# COMBINED CHEMICAL BIOLOGICAL TREATMENT OF BLEACHED EUCALYPT KRAFT PULP MILL EFFLUENT

D. B. Ruas, A. H. Mounteer* , A. C. Lopes, B. L. Gomes, F. B. Dutra, L. M. Girondoli
Civil Engineering Department, Federal University of Viçosa, 36570-000 - Viçosa - MG - Brazil
(Email: ann@ufv.br),

**Abstract.** The effectiveness of ozonation before and after biological treatment for removal of recalcitrant organic matter in bleached kraft pulp effluents was compared. Two industrial ECF bleached eucalypt kraft pulp effluents (E1 and E2) were pretreated with 100 mg $O_3$ /L. Raw and pretreated effluents were treated biologically in bench-scale sequencing batch reactors, under constant conditions. Following biological treatment, the effluents were post-treated with 100 and 200 mg $O_3$/L. Effluent pretreatment increased effluent biodegradability by 10% in E1 and 24% in E2 while ultimate BOD increased only in effluent E1 (36%). Combined $O_3$-biological treated led to small, but significant, increases in COD, BOD and lignin removal over biological treatment alone, but pretreatment had no significant effect on effluent color and carbohydrate removal. Ozone pretreatment did not affect biological activity during treatment of effluent E1 but resulted in a 38% lower specific oxygen uptake rate in effluent E2. At an equivalent dose of 100mg/L, pre-ozonation produced better quality effluent than post-ozonation, especially with regard to COD and color. Likewise, when an equivalent dose of 200 mg/L was applied, splitting the dose equally between pre and post-treatments was more efficient than applying the entire dose in the post-treatment. The potential for combined chemical – biological treatment to improve effluent quality has been confirmed in this study.

**Keywords**. biodegradability, biological treatment, ECF, eucalypt, ozone, recalcitrant COD

## Introduction

Kraft pulp mills produce relatively large volumes of effluents containing recalcitrant organic matter, represented by the chemical oxygen demand (COD) that remains after biological treatment. Increasingly stringent effluent quality requirements are being incorporated into mill operating licenses, especially with regard to COD and color discharges. For example, World Bank guidelines for financing new kraft pulp mills include limits of 300 mg COD $L^{-1}$ and 15 kg COD per ton of pulp (World Bank, 1999). These stricter regulations stem from the fact that model ecosystem studies have indicated a correlation between effluent COD and adverse effects, such as toxicity, observed in receiving waters, which suggests that a decrease in the amount of dissolved organic matter liberated to the environment determines the adverse environmental effects of effluents (Tana & Lehtinen, 1996; Konduru, 2001). However, Archibald et al. (1998) found little or no correlation exists between COD and effluent chronic toxicity. Despite this controversy on the true environmental significance of COD remaining in biologically treated effluents, Brazilian kraft pulp mill operating licenses include effluent COD limits, usually expressed as concentrations (mg/L) and not production loads (kg/ton), which typically vary 350 mg/L to below 150 mg/L. Well-operated pulp mill effluent treatment systems are able to achieve average reductions of 90 to 95 % for BOD, but only 40 to 70% for COD (Yousefian & Reeve, 2000) and the lower COD limits being implemented in Brazil are not readily met using conventional aerobic biological treatment systems.

Ozone ($O_3$) was first applied in tertiary treatment of pulp mill effluents to improve final effluent quality (Hostachy et al., 1997; Zhou & Smith, 1997) but its use in pretreatment to increase effluent biodegradability and improve biological treatment efficiency is currently being investigated (Mansilla et al., 1997; Yeber et al., 1999; Bijan & Mohseni, 2004; Mounteer & Mokfienski, 2005). In pre-treatment, the goal of ozonation is to only partially degrade recalcitrant organic matter and it has recently been shown that ozonation can lead to concomitant increase in the low molecular weight fraction and reduction in the high molecular weight fraction of the organic matter in eucalypt (Mounteer & Mokfienski, 2005) and softwood (Bijan & Mohseni, 2004) ECF bleaching effluents. It has also been shown that, the low molecular weight matter in eucalypt ECF bleaching effluents is more readily removed during biological treatment (Mounteer et al., 2002; Souza et al., 2003), but it remains to be shown that partial degradation of organic matter by ozone will lead to increased biological treatment efficiency, and improved overall effluent quality. The objective of this study was thus to evaluate the potential of combined ozone-biological treatment of bleaching effluents for increasing overall COD removal and to compare the effectiveness of pre and post-ozone treatments for improving final effluent quality.

## Methods

*Effluents*

Effluents were collected at a Brazilian mill producing approximately 2400 ton/d of fully bleached eucalypt kraft pulp in two separate ECF bleaching lines. Combined acid and alkaline filtrates were collected and combined proportionally to produce effluents E1 (DEopDEpD bleaching sequence) and E2 (DEopDP bleaching sequence). Effluents were collected from each of the two production lines on three occasions between October 2004 and May 2005 for use in this study. The effluents were pre-filtered (Whatman qualitative filter paper) and stored at 4ºC until used. The ECF bleaching effluents were treated with ozone both before and after biological treatment in order to compare the relative effects of pre- and post-ozone treatments on final effluent quality. After each treatment, the effluents were characterized by measuring environmental parameters, as well as lignin and carbohydrates, two important classes of organic compounds in bleaching effluents (Herstad-Svard et al., 1997).

*Ozonation*

Ozone treatments were performed in a one liter vertical glass bubble reactor placed in a 35ºC water bath and connected to wash bottle filled with potassium iodide solution (0.1L 1N KI, 0.5L 4N $H_2SO_4$ and 2.5L distilled water).to trap residual ozone. 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 50 to 200 mg/L by increasing contact time. Effluents were preconditioned at a temperature of 35ºC in the water bath before treatment. All ozone treatments were performed in duplicate.

*Biological treatment*

Raw and ozone pretreated effluents were treated biologically in bench-scale sequencing batch reactors consisting of 1000 mL beakers with 600 mL working volumes. Before biological treatment, nitrogen (urea) and phosphorous (phosphoric acid) were added to the effluents at a final $BOD_5$:N:P ratio of 100:5:1, and effluent pH was adjusted to 7 ±0.5. Air was supplied at the bottom of each reactor using porous stones connected to an air pump able to maintain the dissolved oxygen concentration above 2 mg/L. The beakers were placed in a water bath at 35°C. Treatment cycles were 12 hours long (9h aeration + 3 h clarification and rest). Mean cell residence time was kept at 10d by daily removal of an appropriate amount of biomass from the reactor. After each 12 h cycle, treated effluent was withdrawn for COD analysis and replaced with raw effluent. The reactors were inoculated with biomass from the activated sludge plant at the mill where the effluents were collected. Biomass concentration was estimated by measuring volatile suspended solids (VSS), according to the Standard Method (1998). Stable operating conditions were considered reached when the treated effluent COD remained constant (± 10%) for six consecutive cycles (Mounteer et al., 2002;

2003). After stabilization, treated effluent was collected and more fully characterized over six more cycles. In addition, biomass was withdrawn from the reactors for determination of the specific oxygen uptake rate, according to the US Environmental Protection Agency protocol (USEPA, 2001).

*Effluent characterization*

Effluents were characterized by measuring COD, $DBO_5$, TOC, AOX 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). TOC was quantified in a Shimadzu TOC 500 analyzer (Tokyo, Japan) and AOX in a Euroglas 1600 (Delft, Holland) automatic analyzer. All effluent analyses were performed in triplicate and average results are reported.

*Statistical analysis*

Mean effluent parameter values after chemical and biological treatments were compared through ANOVA followed by a one-way comparison of means at a 5% significance level ($p<0.05$) using Tukey´s method using the Statistica software package (Statsoft, Tulsa, OH).

## Results and Discussion

Results of pre-treatment of ECF bleaching effluents E1 and E2 with ozone doses varying from 50 to 200 $mgO_3/L$ are presented in Figure 1. The largest relative effects of increasing the ozone dose in pre-treatment were to reduce effluent color and lignin contents and increase effluent BOD. Effluent COD and AOX were reduced slightly while TOC remained fairly constant. This is important since it implies that organic matter was not being mineralized, but only transformed to a more biodegradable state, which was the goal of the ozone treatment. Initially, carbohydrates increased in effluent E1 and decreased in effluent but the remained constant above a dose of 50 $mgO_3/L$. In fact, effluent biodegradability ($BOD_5$/COD ratio) increased by 17 to 19% in both effluents at an ozone dose of 100 mg/L and did not significantly improve when the dose was doubled to 200 mg/L (Table 1). The increased biodegradability was caused by an increase in BOD and concomitant slight decrease in effluent COD. The observed 5-10% increase in oxidation state of the organic matter (TOC/COD ratio) was consistent with the increase in effluent $BOD_5$. Based on the BOD improvement obtained at 100 $mgO_3/L$, this ozone dose was chosen for the combined chemical-biological treatment.

The effluents were treated at their original pH (pH 7-8), which was considered optimum for the subsequent biological treatment. A preliminary study showed that adjusting to pH10 to promote hydroxyl radical formation (Assalin et al., 2004; Bijan & Mohseni, 2004; Gogate & Pandit, 2004), resulted in only a slight increase in lignin removal, but would imply added cost and thus pH adjustment was not performed.

The results of biological treatment of the raw and ozone treated ECF effluents are shown in Figure 2. Combined ozone-biological treatment led to significant decreases in COD (10% in E1 and 11% in E2) and lignin (20% in E1, 46% in E2) in both effluents and in BOD (40%) of effluent E2. No significant differences were found for effluent color and carbohydrate contents. Although part of the COD was removed by the ozone treatment itself (32mg/L in E1 and 20 mg/L in E2), the transformation of the organic matter to a more readily biodegradable form was also responsible for COD removal during biological treatment, since the absolute amount of COD removed during biological treatment was greater after ozone pre-treatment, in both effluents. Effluent AOX were quite low after biological treatment (<2mg/L), and this parameter was not further studied.

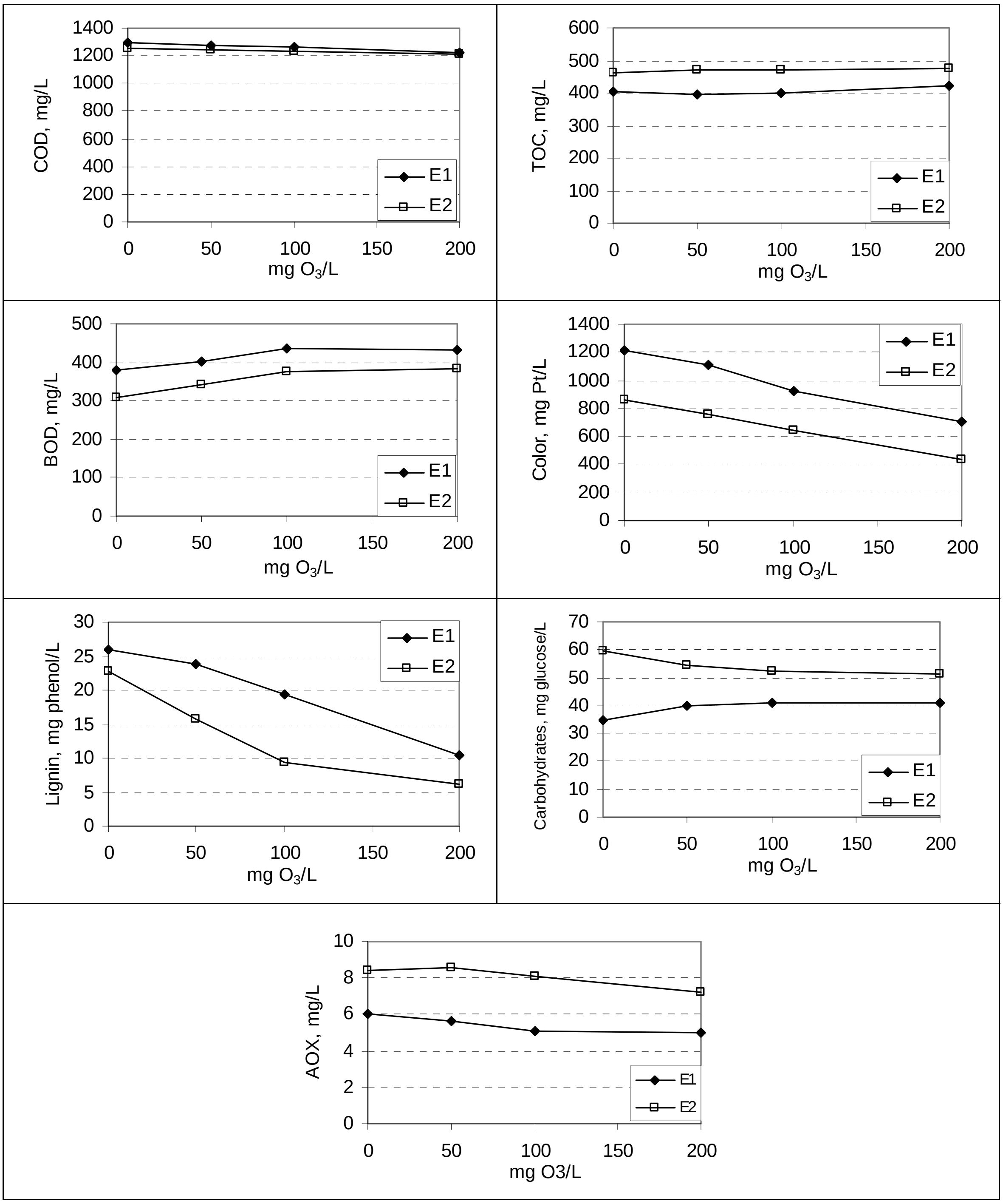



Figure 1 – Effect of ozone dose on environmental parameters upon treatment of two eucalypt kraft pulp ECF bleaching effluents. (Ozonation: 35ºC, 10-11mg $O_3$/min, pH 7-8).

Table 1 – Effect of ozone dose on biodegradability ($BOD_5$/COD) and oxidation state (TOC/COD) of eucalypt ECF bleaching effluents. (Ozonation: 35ºC, 10-11mg $O_3$/min).

| Effluent | Ratio | $O_3$, mg/L | | | |
|---|---|---|---|---|---|
| | | 0 | 50 | 100 | 200 |
| E1 | $BOD_5$/COD | 0.29 | 0.31 | 0.34 | 0.35 |
| | TOC/COD | 0.31 | 0.31 | 0.32 | 0.34 |
| E2 | $BOD_5$/COD | 0.25 | 0.27 | 0.31 | 0.31 |
| | TOC/COD | 0.37 | 0.38 | 0.38 | 0.39 |

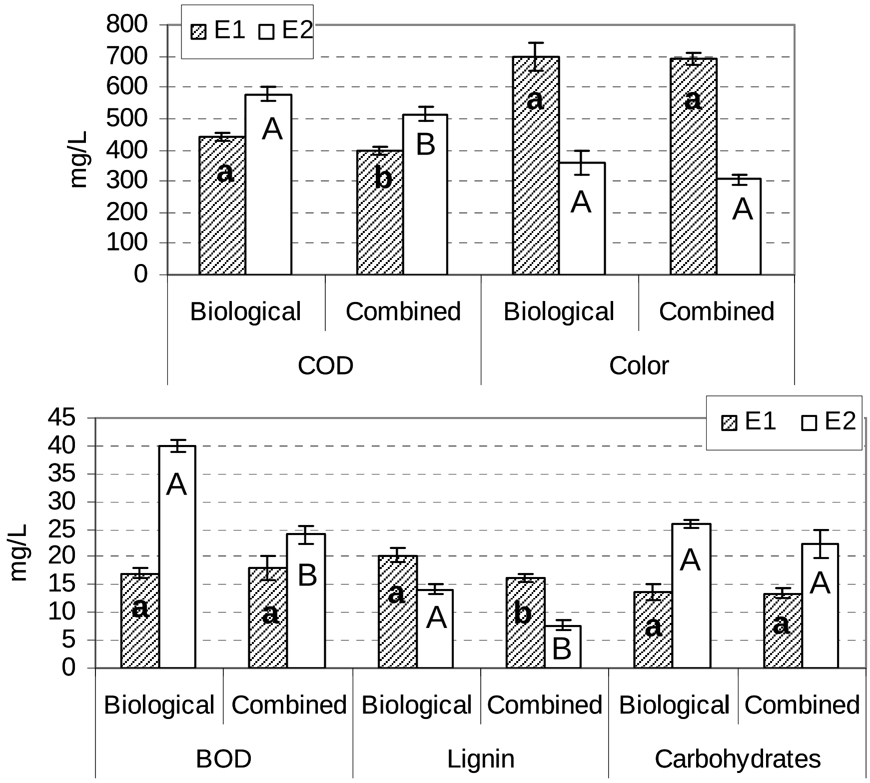



Figure 2 – Comparison of ECF bleaching effluent quality after biological and combined ozone-biological treatments. Error bars represent standard errors (n=6). For each parameter, columns identified by different letters are significantly different (p<0,5). (Ozonation: 100mg$O_3$/L, 11mg$O_3$/min, 35ºC, pH7-8; Biological treatment: 12h, 35ºC, pH7-9).

Ozonation did not effect the biomass concentrations (VSS) established in the reactors treating the raw and pre-treated effluents, although higher biomass concentrations were established in the reactors treating effluent E1 (Table 2) than in those treating effluent E2, probably as a result of the higher biodegradability of effluent E1. However, ozonation did alter the activity of the biomass treating effluent E2, for which the SOUR almost doubled over that in the reactor treating raw effluent E2. This higher activity accounts for the significant reduction in effluent BOD, observed for effluent E2 pretreated with ozone. No such effect was found for effluent E1 and the exact nature of the effect observed for effluent E2 is not yet known.

Table 2 – Volatile suspended solids (VSS) and specific oxygen uptake rate (SOUR) of the biomass in reactors during biological treatment of ECF bleaching effluents with and without ozone pre-treatment (100 mg$O_3$/L). (Values reported are means ± standard deviation).

| Effluent | $O_3$ pre-treatment | VSS, mg/L | SOUR, mg$O_2$/gVSS.h |
|---|---|---|---|
| E1 | no | 1520 ± 228 | 20.5 ± 2.7 |
| | yes | 1570 ± 180 | 20.4 ± 3.1 |
| E2 | no | 1130 ± 145 | 17.0 ± 1.9 |
| | yes | 1020 ± 171 | 31.9 ± 2.4 |

The results of the comparison of the pre and post-treatment with 100 $mgO_3/L$ are presented in Figure 3. Effluent COD and color were higher in both effluents when ozonation followed biological treatment than when it preceded the biological treatment, although only COD in effluent E1 showed a significant difference. The higher color values observed in the post-treatment suggest that the pre-ozonation resulted in destruction of color forming substances during biological treatment. The higher COD values after the post-treatment are also proof of the transformation of organic matter into more readily biodegradable form during ozone pre-treatment. BOD was virtually unaffected in effluent E1, while it was higher in effluent E2 when ozone was used after biological treatment. On the other hand, lignin and carbohydrates were lower in the effluents treated with ozone after biological treatment, with a significant decrease observed for carbohydrates in both effluents.

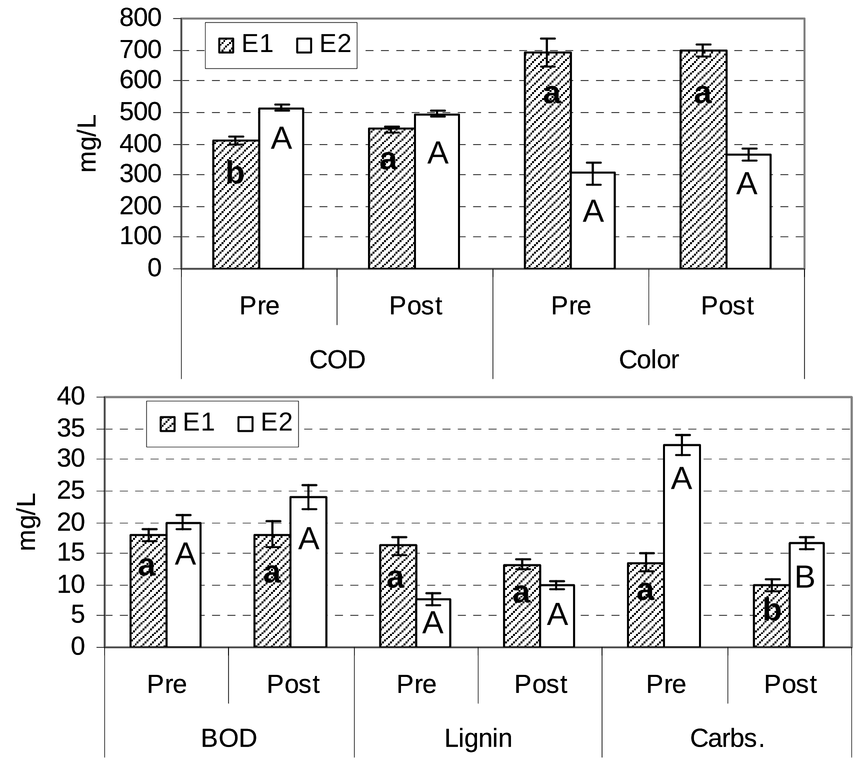
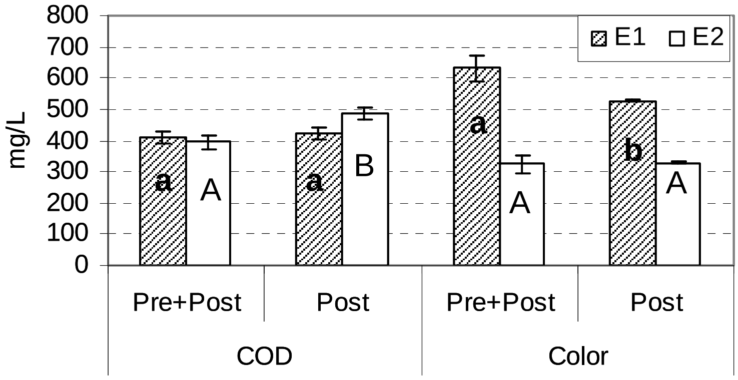



Figure 3 – Effect on quality of ECF bleaching effluents of ozonation (100$mgO_3/L$) before (pre) or after (post) biological treatment. Error bars represent standard errors (n=6). For each parameter, values of columns identified by the same letter are not significantly different ($p<0,5$). (Ozonation: 9-11$mgO_3$/min, 35ºC, pH pre-$O_3$ = 7-8, pH post-$O_3$ = 9; Biological treatment: 12h, 35ºC, pH 7-8).

Since different pre- and post-ozone treatments had opposite effects on the different effluent parameters shown in Figure 3, a final test was run in which the ozone dose was split between pre- and post-treatments (100 $mgO_3/L$ each) and compared to post-ozonation at the same total ozone dose (200mg/L). The results of this study are shown in Figure 4. Both effluents presented significantly lower final BOD when the ozone dose was split between pre- and post-treatments than when only a post-treatment was performed. This illustrates the potentially deleterious effect of post-ozonation on effluent quality, but also suggests the potential for a second biological treatment, as described by Helble et al. (1999). While effluent E2 showed significantly lower COD and lignin and significantly higher carbohydrates after the split ozone treatments, effluent E1 presented a significant decrease in color when all the ozone was applied in a post-biological treatment. No other significant differences were found for effluent E1. Color reduction is considered one of the main benefits of tertiary ozone treatment (Zhou & Smith, 1997), but for effluent E2 ozone pre-treatment apparently destroyed color forming precursors, canceling the beneficial effect normally observed in post-treatment. Overall, the split ozone treatment produced better quality effluent than the post-treatment, although the differing response of the two effluents demonstrates the need to perform pilot studies for each effluent being considered for treatment.



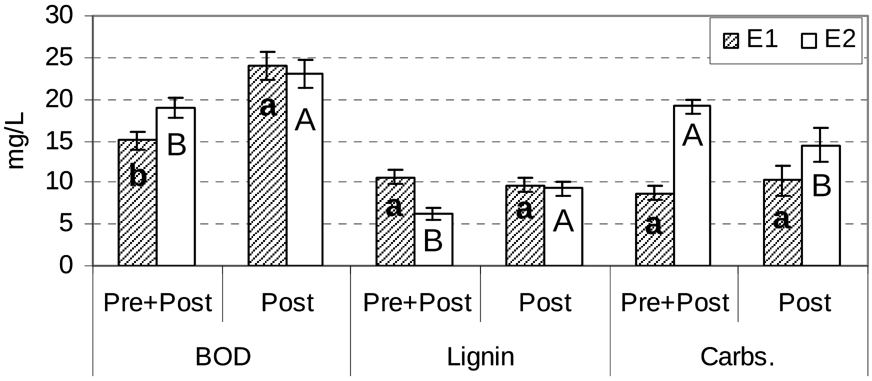




Figure 4 – Final quality of ECF bleaching effluents after combined chemical-biological treatment. Ozonation was performed before and after biological treatment using 100mg$O_3$/L in each stage (Pre+Post) and in a single stage after biological treatment using 200mg$O_3$/L. Error bars represent standard errors (n=4). For each parameter, values of columns identified by different letters are significantly different (p<0,5). (Ozonation: 9-11mg$O_3$/min, 35ºC, pH pre-$O_3$ = 7-8, pH post-$O_3$=9; Biological treatment: 12h, 35ºC, pH 7-8).

## Conclusions

Pre-treatment of eucalypt kraft pulp ECF bleaching effluents with 100mg$O_3$/L led to 10-11% lower final effluent COD after biological treatment, as a result of a 17-19% increase in effluent biodegradability after the ozone stage. Ozone pre-treatment destroyed phenolic lignin structures but did not alter the carbohydrate fraction of the effluents. Ozonation led to higher biomass activity during biological treatment of one of the two effluents tested, resulting in increased BOD removal. At the same ozone dose, pre-treatment or split pre- and post-treatments produced better quality effluents than post-treatment. Ozonation following biological treatment resulted in increased effluent BOD and in only one of four cases led to greater color removal than ozone pre-treatment. The potential for improving effluent quality through combined ozone-biological treatment has been shown. Currently, we are optimizing the biological treatment to maximize the benefits obtained.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