REDUCTION OF THE RECALCITRANT COD OF HIGH YIELD PULP MILLS EFFLUENTS BY AOP. PART 1. COMBINATION OF OZONE AND ACTIVATED SLUDGE

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The aim of this work was to study the effect of ozone, either alone or combined with an activated sludge system, on the reduction of the recalcitrant COD in the effluent of a chemimechanical pulping (NaOH - Na_2SO_3) integrated mill. Several alternative schemes involving ozonation were tested on liquors and effluents of the pulp mill, and on two kinds of effluents were taken at different points of an activated sludge pilot plant. The largest decrease in COD was 33%, whereas that in aromatic compounds (absorbance at 232.5 nm) was of 73%. The most obvious result of the ozone treatment was effluent decolorization. It was not possible to use ozonation as tertiary treatment, as ozone was necessary to treat the BOD generated, and therefore the effluent must necessarily pass through a biological treatment. With a scheme including an intermediate ozonation between two secondary treatments (post-activated sludge and pre-aeration lagoon), the maximum reductions achieved were of 70% in COD, of 93% in aromatics, and of 96% in color. The limits of COD allowed by the environmental regulations (<250 mg/L) could be achieved with the following stages: 1) primary clarifier, 2) activated sludge system, 3) ozonation, 4) aeration lagoon, and 5) stabilization lagoon.

Keywords: COD; Liquid effluents; Color; Ozone; Activated sludge; Chemimechanical pulping mill

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INTRODUCTION

Due to their high yields, chemimechanical (CMP) and semichemical (NSSC) pulping processes do not have recovery systems based on the combustion of dissolved organic matter. As a result, after the biological treatment of the liquid effluents there is a certain amount of organic matter difficult to degrade, called recalcitrant, which is measured as Chemical Oxygen Demand (COD). The documented cases of successful treatments of this recalcitrant organic matter are of doubtful practical applicability, due to their technical, environmental, or economic features. The multiple alternatives that have been reported attempting to solve this problem have been presented in a previous paper (Area et al. 2010).

Although biological systems, such as activated sludge, continue to be the most appropriate treatments to remove biodegradable organic matter, measured as BOD5, they show little ability to remove refractory compounds and color. The maximum decrease reported for CTMP (chemithermomechanical) pulping effluent (12,000 mg/L of initial COD) with the use of activated sludge is 68% (Dufresne et al. 1998). Similar levels have been found for neutral sulfite semichemical pulping (NSSC) effluents (initial COD of 14,200 mg/L) (Magnus et al. 2000). Final COD values indicate that this treatment is insufficient to meet the requirements of the existing environmental regulations.

Advanced oxidation processes (AOP), which are based on the strong oxidizing ability of the hydroxyl radical, involve the generation of sufficient quantities of the radical to oxidize organic compounds in the environment. AOP systems use combinations of ozone, hydrogen peroxide (H_2O_2), ultraviolet light (UV), and catalysts (O_3/H_2O_2, UV/H_2O_2, Fenton: Fe^{2+}/H_2O_2, UV/O_3, heterogeneous photocatalysis: UV/TiO_2, etc.) (Gogate and Pandit 2004).

Advanced oxidation processes involve mainly the hydroxyl radical, which destroys pollutants, degrading the organic matter through the following reactions (Azbar et al. 2004):

$$\begin{array}{ccc}
O_3 + HO^- & \Leftrightarrow & O_2 + HO_2^- \\
HO_2^- + O_3 & \Leftrightarrow & O_3^{\bullet -} + HO_2^{\bullet} \\
HO_2^{\bullet} & \Leftrightarrow & O_2^{\bullet} + H^+ \\
O_2^{\bullet} + O_3 & \Leftrightarrow & O_3^{\bullet -} + O_2 \\
O_3^{\bullet -} + H^+ & \Leftrightarrow & HO_3^{\bullet} \\
HO_3^{\bullet} & \Leftrightarrow & {}^{\bullet}OH + O_2 \\
O_3 + {}^{\bullet}OH & \Leftrightarrow & O_2 + HO_2^{\bullet}
\end{array}$$

Ozone, a powerful oxidizing agent, can react with multiple pollutant species, acting on the double bonds (C = C, C = N, N = N, etc.), but not on the single bonds (C-C, C-O, O-H). It also reacts with the ion S^{-2}, to form SO_3^{-2} and SO_4^{-2} by a simple and rapid mechanism (El-Din et al. 2006).

Most authors agree with the greater effectiveness of the alkaline treatment. The better performance of ozonation at alkaline pH is due to the reaction of almost all organic and inorganic compounds with molecular ozone and radical oxidants, including the hydroxyl radical ($OH\bullet$) (Azbar et al. 2004; El-Din et al. 2006; Bijan and Mohseni 2005). By contrast, ozonation in acidic conditions involves only the selective reaction of ozone with unsaturated organic compounds (El-Din et al. 2006). In agreement with this, some authors have found that oxidation of phenolic compounds is greatest at pH 9 (Bijan and Mohseni 2005). However, other authors have found that the removal of color and COD does not differ significantly at pH 4.5 or 11.0 (Ramírez Cortina 2002). Part of the effective oxidation potential of the radicals is reduced by their reaction with scavengers (i.e. carbonate and bicarbonate) (Roy-Arcand et al. 1991).

The ozone concentration depends on the generator and gas (air or oxygen) used. The increase in the ozone partial pressure increases the rate of degradation, but also the cost of generation. The mass transfer is greatest when the O_2/O_3 gas mixture is introduced into the liquid in the form of very small bubbles, maximizing the reaction zone (gas-liquid interface). The use of diffusers or static mixers maximizes efficiency in terms of time and interfacial contact area. The effect of ozone depends on the degradation mechanism, which may involve direct attack of ozone through chemical bonds or free radicals. In the latter case, the presence of HCO^-_3 radical ions and humic substances decreases the efficiency of degradation. In addition, an increase in temperature decreases ozone solubility, thus reducing degradation, although higher wastewater temperature also can improve degradation, as the kinetic of the reaction is faster and therefore more of the dissolved ozone takes part in the degradation. Degradation is greatest when ozonation is performed at alkaline pH.

The addition of calcium to the ozonation treatment improves COD removal by reducing phenolic products. This is because the calcium ion binds with intermediate reaction products of phenol, forming a precipitate. Also there is a decrease in the reaction time for the same percentage of COD reduction (Hsu et al. 2007). When testing phenol solutions with different concentrations of H_2O_2, varying the pH of the medium, some authors have found that when O_3 and H_2O_2 are combined, the efficiency in alkaline medium is also increased (Ramírez Cortina 2002).

In studies on model compounds of gallic acid, tannin, and lignin, applying ozone prior to the biological treatment and between two biological treatments, an increase in the biodegradation of organic compounds, COD and aromatic reduction has been reported (Saroj 2005). Ozonation processes generate low-molecular weight degradation products, often less toxic and easier to biodegrade (Bijan and Mohseni 2005; Saroj 2005). For example, ozonation after biological treatment removed 20% of the COD, with an increase of 13% in the BOD in the effluent of bleached kraft pulp with an initial COD of approximately 1600 mg/L (Bijan and Mohseni 2005). Ozonation is effective in destructing the chromophore groups. Decreases of 70 to 80% in the color and of 15% in the COD have been reported after ozonation of TMP and CTMP effluents from the primary treatment (mainly resin acids and fatty acids) (Roy-Arcand and Archibald 1997), whereas decreases of 60% in color and of 21% in COD have been reported after ozonation of the effluents from a bleached kraft pulping process (Roy-Arcand et al. 1991).

The COD reduction reported for different types of effluents treated with ozone, with initial COD of 1195 to 108200 mg/L, ranges between 7 and 54%, while ozonation followed by an activated sludge biological treatment reduces initial COD values of 1000-112000 mg/L up to 85% (Chiang 2009).

In the first part of this research, we tested chemical precipitation as a primary treatment and found a decrease of approximately 45% of the initial COD with polyaluminium chloride (PAC) (Felissia et al. 2010). The treatment proved effective for the destruction of chromophores, reaching 80% decolorization. The aim of this work was to study the effect of ozone, either alone or combined with an activated sludge system, on the reduction of recalcitratant COD of a CMP integrated pulp mill effluent.

EXPERIMENTAL

The effluent studied consisted of spent liquor and effluents from an integrated mill that manufactures chemimechanical pulp (CMP: NaOH - Na_2SO_3) and newsprint. At the mill, the chemimechanical pulping effluent is diluted with other liquids of the process (peroxide bleaching, newsprint recycling, and paper mill) before it enters the primary clarifier.

Ozonation was carried out using a Figmay ozone generation system, with a maximum generation capacity of 4.00 g/h. Ozone gas is produced by electric shock when passing a flow of oxygen through the device. The shock produces dissociation of the oxygen molecules into atoms, which, in contact with oxygen molecules, generate ozone.

The experiments were conducted in a 1 L capacity bottle. The dispersion of ozone was carried out through a sintered glass bubbler. The treatment efficiency was verified by quantifying the residual ozone trapped in a potassium iodide solution acidified with acetic acid and titrated with sodium thiosulfate. The ozone generating equipment was adjusted to a rate of 1.42 g O_3/h from pure oxygen.

The pH was measured with a PARSEC pH meter. Total solids were determined according to TAPPI standard (T 629 st). The ash content was determined at 525 ºC. BOD5 and COD were determined using Standard Methods 5210 and 5220-B-B (APHA Standard Methods for the Examination of Water and Wastewater, 1998). Color was quantified by UV-Visible spectroscopy (TECHCOMP spectrometer), measuring the absorbance at 450 nm. The aromatic content was quantified by UV spectrophotometry, by measuring the absorbance at 232.5 nm.

Results were statistically analyzed using Statgraphics software.

Ozonation of Spent Liquors and Effluents

The evolution of the aromatic content in the liquids was monitored by UV spectrophotometry, measuring the absorbance at 232.5 nm, and diluting the samples with water and adjusting the pH to 4-5.

The reducing sugars and volatile acids were determined by HPLC using an Aminex-HPX87H column (BIO-RAD), and the following chromatographic conditions: Eluent: 4 mM H_2SO_4, flow: 0.6 mL/min, temperature: 35 ºC; Detectors: Refractive index and diode array. The composition of the hemicelluloses contained in the liquor was obtained by hydrolyzing a sample of liquor as it was, and determining simple sugars by HPLC. The hexoses were converted to hexosanes by multiplying by 0.90, whereas pentosans were converted to pentoses by multiplying by 0.88.

The experiments were performed according to the following schedule:

Test	Sample	Treatment
a	Concentrated spent liquor	Acidification at pH = 3, with 30% H_2SO_4.
b	Concentrated spent liquor	Alkalization at pH 12, with $Ca(OH)_2$ + centrifugation.
c	Concentrated spent liquor	Filtration and centrifugation, without modification of the original pH.
d	Diluted spent liquor	1 in 4 dilution.
e	Diluted spent liquor	Dilution with other liquids of the process.
f	Diluted spent liquor	Dilution with other liquids of the process + treatment with ozone for 1 hour + centrifugation post ozonation.
g	Diluted spent liquor	Dilution with other liquids of the process + centrifugation and alkalization at pH 8.2 with NaOH.
h	Aerated Lagoon Effluent	As it was.
i	Aerated Lagoon Effluent	Ozone treatment for 1 hour + centrifugation post ozonation
j	Aerated Lagoon Effluent	Centrifugation before the ozone treatment.

Combined Treatments

Ozonation studies were conducted on two types of effluent samples, treated at different points of an activated sludge pilot plant. Each module of the pilot plant has a 5.2 m^3 reactor where the effluent enters along with nutrients and a 1 m^3 clarifier, where part of the thickened sludge is recirculated to maintain good quality.

Sample 1: taken at the end of module 1 (supernatant from the clarifier); it reproduces a treatment with activated sludge fed with the effluent from the aerated lagoon (pH: 8.0, total soluble solids (TSS): 242 (g/L). In this scenario, ozonation emulates a tertiary treatment.

Sample 2: taken at the end of module 3 (supernatant from the clarifier); it reproduces a treatment with activated sludge supplied by the primary clarifier (pH: 8.3, TSS: 64g/L). In this scenario, ozonation emulates an intermediate treatment between two secondary treatments.

The testing involved four types of treatment:

a) Ozonation, using 1.42 g of O_3 every 60 minutes.
b) Addition of 0.5 g/L of $Ca(OH)_2$ and subsequent ozonation.
c) Addition of 17 g/L (0.5 M) of H_2O_2 and subsequent ozonation.
d) Addition of 0.5 g/L $Ca(OH)_2$ before and after centrifugation at 3500 rpm for 5 min.

RESULTS AND DISCUSSION

Ozonation of Liquors and Effluents

The characterization of the liquor and effluent is presented in Table 1.

Table 1. Characterization of Liquor and Effluents of the CMP Mill

Determination	Concentrated black liquor	Diluted black liquor (g)	Aerated lagoon effluent (j)	Final effluent
Centrifuged sedimentable solids (g / L)	7.13	1.25	0.94	0.56
Total solids (TS; g/L)	85.0	6.57	5.12	4.17
Total soluble solids (TSS; g/L)	78.1	5.32	4.18	3.61
pH	9.6	6.1	8.2	7.5
COD (mg/L)	47,000	7,040	3,500	--
COD centrifuged líquid (mg/L)	--	4,940	2,410	--
Ashes at 525 ºC (%TSS)	52.3	46.7	61.0	52.4
Sugars (%TSS)	0.49	1.13	1.56	1.39
Glucose (%TSS)	0.05	1.13	1.56	1.39
Xylose (%TSS)	0.31	n.d.	n.d.	n.d.
Arabinose (%TSS)	0.13	n.d.	n.d.	n.d.
Formic acid (%TSS)	0.51	0.68	0.10	n.d.
Acetic acid (%TSS)	26.04	22.96	0.25	0.67
Hemicelluloses (%TSS)	2.12	6.06	2.67	2.04
n.d. = not detected				

The ozonation experiments performed on the concentrated liquor are presented in Table 2.

Table 2. Ozonation Tests of CMP Liquors

Test	Time (min)	pH	Absorbance at 232.5 nm	Absorbance reduction (%)	Absorbance at 450 nm	Color reduction (%)	COD (mg/L)	COD reduction (%)	BOD (mg/L)	BOD/ COD
a	0	3	0.735	-	1.011	-	48560	-	-	-
a	90	3	0.575	22	0.933	8	46800	3.6	-	-
b	0	12	0.498	-	0.697	-	42880	-	-	-
b	90	12	0.261	48	0.340	51	39860	7.0	-	-
c	0	7.5	0.838	-	1.458	-	47000	-	-	-
c	90	7.5	0.701	16	1.116	23	46550	1.5	-	-
d	0	7.1	0.217	-	0.335	-	13090	-	3670	0.28
d	90	5.6	0.090	58	0.079	76	10870	17	3770	0.35

Conditions of ozonation: 1.34 g/h; 3.65 g O_3 /L liquor (90 min) - specific ozone dosage O_3 dissolved [g O_3-dissolved / g COD-inflow] at 90 min: a) 0.0752; b) 0.0851, c) 0.0776, d) 0.279 (O_3-dissolved = O_3-feedgas – O_3-offgas)

COD in the final effluent comprised 90% of aromatics and about 8% of hemicelluloses that had not been degraded in the secondary treatment (Table 1). The aromatic compounds may have come from lignin fractions, wood extractives, or other sources. The existence of a non-degraded fraction of glucose indicates an insufficient biological treatment.

Treatment "c" was the most unfavorable, followed by treatment "a" (at pH 3). Alkalinization at pH 12 with addition of $Ca(OH)_2$ (treatment "b") generated an initial decrease in COD (precipitated) and a better response to ozonation. Treatment "d" allowed the greatest reduction in COD (Table 2).

We found a high positive correlation between the reduction of absorbance at 232.5 nm and 450 nm (r = +0.97), between the absorbance at 232.5 nm and COD (r = +0.88), and between the absorbance at 450nm and COD (r = +0.90).

To achieve a complete biodegradation, the level of biodegradability (BOD5/COD) of the effluent should exceed 0.4 (Rodrigues et al. 2008). In treatment "d" (diluted liquor), the BOD/COD ratio increased by 20% after 90 minutes of ozonation, in proportion to the reduction of COD. The results indicate that the chemical compounds present in the original liquor changed with ozonation, slightly increasing their biodegradability.

In agreement with the findings of other authors (Roy-Arcand 1991), the treatments allowed a significant reduction in color, with a minor variation in the COD. Under the best conditions (treatment "d", diluted liquor, 90 minutes of treatment), the reductions obtained were 76% in color and of 17% in COD.

Results of ozonation of liquors and effluents are shown in Table 3.

The COD in treatment "f" (4,730 mg/L, sample of diluted liquor treated with ozone for 1 hour and centrifuged) and "g" (4,940 mg/L, sample of liquor centrifuged) was similar. This means that approximately 30% of COD decreased by centrifugation alone (from 7,040 mg/L to less than 5,000 mg/L). The same can be said about treatment "h" (sample from the aerated lagoon), in which the COD decreased from 3,500 mg/L to 2,312 mg/L after ozonation and centrifugation, and about treatment "i" (only centrifuged), which decreased to 2410 mg/L.

In samples that were not initially centrifuged, ozone was consumed in degrading the suspended organic matter, reducing the treatment efficiency. It is therefore essential to make a pre-treatment, which can include effluent centrifugation (approximately 30% decrease in COD), or a primary treatment (clarifier) including chemical precipitation with PAC (reduction of about 45%) (Felissia et al. 2010).

Table 3. Test Results of Ozonation of Liquor and Effluent

Test	Time (min)	pH	Applied O_3 (g)	g O_3-dissolved / g COD-inflow	Consumed O_3 (% applied)	COD (mg/L)	COD reduc-tion (%)	Absorb-ance - 232.5 nm	Absorb-ance reduction (%)	Color	Color reduc-tion (%)
e	0	6.1	0			7040	--	--	--	1.461	
	60	5.3	1.42	0.14	40.2%	6950	1.3%	--	--	0.600	59
f	60	5.3				4730	33%	--	--	0.502	66
g	0	8.2	0			4940	--	0.963	--	1.578	
	60	5.8	1.42	0.34	70.6%	--	--	0.483	50	0.590	63
	120	5.4	2.84	0.64	66.5%	4150	16%	0.345	64	0.710	55
	180	5.4	4.26	0.96	66.4%	4130	16%	0.324	66	0.364	77
h	0	8.2	0			3500	--	--	--	1.795	
	60	7.8	1.42	0.500	73.6%	2730	22%	--	--	0.531	70
i	60	7.7				2312	34%	--	--	0.491	73
j	0	7.6	0			2410	--	0.808	--	2.212	
	60	7.5	1.42	0.79	80.3%	--	--	0.332	59	0.714	68
	120	7.6	2.84	1.43	72.5%	--	--	0.296	63	0.560	75
	180	7.6	4.26	2.08	70.2%	1920 **	20%	0.219	73	0.432	80

**: BOD_5: 275 mg/L; color: Absorbance at 450 nm

The maximum COD reduction due to ozonation, after 180 min of treatment, was 16.4% for treatment "g" (diluted liquor) and 20.3% for treatment "j" (sample from the aerated lagoon).

In all the cases, the absorbance at 450 nm (indicating the color of the effluent) varied significantly with ozone application between 0 and 60 minutes ($p = 0.0014$), time after which the decline was much slower (Fig. 1). The maximum decolorization obtained was 80%.

The reduction of COD with ozonation of both liquids (diluted liquor, and effluent from the aerated lagoon) followed the same equation. The largest decrease in aromatic compounds occurred between 0 and 60 minutes.

The reaction kinetics of ozone with the substances of interest is very fast. Therefore, the reported effect is most probably a consequence of the ozone dosage applied at a given time, rather than an effect of the time of treatment.

The changes in the absorbance curves with the progress of ozonation of the diluted liquor and the effluent from the aerated lagoon are shown in Figs. 2 and 3, respectively. Table 4 shows the evolution of carbohydrates and organic acids with the ozonation treatment.

The shape of the spectrum varied with the application of ozone, which makes evident a change in the structure of the aromatic compounds (Figs. 2 and 3).

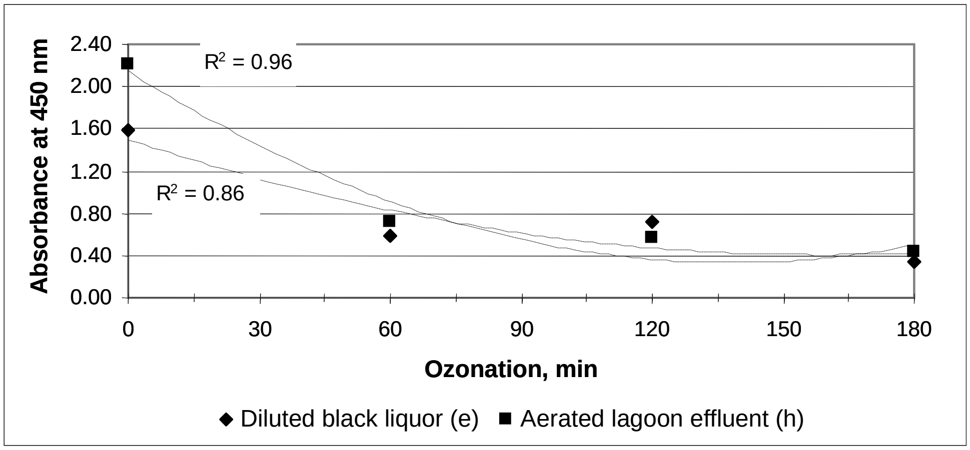

Figure 1. Evolution of decolorization with the ozonation treatment

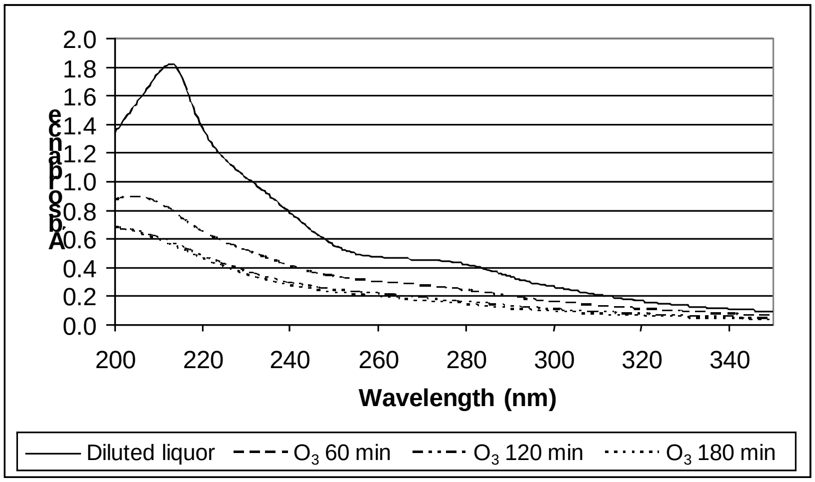

Figure 2. Spectrogram of ozonation of diluted liquor (dilution 1 / 50, COD reduction: 16.4%)

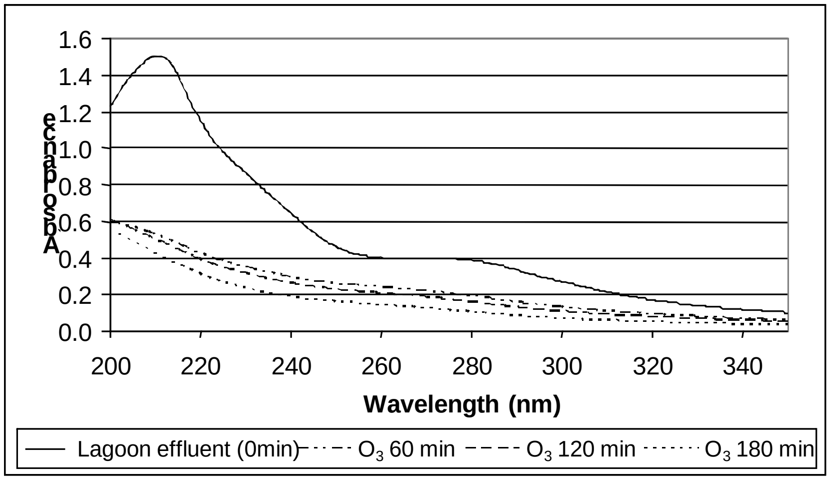

Figure 3. Spectrogram of ozonation of the effluent from the aerated lagoon (dilution 1 / 50, COD reduction: 20.3%)

Table 4. Evolution of Sugars and Organic Acids of the Centrifuged Liquid Incoming to the Clarifier and of the Effluent from the Aerated Lagoon (g/L) with the Ozone Treatment

Liquid	Time (min)	Glucose	Xylose	Arabinose	Formic acid	Acetic acid	Oxalic acid
g	0	0.060	n.d.	n.d.	0.036	1.224	n.d.
	60	0.056	0.004	0.004	0.064	1.196	0.048
	180	0.052	0.012	0.004	0.100	1.220	0.152
j	0	0.062	n.d.	n.d.	0.004	0.010	n.d.
	60	0.056	0.004	n.d.	0.012	0.016	0.098
	180	0.058	0.004	0.008	0.060	n.d.	0.200
n.d. = not detected							

During ozonation there were no changes in glucose or acetic acid, but the content of formic acid, xylose, and arabinose was increased by hemicellulose degradation. At 180 minutes of ozonation a large amount of acetic acid remained in the diluted liquor, whereas the secondary treatment removed it by 99%. However, oxalic acid significantly increased with the ozonation of the effluent from the aerated lagoon (Table 4).

In kraft pulp bleaching with ozone, lignin has been considered to be the main source of oxalic acid formation. Some authors have shown that the amount of oxalic acid generated during bleaching correlates well with the decrease in the kappa number. However, other authors who ozonated model compounds of xylans, cellulose, and lignin consider that part of the oxalic acid formed is due either to the HexA acid content or to the contribution of xylans (Roncero Vivero 2001). Other authors ozonated effluents from a sulfite pulping mill and found that 75% of lignin's aromatic rings were opened up after 5 h of ozonation (both at acid and alkaline pHs) and that they almost disappeared after 10 h of ozonation (Nakamura et al. 2004). Studying the mechanisms of ozonolysis of lignin model compounds, these authors found two ways of breaking the aromatic ring. The first involves the rupture between carbons C-1 and C-2 and the formation of muconic acid and its methyl ester, which subsequently breaks down to produce low molecular weight carboxylic acids and their esters. The other route is the direct formation of oxalic acid and its methyl ester (Fig. 4).

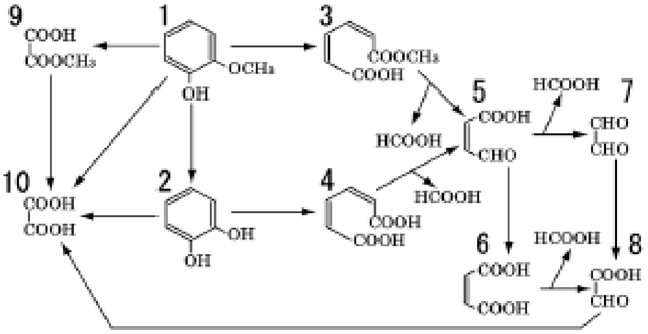

Figure 4. Mechanism of ozonolysis of guaiacol. 1: Guaiacol, 2: Catechol, 3: Monomethyl ester of muconic acid, 4: Muconic acid, 5: Malealdehydic acid, 6: Maleic acid, 7: Gloxal, 8: Glyoxylic acid, 9: Monomethyl ester of oxalic acid, 10: Oxalic acid (Nakamura et al. 2004)

The formation of oxalic acid could be one explanation for the change of shape of the spectrum of aromatic compounds during ozonation. One of the most interesting aspects is that these organic acids can be completely biodegraded in an activated sludge treatment.

The most obvious result of the ozone treatment was the decolorization of the effluent (Fig. 5).

Figure 5. Ozonation of centrifuged samples of diluted liquor and of effluents from the aerated lagoon

Combined Treatments

Results obtained after ozonation of samples from the initial effluent and Sample 1 (activated sludge post-aeration lagoon) are presented in Table 5.

Table 5. Ozonation of Sample 1

Time (min)	pH	g O_3-dissolved / g COD-inflow	Consumed O_3 (% applied)	COD (mg/L)	COD reduction (%)	BOD (mg/L)	BOD/ COD	Absorbance at 232.5 nm	Absorbance reduction (%)	Color	Color reduction (%)
0	8.00	--	--	2,200	--	80	0.04	0.933	--	2.474	--
60	7.85	0.78	72.2	1,170	47	--	--	0.298	68	0.446	82
120	8.12	1.78	82.8	960	56	--	--	0.198	79	0.226	91
180	8.18	2.62	81.3	1,020	54	158	0.15	0.132	86	0.127	95

color: Absorbance at 450 nm

In the ozonation performed on Sample 1, 81% of the ozone applied was consumed after 180 minutes of treatment. The variation of COD was not significant between 120 and 180 minutes of treatment, but aromatic compounds and color decreased notably.

About 55% of the COD, 86% of the aromatic compounds, and 95% of the color decreased after 180 minutes of treatment. However, the effluent final COD was 1020 mg/L, i.e., still far from what is allowed by most provincial regulations in Argentina (<250 mg/L). Following ozonation, BOD, which was initially close to 50 mg/L, a value allowed by most provinces in Argentina, increased to 180 mg/L due to the increased degradability of compounds by aromatic ring breakage (Nakamura et al. 2004).

Ozonation transformed hardly biodegradable compounds into more easily biodegradable forms, as indicated by the BOD/COD ratio, which increased from 0.04 to 0.15, but not resulting in completely biodegradable compounds (Rodrigues et al. 2008).

This arrangement, which represents a tertiary treatment, means that the effluent has passed sequentially through the following stages: 1) primary clarifier; 2) aerated lagoon, 3) activated sludge system, and 4) ozonation. As the only remaining step is the stabilization basin, the treatment will not be enough to degrade the organic matter generated by ozonation. The treatments carried out on Sample 2 (activated sludge after the primary clarifier) are presented in Table 6.

Table 6. Ozonation of Sample 2

Time (min)	pH	g O_3-dissolved / g COD-inflow	Consumed O_3 (% applied)	COD (mg/L)	COD reduction (%)	BOD (mg/L)	BOD/COD	Absorbance at 232.5 nm	Absorbance reduction (%)	Color	Color reduction (%)
0	8.30	--	--	1,440	--	66	0.04	0.783	--	1.884	--
60	8.07	0.76	46.0	800	44	--	--	0.206	78	0.257	86
120	8.40	2.67	81.0	600	58	--	--	0.108	88	0.120	94
180	8.46	4.34	87.9	430	70	100	0.23	0.063	93	0.077	96
0	8.10	--	--	1,440	--	66	0.05	0.783	--	1.884	--
60*	9.40	--	64.2	--	--	--	--	0.179	81	0.204	89
120*	9.14	3.00	91.0	450	69	100	0.22	0.078	92	0.095	95
0	8.10	--	--	1,440	--	66	0.05	0.783	--	1.884	--
60**	8.07	--	46.0	--	--	--	--	0.206	74	0.069	96
120**	8.00	2.67	81.0	770	47	n.d.	--	0.104	87	0.027	99
120 ** +	8.46	2.69	81.8	590	59	n.d.	--	0.092	88	0.037	98

* $O_3 + Ca(OH)_2$+ centrifugation
** $O_3 + H_2O_2$
+: $O_3 + H_2O_2 + Ca(OH)_2$+ centrifugation
n.d.: could not be determined because of the presence of hydrogen peroxide

In the ozonation performed on Sample 2 without additives (intermediate ozonation between two secondary treatments), 88% of the ozone applied was consumed at 180 minutes of treatment. Ozone consumption was almost constant between 120 and 180 minutes, but the decrease in COD and aromatics that occurred during this period was very important (Table 6).

The application of ozone for 180 minutes to Sample 2 resulted in a decrease of 70% in the COD, reaching 430 mg/L. The decrease in aromatic compounds was slightly above 90% and decolorization was 95%. Similar results were obtained with 120 minutes of ozonation, adding calcium hydroxide and centrifuging the system. This reduction of the treatment time in the presence of calcium is consistent with that reported by other authors (Hsu et al. 2007).

The ozone treatment applied subsequently to an activated sludge system caused a decrease in COD of 70%, whereas the ozonation of the effluent without the activated sludge plant caused a decrease that did not exceed 35%. It can be concluded that the microbiological treatment applied in the pilot plant allowed for a more significant change in the structure of aromatic compounds. These results agree with those found by other authors, who worked with model compounds (Saroj et al. 2005).

The degradability of the effluent increased significantly, since the BOD/COD ratio increased from 0.04 to 0.23, i.e., which was more than in the treatment of Sample 1. The modification of chemical species during the ozonation treatment can be observed through the changes in the absorption spectra in the UV region between 190 and 350 nm (Figs. 6 and 7).

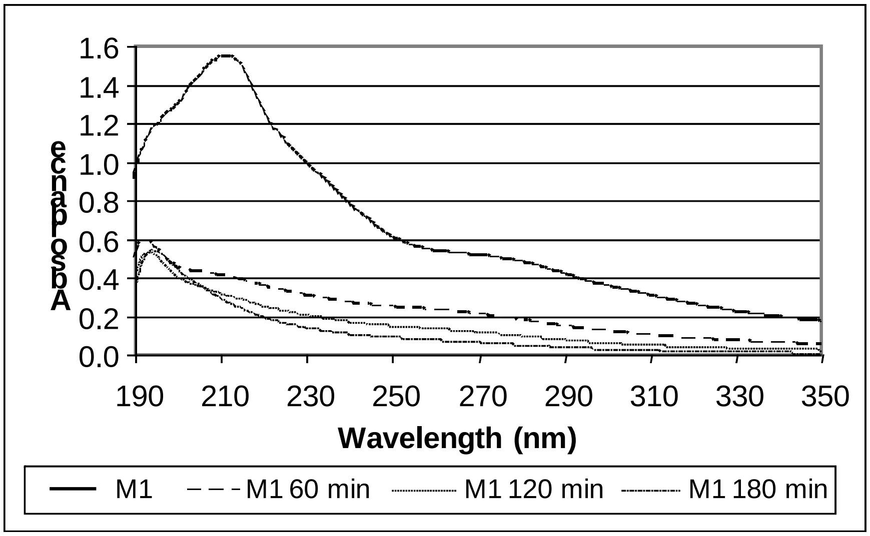

Figure 6. Absorbance spectra of the treatment of Sample 1

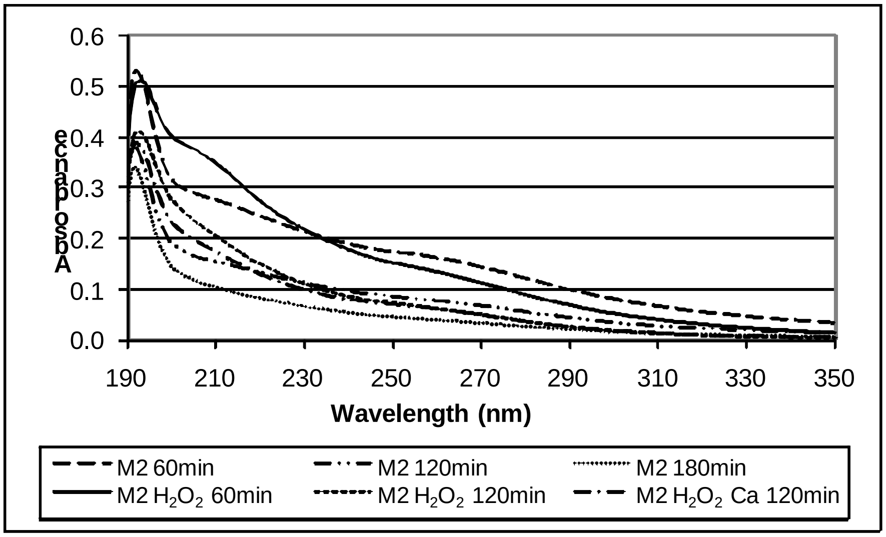

Figure 7. Absorbance spectra of the treatment of Sample 2 (the spectrum of the initial sample was eliminated to improve visualization)

In Sample 1, the relationship between the decrease in COD and the increase in BOD was nearly 1:1 (50% decrease in COD caused 50% increase in BOD). However, in the case of Sample 2, the ratio was 2:1 (70% decrease in COD generated 35% increase in BOD). This implies that each effluent contained different kinds of chemical species. The second relationship is more similar to that found by other authors (for example, 21% reduction in COD and 13% increase in BOD5, ratio: 1.6:1, in kraft bleaching effluents) (Bijan and Mohseni 2005). Unlike results obtained by other authors (Ramírez Cortina 2002), under these experimental conditions, hydrogen peroxide caused only a rapid decoloration effect, without further action on COD (Fig. 8).

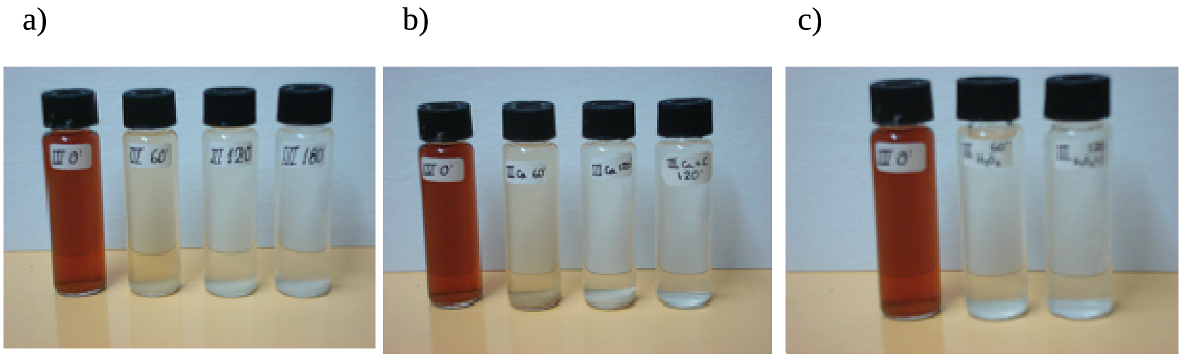

Figure 8. Treatments applied to Sample 2: a) O_3 (0, 60, 120, 180 min); b) O_3 + $CaOH_2$ (0, 60, 120 and 120 min, centrifuged); c) O_3 + H_2O_2 (0, 60 and 120 min)

The treatment scheme involving the experiments with Sample 2 (simulation of an intermediate ozonization between two secondary treatments), which consisted of the following steps: 1) primary clarifier; 2) activated sludge system, 3) ozonation, 4) aerated lagoon, and 5) stabilization basin, was able to remove the BOD generated in the process of ozonation and the residual COD, composed mainly of oxalic acid.

Given that maximum COD reductions expected with ozonation are 70 to 80%, the COD entering the system should be approximately 1000 to 1500 mg/L, which could be achieved by optimizing the activated sludge treatment.

On the basis of what has been found so far (Felissia et al. 2010, and this work), a proposed scheme for the treatment of the CMP mill effluent would involve:

1. A pre-treatment of the effluent, to decrease COD to levels compatible with those of the ozonation treatment.
    a) Centrifugation of the spent liquor, diluted with other liquids of the process (i.e., from the paper mill), decreasing COD levels by approximately 30%, from 7,000 mg/L to 5,000 mg/L.
    b) A primary treatment for the sedimentation of suspended solids that performs well, using chemical precipitation with PAC (COD decreases by approximately 45%, to 3,000 mg/L).
    c) An optimized activated sludge treatment (COD decreases approximately 70%, to 1,000 mg/L).
2. Ozonation with or without addition of $Ca(OH)_2$, depending on time requirements (COD decreases approximately 70%, to 300 mg/L).
3. A subsequent secondary treatment in the aerated lagoon, to degrade the BOD generated during ozonation (COD decreases approximately 30%, to 210 mg/L).
4. If using $Ca(OH)_2$, a recovery system might be implemented.

A similar treatment scheme has been incorporated into a full-scale production facility at the SCA Graphic Laakirchen AG mill (Kaindl et al. 1999; Kaindl and Liechti 2008). Its economic viability has been proved for more than 6 years of continuous operation, which is ongoing. Nevertheless, other options for COD reduction will be explored.

CONCLUSIONS

1. Acceptable levels of COD (allowed by environmental regulations) can be achieved (<250 mg/L) with the following stages: 1) primary clarifier; 2) activated sludge system, 3) ozonation, 4) aeration lagoon, and 5) stabilization basin.
2. Oxalic acid increased markedly in the ozonated liquid. Therefore, it is not possible to use ozonation as the last treatment, because it is necessary to eliminate the generated BOD after ozonation. As a consequence, the effluent must pass again through a biological treatment.
3. Ozonation between two secondary treatments (after the activated sludge and before the aerated lagoon) causes maximal decreases of 70% in COD, of 93% in aromatics and of 96% in color.
4. Ozonation of the CMP spent liquor, directly after the pulping system, is inefficient. In uncentrifuged samples, the ozone is consumed in degrading the suspended organic matter. Centrifugation causes an initial decrease in the COD of approximately 30%, whereas filtering the liquor causes a decrease in the COD of 21% over the original. Alkalinization at pH 12 with addition of $Ca(OH)_2$ causes an initial decrease in COD (precipitated) and a better response to ozonation. The largest decrease obtained for COD was 33%, whereas that of aromatic compounds (which absorb at 232.5 nm) was 73%.
5. The most obvious result of the ozone treatment was the decolorization of the effluent (80%).
6. Calcium incorporation increased the reaction rate, while the addition of hydrogen peroxide resulted only in decolorization.

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