

ADVANCED OXIDATION OF BLEACHED EUCALYPT KRAFT PULP MILL EFFLUENT

A. H. Mounteer, R. O. Pereira, A. A. Morais, D. B. Ruas D. S.A. Silveira, D. B. Viana, R. C. Medeiros
Civil Engineering Department, Federal University of Viçosa, 36570-000 - Viçosa - MG – Brazil
(Email: ann@ufv.br)

Abstract In this study a poorly biodegradable (BOD/COD = 0.3) industrial alkaline ECF bleaching filtrate was treated using different advanced oxidation processes to evaluate their use in combined chemical-biological treatment aimed at increasing recalcitrant COD removal and improving final effluent quality. Oxidative treatments included ozonation combined with hydrogen peroxide (2, 5, 10, 20mM O₃/0.7, 2, 5, 10 mM H₂O₂) and photocatalysis with hydrogen peroxide (UV/2, 4 and 8 mM H₂O₂) and with TiO₂ (UV/TiO₂/0.7 and 4mM H₂O₂). The O₃/H₂O₂ process increased effluent biodegradability by up to 68% as a result of increasing BOD and decreasing COD. Increasing the O₃ dose had a greater effect on biodegradability improvement and lignin and color removal efficiencies than increasing the H₂O₂ dose. A combined oxidant dose of 5mM O₃ and 2mM H₂O₂ resulted in 75% lignin removal, 40% color removal and 6% carbohydrate loss without mineralizing the organic carbon. The photocatalytic processes generally led to a decrease in effluent biodegradability as a combined result of decreasing BOD and increasing COD and did not result in efficient lignin or color removal. Photocatalytic oxidation was apparently inhibited by the high chloride (870 mg/L) and COD (1867 mg/L) levels in the alkaline filtrate, and may be more efficient in recalcitrant COD removal if performed after biological.

Keywords advanced oxidation processes, ECF bleaching, eucalypt, ozonation, photocatalysis, recalcitrant organic matter

Introduction

Biological treatment typically achieves from 40 to 70% removal of chemical oxygen demand (COD) in bleached kraft pulp mill effluents (Pokrel & Viraraghavan, 2004) and the recalcitrant organic matter remaining after effluent treatment has become the focus of increasingly strict legislation worldwide (Konduru et al., 2001). Among the technologies developed in recent years to increase effluent treatment efficiency, advanced oxidation processes (AOPs) have received much attention given their proven potential oxidize toxic and/or recalcitrant organic compounds found in bleaching effluents, such as lignin and chlorophenols, and thereby increase effluent biodegradability (Mansilla et al., 1997; Yeber et al., 1999; Chang et al., 2004). It has been reported that the heterogeneous photocatalytic process catalyzed by titanium dioxide (UV/TiO₂) efficiently removes color and total organic carbon (TOC) from ECF bleaching effluents and lignin containing solutions and that addition of small amounts of hydrogen peroxide (UV/TiO₂/H₂O₂) can improve chemical oxygen demand (COD) removal, especially at pH <7.5 (Peralta-Zamora et al., 1998; Pérez et al., 2001; Machado et al., 2003; Chang et al, 2004). However, Yeber et al. (1999) reported that homogeneous processes using ozone (O₃ and O₃/UV) are more effective than the heterogeneous systems for increasing bleaching effluent biodegradability and ozone is more efficiently applied at pH>10 (Gogate & Pandit, 2004).

Use of AOPs for pulp and paper mill effluent treatment will only be economically attractive if combined with biological treatment (Möbius & Cordes-Tolle, 1997; Sarria et al., 2002). All AOPs are based on the formation of hydroxyl radicals, strong oxidizing agents that can break down complex organic structures into simpler compounds, thus facilitating their removal during subsequent biological treatment (Marco et al., 1997). However, Balcioglu and Çeçen (1999) observed that heterogeneous photocatalytic systems are only applicable to bleaching effluents with relatively low COD and chloride contents, and therefore suggested that biological treatment should be used prior to this AOP in order to reduce the levels of these two parameters. It is highly recommended that pilot studies be performed for each effluent under consideration, since oxidative treatment efficiency is strongly influenced by effluent chemical composition and AOPs may be inhibited by certain inorganic substances,

such as chloride ions that react with hydroxyl radicals to form chlorine radicals (Balcioglu & Çeçen, 1999; Gogate & Pandit, 2004a,b). This study was thus undertaken to identify AOP alternatives for use in combination with biological treatment to increase removal of recalcitrant organic matter and improve final effluent quality of eucalypt bleached kraft pulp effluents.

Material and Methods

Effluent

Alkaline bleaching filtrate was collected in May and October, 2005 from the DEopDP bleaching line of a Brazilian mill producing approximately 2400 ton/d of fully bleached eucalypt kraft pulp. The effluent was pre-filtered (Whatman qualitative filter paper) and stored at 4°C until used. Chemical characteristics of the effluent are listed in Table 1. The filtrate presented low biodegradability (BOD/COD = 0.3), making it a good candidate for AOP treatment.

Table 1. Chemical characteristics of the ECF alkaline filtrate evaluated. (Values reported are means \pm standard deviation for the two sampling dates).

Parameter	Value
COD	1867 \pm 72
TOC	894 \pm 192
BOD	556 \pm 45
Lignin, mg phenol/L	14 \pm 1.6
Carbohydrates, mg glucose/L	111 \pm 5
Color, mg Pt/L	604 \pm 42
Chloride, mg Cl ⁻ /L	870
pH	10.7

Advanced Oxidation Processes

Given that the alkaline filtrate had a residual of 0.7mM H₂O₂, AOPs containing H₂O₂ and previously reported as capable of removing COD and color from bleaching effluents were evaluated. These were: O₃/H₂O₂, UV/H₂O₂ and UV/TiO₂/H₂O₂.

Ozone treatments were performed in a one liter vertical glass bubble reactor placed in a 70°C water bath and connected to wash bottle filled with potassium iodide solution to trap residual ozone, and used to calculate true ozone consumption. Ozone was produced from pure oxygen in a laboratory ozone generator (Sumitomo Precision Products, Hyogo, Japan). Ozone flow was adjusted to 9-11 mg/min, and ozone doses were varied from 100 to 1000 mg/L by increasing contact time. The desired amount of a 30% (w/v) solution of H₂O₂ was added to the reactor before applying the ozone. Effluents were preconditioned at a temperature of 70°C in the water bath before treatment.

Photocatalysis was performed in a glass reactor with a 1.8 liter working volume, equipped at its center with a 125W mercury vapor lamp (glass cover removed) encased in a quartz sleeve. Effluent was circulated through a 500mL beaker held in an ice bath to maintain temperature within the reactor at 30-35°C. The desired amount of a 30% (w/v) solution of H₂O₂ was added to the reactor before starting irradiation. For heterogeneous photocatalysis tests, a film of TiO₂ (Degussa P25) was immobilized on the inner surface of the reactor by thermal fixation (three cycles of 1h at 250°C). Effluent samples were removed after 0.5, 1, 2, 4 and 8 h of irradiation for characterization.

Effluent Characterization

Effluents were characterized by measuring COD, DBO₅, dissolved organic carbon (DOC), and lignin according to the Standard Methods (1998), color by the Canadian Pulp and Paper

Association proposed method (CPPA, 1993) and carbohydrates by the modified anthrone procedure (Jenkins et al., 1993). DOC was quantified in a Shimadzu TOC 500 analyzer (Tokyo, Japan). Effluents were filtered (Whatman qualitative filter paper or Millipore AP40 membrane) before analyses, which were performed in triplicate and are reported as average values.

Chemical residuals (O_3 and H_2O_2) were measured by the appropriate iodometric titrations after each oxidative treatment. Oxidant residuals were destroyed by adding a stoichiometric equivalent of sodium bisulfite to the effluents before performing COD and BOD analyses.

Results of the advance oxidation processes were interpreted based on values of environmental parameters as well as the by biodegradability (BOD/COD ratio) and average oxidation state (AOS), which was calculated by the equation $AOS = 4 \cdot [(DOC - COD)] / DOC$ (Sarria et al., 2002). The AOS can be used to determine oxidant doses, based on the assumption that addition of oxidant beyond the point at which the AOS value levels off would be wasteful.

Results and Discussion

Results of O_3/H_2O_2 treatment of the alkaline filtrate are presented in Figures 1 and 2. Effluent pH dropped by about one unit when the ozone dose increased from 2 to 20 mM. The pH drop was 0.2 - 0.3 units greater when the peroxide dose was raised from 0.7 to 10 mM H_2O_2 , at a given ozone dose. Ozone residuals (expressed as percent of initial dose) rose with the increase in ozone dose but were less than 15% of the initial charge, even at a dose of 20 mM O_3 . For given ozone dose, increasing the peroxide dose resulted in lower ozone residuals, suggesting that peroxide led to more rapid ozone degradation (Gogate & Pandit, 2004b). Peroxide residuals were only found when 10mM H_2O_2 was charged.

COD removal reached 19-21% at a combined oxidant dose of 10mM $O_3/4mM H_2O_2$. Raising the ozone dose had a more pronounced effect on decreasing COD than raising the hydrogen peroxide dose, since 200-250 units of COD were lost when ozone increased from 0 to 10 mM O_3 for a given peroxide dose, while only about 60 units of COD were lost when the peroxide dose was increased from 0 to 10 mM H_2O_2 for a given ozone dose. BOD rose initially, with a 33-42% increase at a dose of 5mM O_3 , and then dropped off to a 9-26% increase at 20mM O_3 . Once again, the ozone dose had a greater effect on BOD behavior than the peroxide dose. DOC was affected only slightly by the oxidative treatment, presenting a loss of about 3% at a dose of 5mM O_3 and a loss of 6% at 20mM O_3 . H_2O_2 had little effect on the DOC content except at the highest dose tested (10mM). At this peroxide dose a smaller loss in DOC was observed when the ozone dose was 10mM O_3 or greater. The small DOC loss indicates that although organic matter was oxidized (loss in COD), it was not mineralized, and thus oxidant was not wasted on a transformation that is more economically achieved during biological treatment (Sarria et al., 2002; Pokhrel & Viraraghavan, 2004).

Color decreased continually with the increase in ozone and at 20mM O_3 , color removal reached 70% when the peroxide dose was 2mM H_2O_2 or greater. There was a 40-47% color loss at 5mM O_3 , regardless of peroxide dose. Ozone clearly had a much greater effect on color removal than peroxide dose, but this effect decreased at ozone doses of 10mM O_3 or greater. Lignin removal was directly proportional to the ozone dose, and reached 65-80% at a dose of 5mM O_3 . Increasing the peroxide dose resulted in a slightly lower lignin removal at a given ozone dose. Carbohydrate content also fell with the increase in ozone but to a proportionally lesser extent than the lignin phenolic fraction, presenting only an 18% loss at a dose of 20mM O_3 . No clear relation was observed between peroxide dose and carbohydrate removal. Color removal by ozone is well documented in the literature (Zhou & Smith, 1997). Preferential attack of ozone on lignin as compared to carbohydrates in ECF bleaching effluents has also been reported (Mounteer & Mokfienski, 2005).

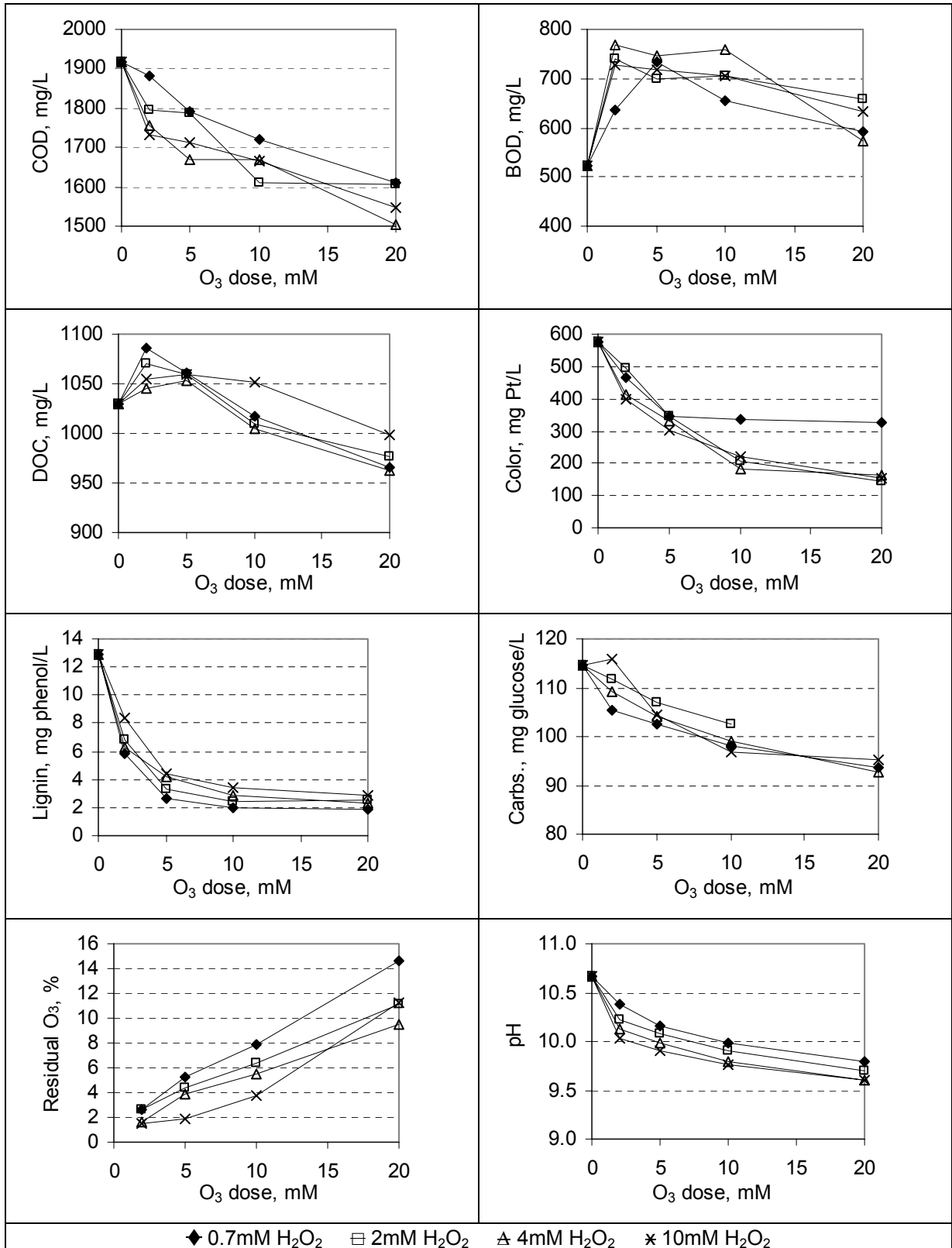


Figure 1. Effects of O₃ and H₂O₂ doses on effluent quality after advanced oxidation of alkaline ECF bleaching filtrate by the O₃/H₂O₂ process.

As presented in Figure 2, effluent biodegradability increased by 26-68%, reaching maximum values at doses of 2 to 10mM O₃, and then dropped off slightly. The increases in biodegradability resulted from increases in BOD and concomitant decreases in COD. Relatively smaller increases were observed for the ozone treatments without added H₂O₂ than when at least 2mM H₂O₂ was applied. It has previously been shown that the increase in biodegradability produced by ozone treatment results both from transformation of high molecular mass matter into low molecular mass matter (Bijan & Mohseni, 2004; Munteer & Mokfienski, 2005) and increased biodegradability of the high molecular mass fraction (Bijan & Mohseni, 2004). Effluent average oxidation states increased by 0.7-1.2 units with the increase in ozone dose up to 5mM O₃, and then leveled off (Figure 2). Once again, adding at least 2mM H₂O₂ had a beneficial effect on increasing the average oxidation state.

The graphs presented in Figure 2 clearly show that for the alkaline filtrate evaluated, the optimal oxidant charges for O₃/H₂O₂ pretreatment are 2-5mM O₃/2mM H₂O₂. The relatively large increases in BOD combined with efficient removal of the potentially toxic phenolic fraction and the relatively small mineralization rate observed using these oxidant doses are desired characteristics for AOP pretreatment of industrial effluents (Marco et al., 1997). Combining the pretreatment with an aerobic biological treatment is expected to lead to improved overall effluent quality.

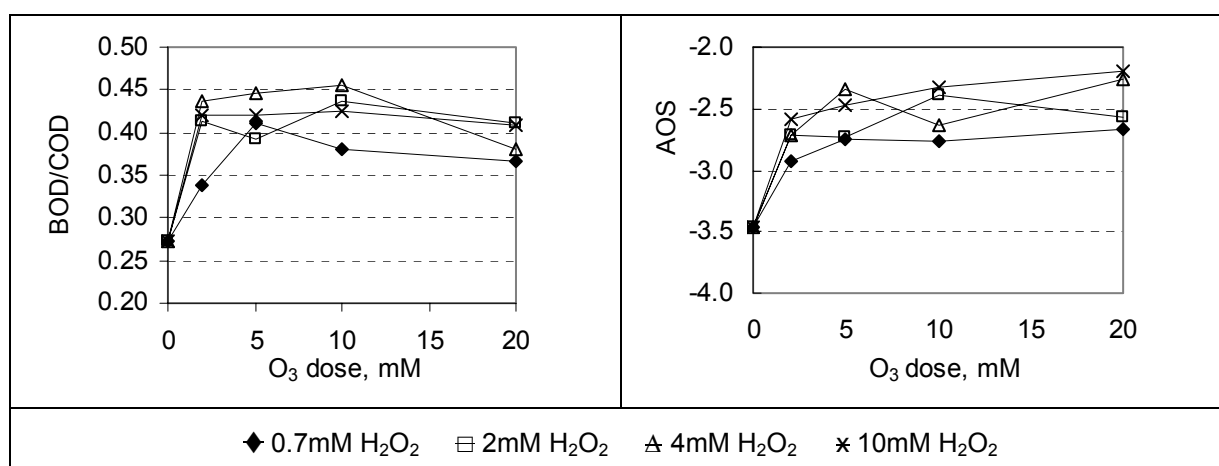


Figure 2. Effects of O₃ and H₂O₂ doses on effluent biodegradability (BOD/COD) and average oxidation state (AOS) after advanced oxidation of alkaline ECF bleaching filtrate by the O₃/H₂O₂ process. (Constant conditions: temperature = 70C, initial pH10,7).

Results of photocatalytic treatment of the alkaline ECF bleaching filtrate are presented in Figures 3 and 4. Peroxide consumption occurred for up to four hours of irradiation under all conditions tested, and then stabilized for all conditions except the heterogeneous process without added peroxide. This condition was the only one in which all original peroxide (0.7mM H₂O₂) was consumed after 8h of irradiation. Effluent pH fell by 0.7 to 1.5 units after 8h irradiation, and the pH drop increased with the increase in H₂O₂ dose in both the homogeneous and heterogeneous processes.

Effluent behavior varied considerably in both the homogeneous (UV/H₂O₂) and heterogeneous (UV/H₂O₂/TiO₂) treatments, especially within the first two hours of irradiation, after which values of effluent parameters tended to stabilize. In the presence TiO₂ catalyst, effluent COD decreased by up to 8%, whereas in its absence, COD increased by up to 16% (8mM H₂O₂, 4h irradiation). Effluent BOD increased by 23% after 2h in the presence of TiO₂/0.7mM H₂O₂ but decreased by 25% after 2h using 8mM H₂O₂ but no TiO₂. Effluent DOC generally increased with the increase in peroxide dose (32% at 8mM H₂O₂, 2h), but increases were lower in the presence of TiO₂. Lignin phenolic content increased under all conditions, except UV/TiO₂/0.7mM H₂O₂, while carbohydrates exhibited a mixed response under the various conditions tested.

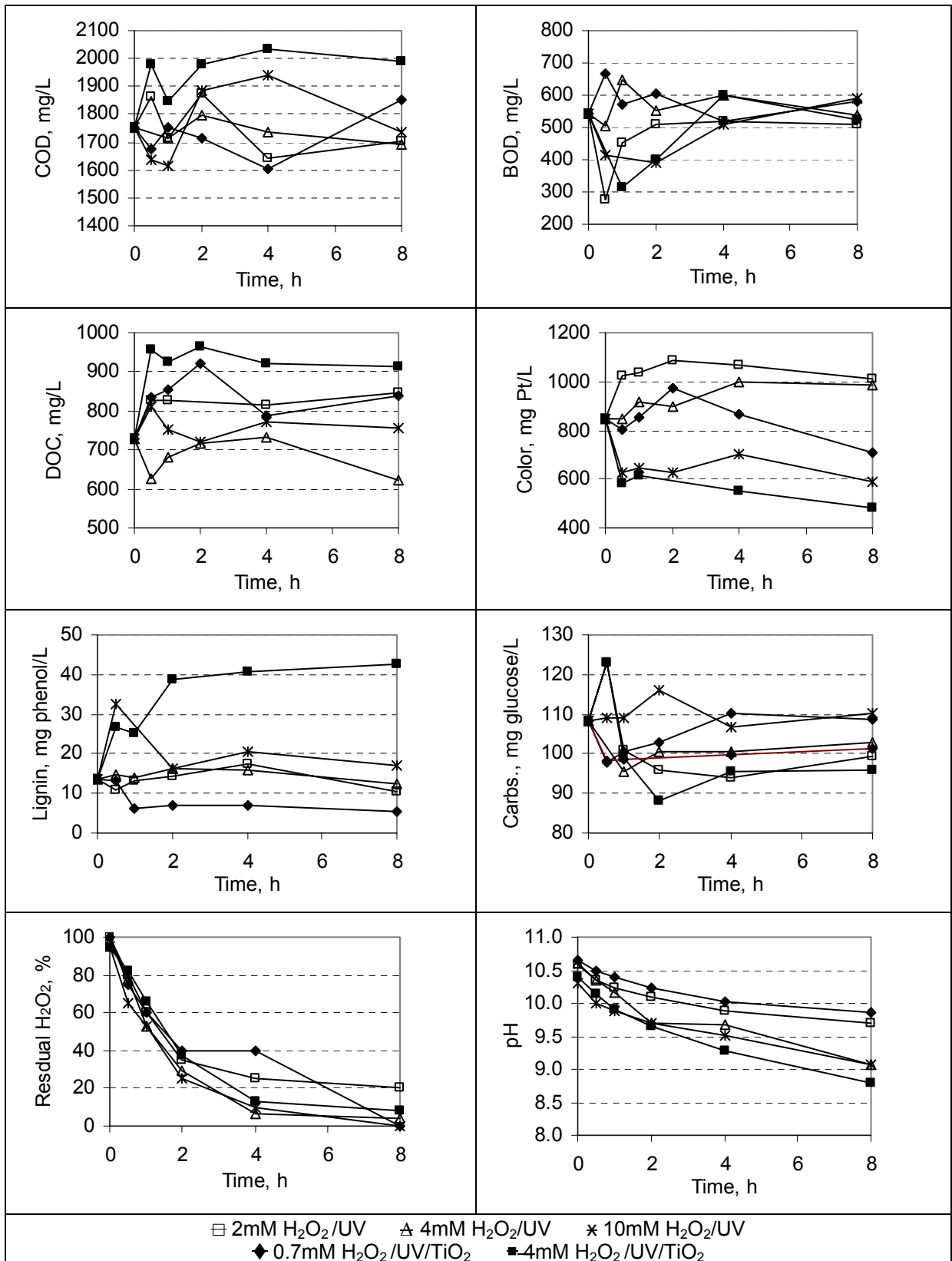
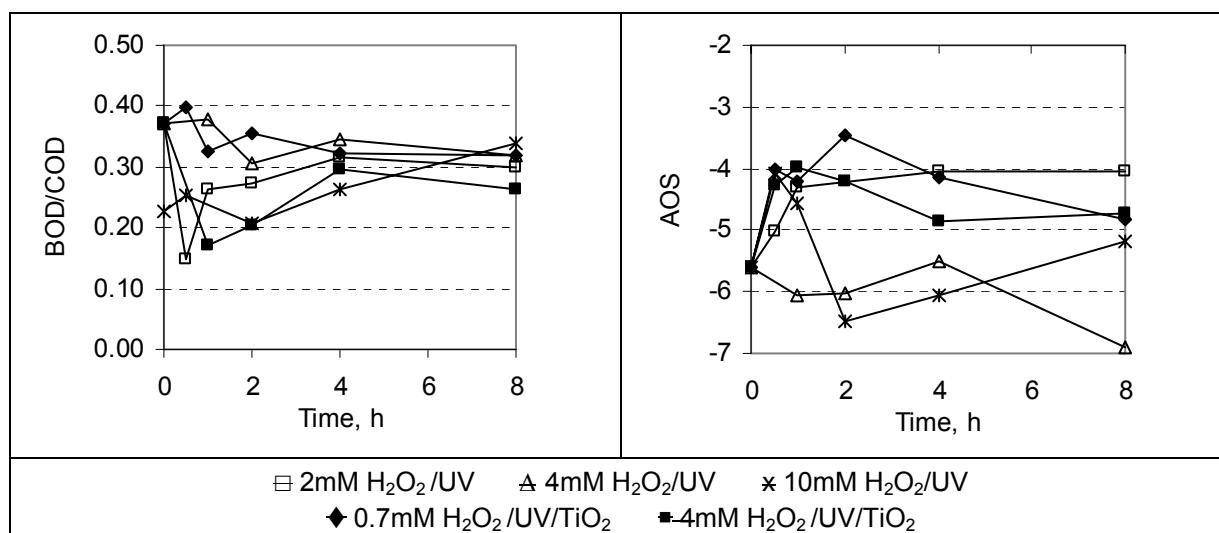


Figure 2. Results of photocatalytic treatment of eucalypt kraft pulp alkaline bleaching filtrate by UV/H₂O₂ and UV/H₂O₂/TiO₂ processes. (Temperature 30-35C, initial pH 10,7).

Effluent color increased by up to 28% during homogeneous photocatalysis at low peroxide doses (2 and 4 mM H₂O₂), but decreased by over 25% using the highest peroxide dose (8mM H₂O₂) and in the heterogeneous process (4mM H₂O₂/TiO₂). Chang et al. (2004) showed that the UV/TiO₂ process at pH 3 (<7.5) could remove up to 99% of the color of lignin containing effluent color, while Peralta-Zamora et al. (1998) reported removal of 60% of the color after 60 min UV irradiation of alkaline effluent at pH 5.1, using 1g TiO₂/L. We studied the effect of pH by treating the alkaline filtrate using the UV/TiO₂ process after adjusting filtrate pH to 4 and 7, but no beneficial effect was observed on any effluent parameter (data not shown).

The increases observed in organic matter content may result from transformation of colloidal matter (that did not originally pass through the membrane used to filter the effluents) into soluble matter during the oxidative treatment. Transformation of high molecular mass organic matter into low molecular mass matter during heterogeneous photocatalysis of eucalypt kraft pulp ECF bleaching filtrates has already been reported (Mounteer & Pereira, 2004).

Effluent biodegradability decreased under all photocatalytic conditions tested, as shown in Figure 4. The loss in biodegradability occurred as a combined result of increase in COD and decrease, or smaller percent increase, in effluent BOD. The average oxidation state of the effluent increased for the heterogeneous processes and the homogenous process with 2mM H₂O₂, indicating that the COD increased proportionally less, or decreased in relation to the effluent DOC, a desired effect. Photocatalytic oxidation did not result in significant lignin, color and COD removals, as have previously been reported for bleaching effluents (Peralta, Zamora et al., 1998; Yeber et al., 1999; Pérez et al., 2001; Machado et al., 2003; Chang et al., 2004;) Balcioğlu and Çeçen (1999) reported that photocatalytic oxidation of bleaching effluents is inhibited by both high levels of COD and chlorides. The high chloride ion (870mg/L) and COD (1867 mg/L) levels of the alkaline filtrate evaluated in the present study apparently interfered with the photocatalytic process, which suggests that this process may be more effective when used after biological treatment to remove the residual recalcitrant COD.



Conclusion

Advanced oxidation of an industrial alkaline ECF bleaching filtrate by the O₃/H₂O₂ process increased effluent biodegradability by up to 68% as result of increasing BOD and decreasing COD, without mineralizing organic carbon. Increasing the O₃ dose resulted in greater increases in BOD and greater reductions in lignin and color than increasing the H₂O₂ dose. Homogeneous (UV/H₂O₂) and heterogeneous (UV/TiO₂/H₂O₂) photocatalytic treatment was not effective in increasing effluent biodegradability since it resulted in BOD removal.

Furthermore, photocatalysis did not result in lignin or color removal, and was apparently inhibited by the high chloride and COD contents of the alkaline filtrate. The results of this study illustrate the need for pilot studies to evaluate the potential application of AOPs for removing recalcitrant organic matter in pulp bleaching effluents.

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