) Dechlorination of chlorophenols found in pulp bleach plant E-1 effluents by advanced oxidation processes. *Bioresour Technol* 96:897–906
- Xu MJ, Wang QS, Hao YL (2007) Removal of organic carbon from wastepaper pulp effluent by lab-scale solar photo-Fenton process. *J Hazard Mater* 148:103–109
- Yeber MC, Rodríguez J, Baeza J, Freer J, Zaror C, Duran N, Mansilla HD (1999a) Toxicity abatement and biodegradability enhancement of pulp mill bleaching effluent by advanced chemical oxidation. *Water Sci Technol* 40:337–342
- Yeber MC, Rodríguez J, Freer J, Baeza J, Duran N, Mansilla HD (1999b) Advanced oxidation of a pulp mill bleaching wastewater. *Chemosphere* 39:1679–1688
- Yeber MC, Rodríguez J, Freer J, Duran N, Mansilla HD (2000) Photocatalytic degradation of cellulose bleaching effluent by supported TiO₂ and ZnO. *Chemosphere* 41:1193–1197
- Yeber MC, Onate KP, Vidal G (2007) Decolorization of kraft bleaching effluent by advanced oxidation processes using copper (II) as electron acceptor. *Environ Sci Technol* 41:2510–2514
- Zahrim AY, Gilbert ML, Janaun J (2007) Treatment of pulp and paper mill effluents using photo-Fenton's process. *J Appl Sci* 7: 2164–2167